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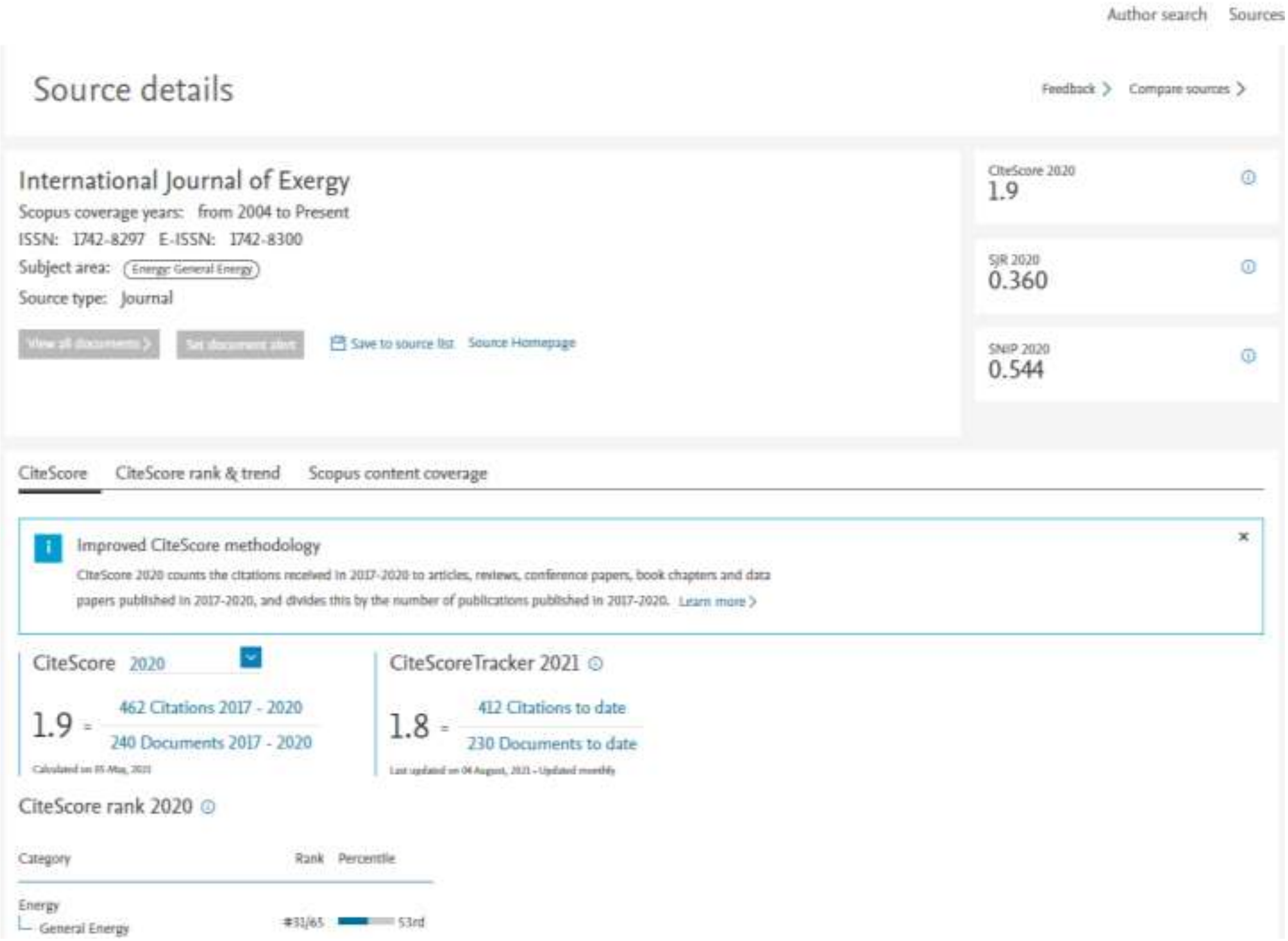

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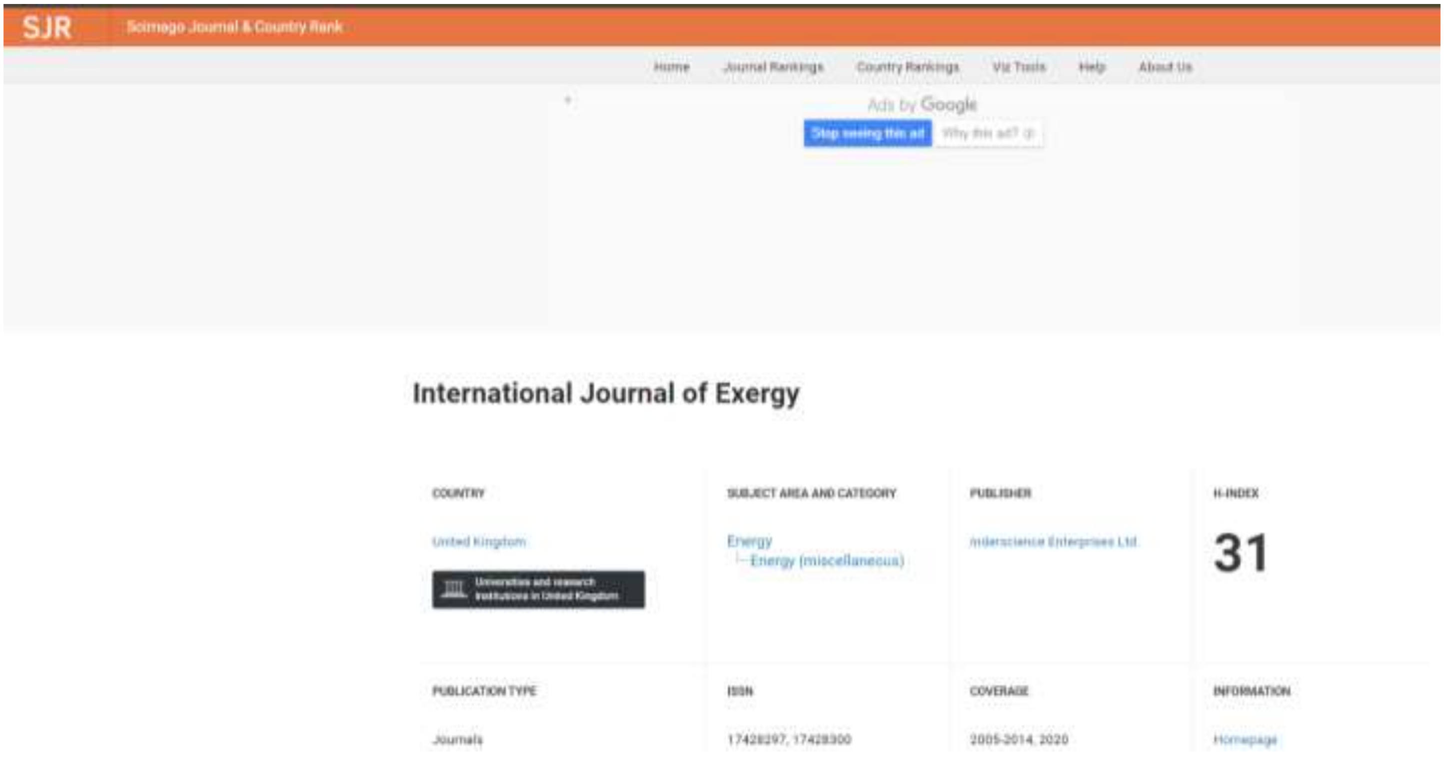

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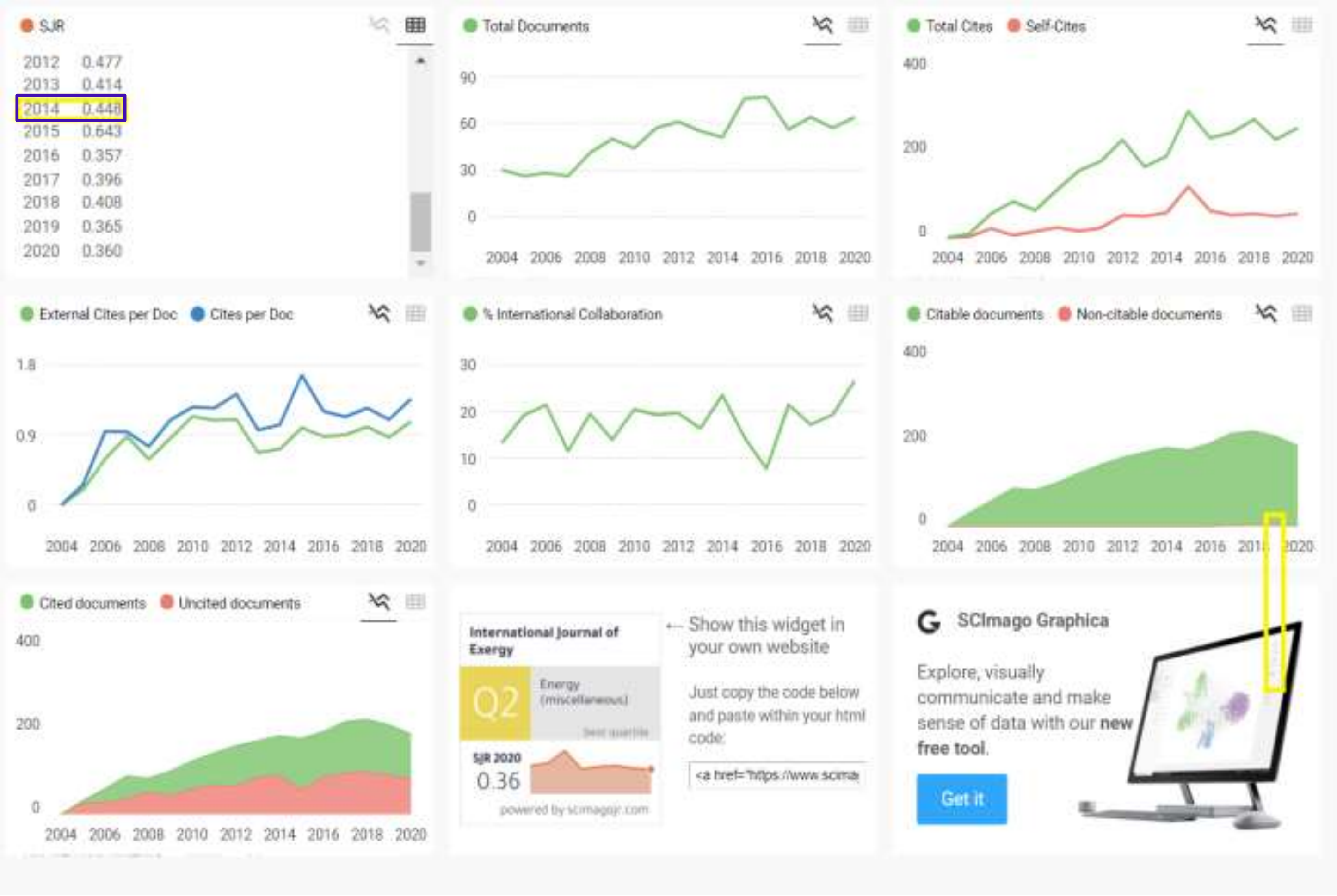

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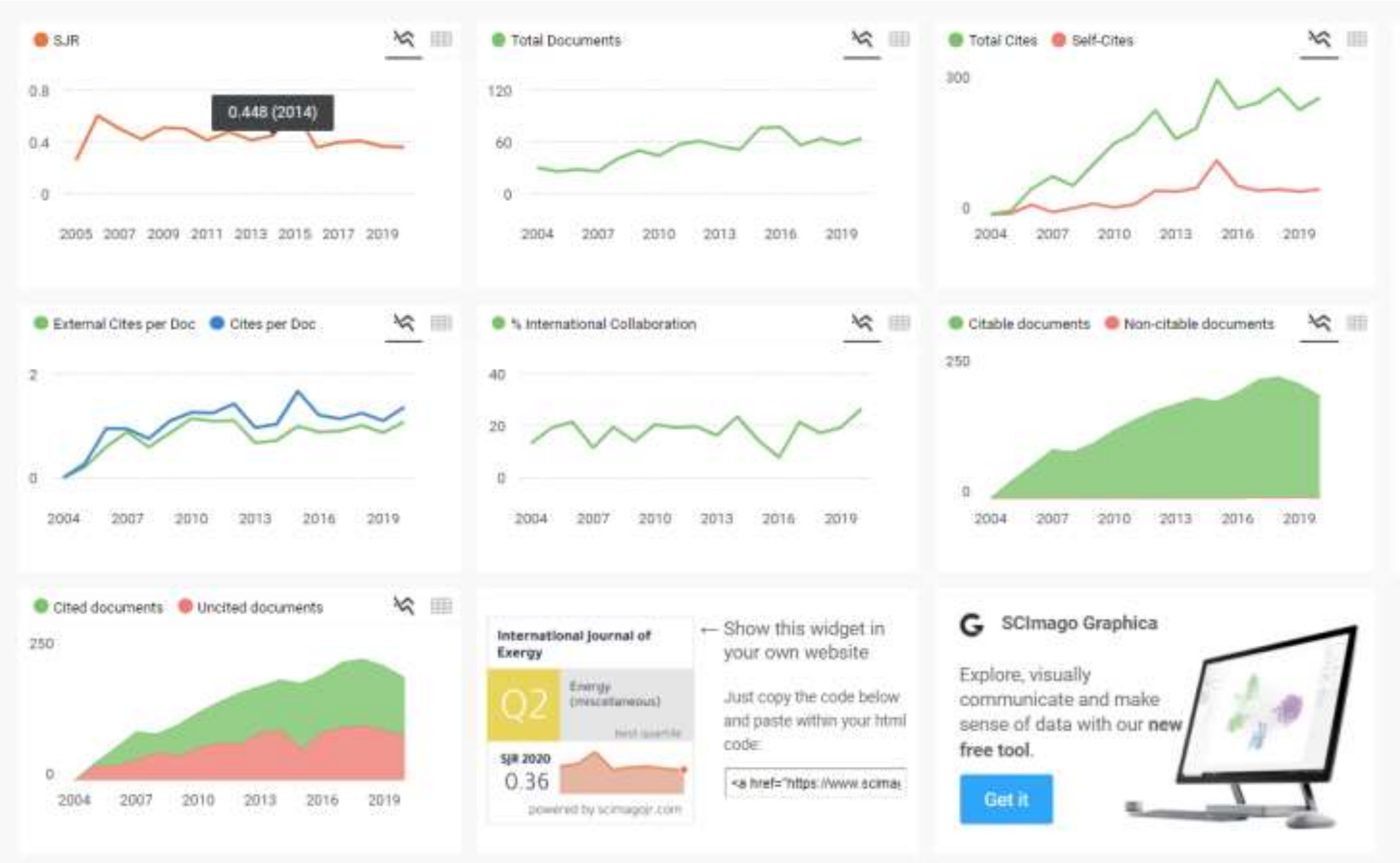

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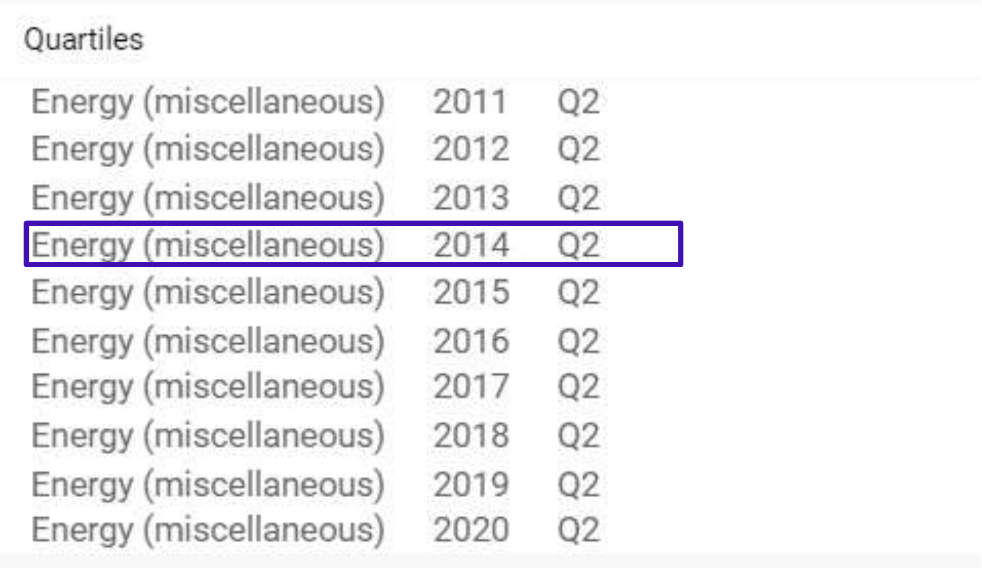

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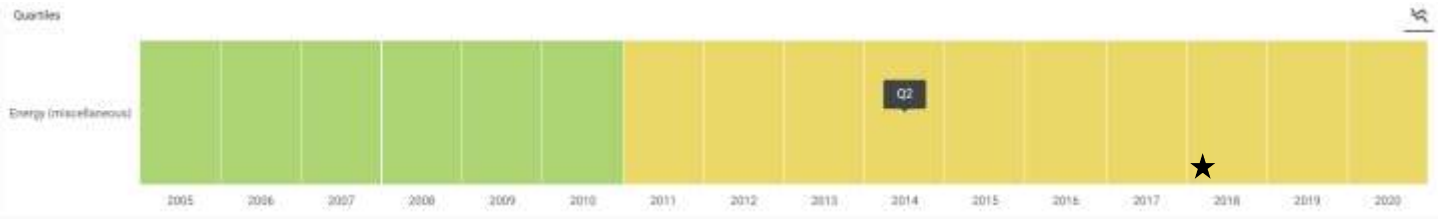

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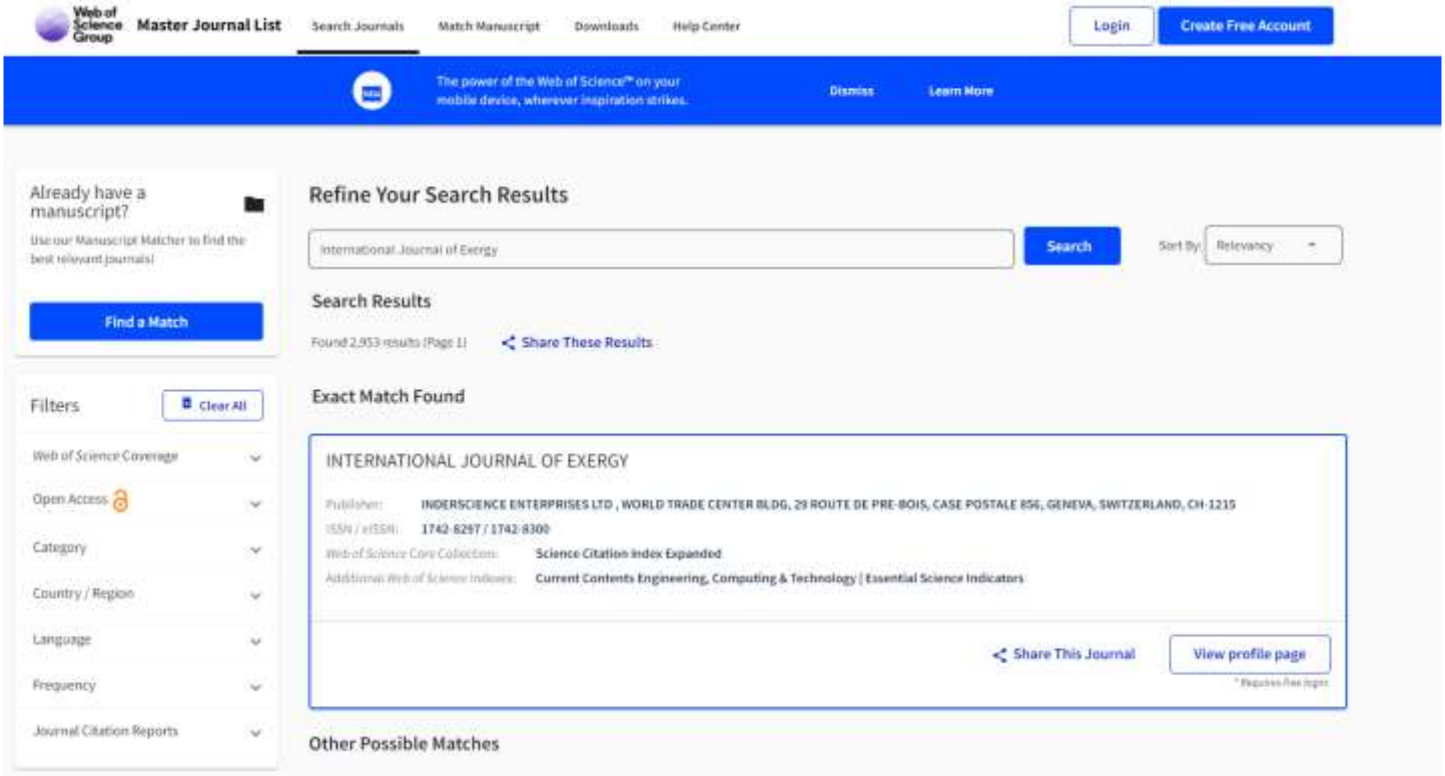

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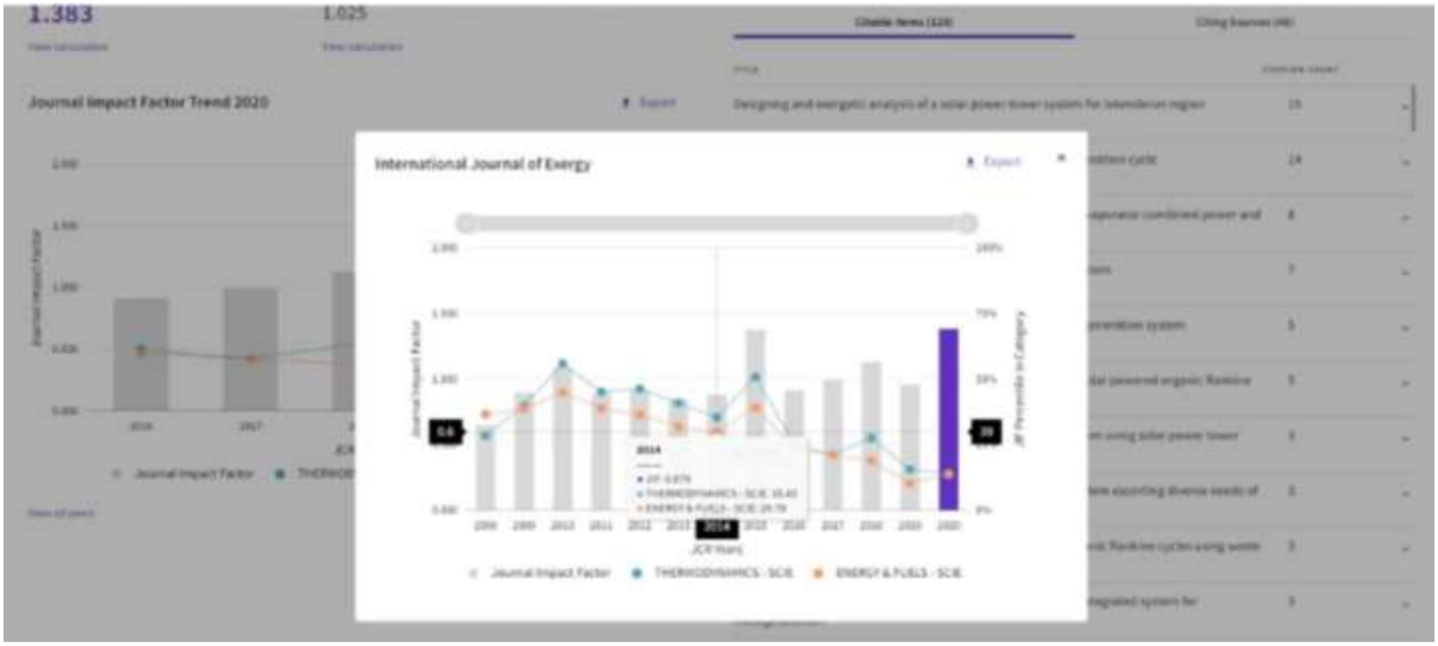

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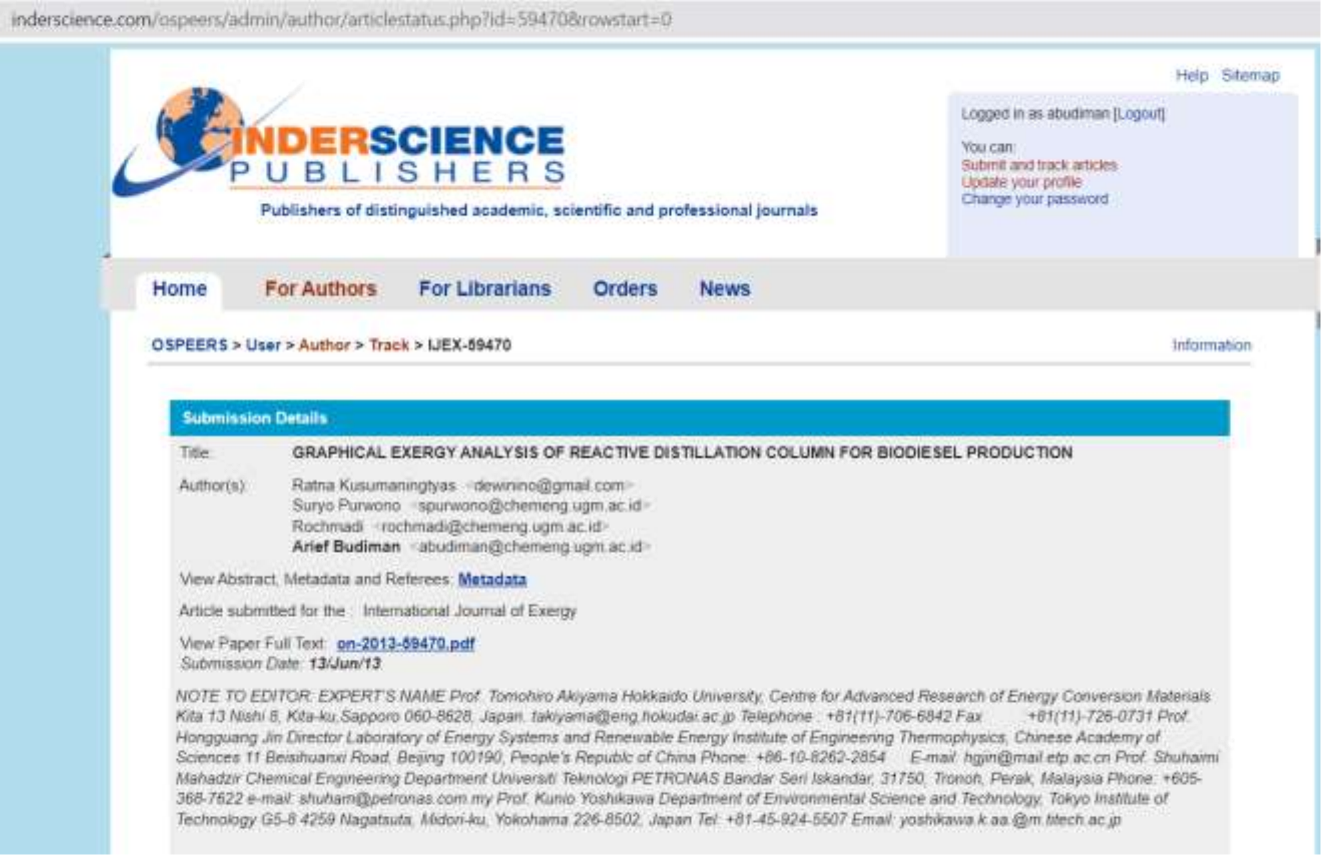

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Author(s):
Ratna Kusumaningtyas <dewinino@gmail.com>
Suryo Purwono <spurwono@chemeng.ugm.ac.id>
Rochmadi <rochmadi@chemeng.ugm.ac.id>
Arief Budiman <abudiman@chemeng.ugm.ac.id>

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NOTE TO EDITOR: EXPERT'S NAME Prof. Tomohiro Akiyama Hokkaido University, Centre for Advanced Research of Energy Conversion Materials Kita 13 Nishi 8, Kita-ku,Sapporo 060-8628, Japan. takiyama@eng.hokudai.ac.jp Telephone : +81(11)-706-6842 Fax +81(11)-726-0731 Prof. Hongguang Jin Director Laboratory of Energy Systems and Renewable Energy Institute of Engineering Thermophysics, Chinese Academy of Sciences 11 Beisihuanxi Road, Beijing 100190, People's Republic of China Phone: +86-10-8262-2854 E-mail: hgjin@mail.etp.ac.cn Prof. Shuhaimi Mahadzir Chemical Engineering Department Universiti Teknologi PETRONAS Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia Phone: +605-368-7622 e-mail: shuham@petronas.com.my Prof. Kunio Yoshikawa Department of Environmental Science and Technology, Tokyo Institute of Technology G5-8 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan Tel: +81-45-924-5507 Email: yoshikawa.k.aa.@m.titech.ac.jp

GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi, and Arief Budiman*
Chemical Engineering Department, Faculty of Engineering,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: ratnadewi_unnes@yahoo.co.id
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed Reactive Distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column is performed based on the non-equilibrium model of a three phase packed RD system. The graphical Ex-N-A method is utilized to evaluate exergy features of the internal RD column. This technique is rigorous to demonstrated the value of exergy losses at each increment of the column, *i.e.* losses due to the temperature change, phase change, mixing in liquid and vapour phases, and chemical reaction. The effects of the the molar ratio of the reactant and the height of the packed column to the conversion and exergy losses are examined and displayed in a simple figure.

Key words: Exergy analysis, reactive distillation, esterification, Ex-N-A, biodiesel

Biographical notes: Ratna Dewi Kusumaningtyas is a PhD students at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor’s and Master’s Degree from the same department in 2000 and 2004, respectively. She is also an Erasmus Mundus Euro Asia awardee for PhD exchange program in Politecnico di Torino, Italy (2010-2012). She is author and co-author of 12 journal and international conference paper during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD Degree from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario, Canada (1993). His research focuses on distillation, petroleum, and renewable energy development. He is author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi is Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK (1991). His research topic is polymer and biofuel development. He is author or co-author of 55 scientific papers.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan (1997). His research focuses on thermodynamics and exergy analysis for system engineering. He is author or co-author of 30 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009, and 2011) and Visiting Professor at Kyushu University (2012).

EXPERT'S NAME

Prof. Tomohiro Akiyama
Hokkaido University,
Center for Advanced Reserch of Energy Conversion Materials
Kita 13 Nishi 8, Kita-ku,Sapporo
060-8628, Japan. takiyama@eng,hokudai.ac.jp
Telephone : +81(11)-706-6842
Faz :+81(11)-726-0731
Expertise: Development materials for dense storage, transportation and efficient conversion of energy from the viewpoints of cascade utilization and process integration.

Relationship: I visited his laboratory in 2005 and we organized Japan-Indonesia Bilateral Symposium on Sustainable engineering that be held in Yogyakarta, Indonesia, on May 14, 2007.

Prof. Hongguang Jin
Director Laboratory of Energy Systems and Renewable Energy
Institute of Engineering Thermophysics, Chinese Academy of Sciences
11 Beisihuanxi Road, Beijing 100190, People's Republc of China
Phone: +86-10-8262-2854 E-mail: hgjin@mail.etp.ac.cn
Expertise: Developments and innovations in energy and power systems. He published exergy paper in several journals.
Relationship: He was my research partner when I was doctor student in Tokyo Institute of Technology, Japan (1994-1997)

Prof. Shuhaimi Mahadzir
Chemical Engineering Department
Universiti Teknologi PETRONAS
Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia
Phone: +605-368-7622
e-mail: shuham@petronas.com.my
Expertise: Energy efficient processes. He published energy-exergy paper in several journals.
Relationship: I visited his department as an external examiner for his PhD student (September 2012)

Prof. Kunio Yoshikawa
Department of Environmental Science and Technology,
Tokyo Institute of Technology G5-8
4259 Nagatsuta, Midori-ku,
Yokohama 226-8502, Japan
Tel: +81-45-924-5507
Fax: +81-45-924-5518
Email: yoshikawa.k.aa.@m.titech.ac.jp
Expertise: Separation process, biodiesel technology. He published related paper in several journals.
Relationship: I visited his laboratory as visiting professor (Dec 2012)

Finally, this article is our original unpublished work and it has not been submitted to any other journal for review.

Sincerely,
Arief Budiman

GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed Reactive Distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column is performed based on the non-equilibrium model of a three phase packed RD system. The graphical Ex-N-A method is utilized to evaluate exergy features of the internal RD column. This technique is rigorous to demonstrated the value of exergy losses at each increment of the column, *i.e.* losses due to the temperature change, phase change, mixing in liquid and vapour phases, and chemical reaction. The effects of the the molar ratio of the reactant and the height of the packed column to the conversion and exergy losses are examined and displayed in a simple figure.

Key words: Exergy analysis, reactive distillation, esterification, Ex-N-A, biodiesel

1. Introduction

Reactive Distillation (RD) is a promising alternative process for equilibrium limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dimian *et al*., 2009; Dragomir and Jobson, 2005; Gomez-Castro *et al*., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognized as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient to examine the energy quantity and quality of a process accurately (Suphanit *et al.*, 2007). This analysis can also facilitate the engineer to identify the specific location and source of inefficiency of the process, and subsequently it plays an important role for designing, developing, optimizing an energy-efficient RD process, (Budiman and Ishida, 2004). as well.

Various method of exergy analysis has been proposed for distillation process. Le Goff *et al*. (1996) introduce the *Carnot factor-specific enthalpy diagram*. This methods is easy to utilize for calculating the exergy target, but it cannot describe the stage by stage exergy characteristic. Later, Dhole and Linnhoff (1993) propose a procedure for composing a T-H curve called the *Column grand composite curve* or the CGCC. Demirel (2006) suggest that the CGCC and exergy loss profiles is useful for exploring the energy-saving potential, determining the targets for column modifications, and recommending a retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method is developed by Taprap & Ishida (1996), named *Energy Utilization Diagram* (EUD). This method is functional for analyzing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXL), namely EXL due to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenience when the number of plates in a column is increased. The EUD method is then modified by Budiman dan Ishida (1998) into a more compact graphical method called *Integrated Energy Utilization Diagram* (IEUD). This method exhibits all the different types of exergy losses in a simple diagram. The IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance.
To overcome this drawback, Budiman and Ishida (2004) introduce the *Material-Utilization Diagram* (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-process exergy loss is much larger than the other. Therefore, it is necessary to compose such a simpler and easy to understand diagram for a complex RD process. For that reason, the application of Ex-N-A method for exergy analysis in RD system is studied in this work. The graphical Ex-N-A is constructed to display the exergy characteristic of a packed RD column in a simpler diagram. This graphical diagram is easy to understand even in a case when one of the sub-process exergy loss is much larger than the other.

A thermodynamic analysis using the graphical Ex-N-A Diagram to a packed RD column for biodiesel production is performed in this work. Biodiesel is produced via an esterification reaction of fatty acid with methanol. This route is preferred rather than transesterification of triglyceride scheme since today employing waste and non-edible feedstock is an obligatory to meet with the ecological and ethical requirement for bio-fuels (Dimian *et al.,* 2009). Waste oil and low grade feedstock contains a considerable value of free fatty acid (FFA). Therefore, the esterification of fatty acid will be the best scheme for biodiesel production using waste and non-edible oil as feedstocks. Biodiesel production in this work is carried out continuously using packed RD column. The non-equilibrium (NEQ) model with three phase approach is applied for the RD system. The combination of the three phases and NEQ models has been previously studied by Higler *et al.* for a distillation system without any reaction involved in the system (2004). This paper is aimed at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the packed RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss are also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the reaction conversion as well as improve the energy efficiency of the RD system.

2. Model and Simulation for Reactive Distillation Column

A packed RD column is utilized for the biodiesel production via fatty acid esterification. In this case, oleic acid is taken as a compound representing the FFA. As a case study, esterification of oleic acid and methanol in the present of solid acid catalyst namely acid ion-exchange polymeric resin of relite CFS (Tesser *et al.,* 2005) in a packed RD column is examined. The generic esterification reaction between a fatty acid and methanol, which is the most used alcohol, is shown below:

$$\mathrm{RCOOH\ (A)\ +\ CH_3OH\ (B)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCOOCH_3\ (C) + H_2O\ (D)} \qquad (1)$$

For the RD simulation, the following pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser *et al.* , 2005)

$$r = \left(k_1 x_A x_B - k_2 x_C x_D\right) C_{cat} \qquad (2)$$

The values of the pre-exponential factors (k_0) and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction results slightly endothermic with ΔH_r = 2.68 kcal/mol.

Table 1. Kinetic parameters of the pseudo-homogeneous model

	Ln k_0	E_a (kcal/mol)
k_1 (mol·cm^3·g$_{cat}^{-2}$·min^{-1})	12.93	14.00
k_2 (mol·cm^3·g$_{cat}^{-2}$·min^{-1})	8.76	11.32

The compounds involved in the reaction is oleic acid and methanol as reactant, on the other hand water and methyl oleate (biodiesel) as products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 2. Molecular structure and normal boiling points of all the chemical compounds

Oleic Acid (A)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	T_b=359.85 °C
Methanol (B)	CH_3OH	T_b=64.7 °C
Methyl-oleate (C)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	T_b=343.85 °C
Water (D)	H_2O	T_b=100.0 °C

The esterification reaction is carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top are condensed, subsequently they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the the column, on the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in **Figure 1**. The RD Column is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the column starts from the top, hence N = 0 meter is the top of the column and N = n meter is the lowest part of the column. The base case condition employs the packed column with the height of 3 meter with the column diameter of 0.5 m. The ratio of oleic acid and total methanol entering the column is set constant 2:1 inside the column. Flowrate of oleic acid introduced to the column is 300.00 kmole/ hr and total methanol inputted to the column is 600 kmole/ hr. The flowrate of the total vapor leaving the column is 666 kmole/ hr and the flowrate of the product discharging from the reboiler is 250.26 kmole/ hr.

The simulation of the packed RD column is performed based on the novel NEQ model combined with three phase approach. The unit cell for the NEQ model for threephase RD is shown in **Figure 2.** It is an innovative approach for a packed RD simulation since the previous work using this sophisticated approach has merely been proposed for the conventional tray distillation column (Higler, 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester, and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible and will separate into two liquid phases. Thus, the three phases are defined as vapour phase which contains only methanol and water, alcoholic liquid phase which contains mainly water and methanol, and organic liquid phase which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

The equations applied for the NEQ model of three phase RD are summarized as follows. The mass balances of each compounds in the vapour, Liquid-1, and Liquid-2 phases are formulated in the equations (3), (4), and (5), respectively:

$$\frac{dy_j}{dz} = \frac{\left(-R_{j,G}\right) - y_j \dfrac{dV'}{dz}}{V'} \tag{3}$$

$$\frac{dx_j}{dz} = \frac{-\left(-R_{j,L_1}\right) - x_j \dfrac{dL_1'}{dz}}{L_1'} \tag{4}$$

$$\frac{dx_j}{dz} = \frac{-\left(-R_{j,L_2}\right) - x_j \dfrac{dL_2'}{dz}}{L_2'} \tag{5}$$

Meanwhile, the total mass balance of the vapour, Liquid-1, and Liquid-2 phase are presented in the equations (6), (7), and (8), respectively:

$$\frac{dV'}{dz} = -\sum R_{j,G} \tag{6}$$

$$\frac{dL_1'}{dz} = -\left(-\sum R_{j,L_1}\right) \tag{7}$$

$$\frac{dL_2'}{dz} = -\left(-\sum R_{j,L_2}\right) \tag{8}$$

To solve the equations (3) to (8), the rate processes equations are necessary. The rate processes equations for the gas, Liquid-1, and Liquid-2 phases are equations (9), (10), and (11), respectively.

$$R_{j,G} = -\left(N_j^{GL1} + N_j^{GL2}\right) \tag{9}$$

$$R_{j,L_1} = N_j^{GL1} - N_j^{L1L2} \qquad (10)$$

$$R_{j,L_1} = N_j^{GL2} + N_j^{L1L2} + \upsilon_j Rc \qquad (11)$$

The result outputted from the RD simulation is utilized for the exergy analysis by means of the graphical Ex-N-A methods. The graphical Ex-N-A thermodynamic analysis is a rigorius method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of exergy loss (EXL) at each increment of the RD packed column, i.e. EXL due to the temperature change, phase change, mixing in liquid and vapour phase, and chemical reaction. The loss in reboiler and condenser are also examined. EffectS of the main parameters, specifically molar ratio and the column height, on the conversion and exergy loss inside the column are also analyzed incremently.

3. Graphical Ex-N-A Methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Srinophakun *et al.*, 2001; Suphanit *et al.*, 2007). The formula of non-chemical exergy loss calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, *i.e.* EXL due to the change of the concentration (mixing), phase change of the component, and the temperature change has been described in their work and are adopted for the calculation in this study. On the other hand, the formula for finding out the EXL due to the chemical reaction starts from the concept of the energy level. A new intensive parameter, called availability factor or energy level (A), is explained as (Srinophakun *et al.*, 2001):

$$\boldsymbol{A = \frac{EXL}{\Delta H}} \qquad (12)$$

EXL is then defined by the following equation.

$$\boldsymbol{EXL = \Delta H - T_0 \Delta S} \qquad (13)$$

Hence,

$$\boldsymbol{A \;\; = (1 - T_0 \frac{\Delta s}{\Delta H})} \qquad (14)$$

It illustrates the maximum fraction of energy which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{Chem} = (1 - T_0 \frac{\Delta s}{\Delta H}) \tag{15}$$

On the equilibrium condition in which the reaction doesn't occurs, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T} \tag{16}$$

In this condition, level A can be written as:

$$A \ = (1 - \frac{T_0}{T}) \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{Liq} = (1 - \frac{T_0}{T}) \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{Gas} = (1 - \frac{T_0}{T}) \tag{19}$$

T in the energy level formula depends on the phase. T is gas temperature for the energy level of the gas and liquid temperature for the energy level of the liquid. Meanwhile, the reaction takes place in the liquid phase. Thus, EXL due to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Thus, the EXL loss due to the chemical reaction can be written as:

$$EXL_{Chem} = (A_{Liq} - A_{Chem})\, \Delta H \tag{24}$$

4. Display of Packed Reactive Distillation Column on graphical Ex-N-A Diagram

4. 1. Base Case Analysis

Ex-N-A Diagram is an-exergy features based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation is developed based on the fundamental concept of the previous graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work related to MUD application, Budiman and Ishida (2004), Budiman (2008), and Budiman *et al.* (2011) composes the graph for EXL due to the concentration, phase and temperature change by putting the mole number (n_j) as abscissa and $\Re T_0 ln x_j$ as ordinate for the liquid phase and $\Re T_0 ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A Diagram is made by placing the two types of diagram in a single feature. The height of the column (N) is put as ordinate while the total EXL, the non-chemical reaction EXL, and A (energy level) is placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consist of N as ordinate while total EXL and non chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which N is putted as ordinate and A is set as abscissa. The two other diagram exhibiting the correlation between the column height with the total exergy loss and reaction conversion are also composed.

This Ex-N-A diagram is developed by adopting the principle of energy-utilization diagrams (EUD). The EUD methodology, proposed by Ishida (1982), has a fundamental concept based on the combination of the first law and the second law of thermodynamics. In EUD technique, its abscissa shows the amount of the transformed energy/enthalpy of the process. Every process must donate or accept energy. The process donating energy is called the energy donor and the one accepting energy is called the energy acceptor. The energy level difference between A_{Ga} and A_{Liq} ($A_{Gas} – A_{Liq}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). This graphical methodology can exemplifies the driving force as the energy level difference and exergy consumption as the shaded area in the diagrams.

In composing the Ex-N-A diagram, column height (N) is plotting as abscissa against the total EXL, non-chemical reaction EXL, and energy level. Based on this diagram, the graphical correlation between total EXL, non-chemical reaction EXL, and energy level difference between gas and liquid (A_{gas}-A_{liq}) is revealed incremently along the column. The Ex-N-A diagram is illustrated in the form of a bar graph and it consists of the two graphs, namely the Ex-N and the N-A graphs. The Ex-N graph also splitted into two types of Ex-N graph. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL due to the chemical reaction, and non-chemical EXL (*i.e* losses due to the temperature change, mixing, and phase change) incremently from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, *i.e.* losses due to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase, and temperature change in the gas phases, are illustrated in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non chemical reaction EXL.

It consists of losses due to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase, and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incremently. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is put at the lower position. Based on this N-A graph, the energy level difference between gas and liquid (A_{gas}-A_{liq}) incremently can be exposed.

Figure 3 demonstrates the Ex-N-A Diagram over the whole column for the base case studied when the height of the column (N) is 3 meter and the molar ratio of methanol to oleic acid is 2:1, which results in total oleic acid conversion of 30.76 %. The EXL profile shows large EXL at the condenser and reboiler compared to the other parts of the column. This is as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s while in condenser is 769351.3847 J/s. In **Figure 3a**, EXL of the reboiler and condenser are shown by the scale of 1/5 because of their large values. The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa *et al.* (2010).

The incremently assessment on the RD column using Ex-N-A Diagram is also depicted in **Figure 3**. The Ex-N diagram in **Figure 3a** shows on that the non chemical EXL, *i.e.* the summation of EXL due to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, start from N= 2 meter from the top, the non-chemical exergy loss turns into a very small quantity. This tendency agrees with the A-N Diagram in **Figure 3b**, which displays the profile of the energy level difference between gas and liquid (A_{gas}-A_{liq}) inside the column or so-called driving force. The energy level difference between gas and liquid strongly corresponds to the temperature profile along the packed RD column. The difference temperature between gas and liquid will result in the difference energy level.

Based on the A-N diagram in **Figure 3b**, it is disclosed that there is a large gas-liquid temperature difference at the top, then it gets smaller towards the bottom. Subsequently, at the height of 2 meter from the top (N=2), the liquid temperature almost reaches the similar temperature to the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, all the losses influenced by temperature is zero, hence simply the EXL due to the mixing which exists at N= 2 meter downwards. EXL due to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL due to the temperature and phase change are absolutely depends on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near equilibrium condition is reached. In this condition, a macro heat transfer between the two phase does not occurs. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium zone, and the second one is the close-to-equilibrium zone.

Two regions, non-equilibrium zone and close to equilibrium zone, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column and the close to equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small difference temperature between gas and liquid, which also results in a very small (near to zero) energy level difference. Pinto *et al.* (2011) calls the condition where the energy level difference or the driving force is very small (or let's say "zero") as the ideal column with minimum thermodynamic condition. This condition has brought about the close-to-equilibrium zone on this lower part of the column. The intensive discussion on close-to-equilibrium zone, or sometimes called as close-to-equilibrium point (CEP), has also been presented by Budiman *et al.* (2011). In their work, CEP has been shown on MUD for the minimum reflux ratio. Budiman *et al.* (2011) and Pinto *et al.* (2011) suggested that the procedure to improve the energy efficiency of distillation columns should involve the use of the so-called minimum thermodynamic condition of columns.

The non-equilibrium zone is emerging at the upper part of the column. At the top of the column, all feed are introduced, both the fresh feed of methanol and oleic acid, as well as the methanol reflux. The abundant liquid stream that enters the column has drastically changed the gas-liquid composition and bring about a distance between the actual condition with the near to equilibrium condition. It also causes an inefficient heat transfer between the gas flowing from the lower increment to the liquid stream. Thus, there will be a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is depicted by the large energy level difference (driving force) between gas and liquid at the top of the column (A-N Diagram in **Figure 3b**). The difference energy level is decreasing from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the Close-to-Equilibrium zone. The profile of A-N diagram agrees with the non-chemical reaction exergy loss profile as demonstrated on Ex-N diagram in **Figure 3a**. The diagram show that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on the packed RD column design and modification.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis due to the chemical reaction. However, assessment on the EXL loss due to chemical reaction incremently never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N Diagrams in **Figure 3b** exhibits a different tendency between the profile of the total EXL and EXL due to the chemical reaction on one side, and EXL due to non-chemical reaction on the other side. The profile of total EXL and EXL due to chemical reaction is increasing from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL due to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL due to chemical reaction profile.

Based on the Ex-N diagram, it is revealed that the amount of EXLs due to chemical reaction is increasing from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher mole reacts, the higher EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL due to chemical reaction as well as the total EXL increase from the top to the bottom.

Fitzmorris and Mah (1980) underlines that analyzing EXL in a distillation column can provide a useful understanding and insights, which will lead to a better design of a distillation system. Thus, in order to acquire an in-depth understanding of the thermodynamic aspects of the packed RD column, examination on the influence of the main process parameters should be conducted. The parameters observed in this study are molar ratio of the reactants and height of the column (N). The knowledge of their influence on the RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimization graphically.

4. 2. Effect of the Molar Ratio of the Reactants inside the Packed RD Column

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, firstly, the molar ratio of methanol and oleic acid in the whole column is changed from 2:1 to 6:1 at the same column height 3 meter (N = 3). By employing the molar ratio of 6:1, it is exhibited that the reaction conversion enhances about twice times from 30.76% to 66.41%. However, the Ex-N diagram in **Figure 4a** demonstrates that the profile of non-chemical EXL does not change so much compared to the result given by the molar ratio of 2:1. At molar ratio of 6:1, the area in the packed RD column is split into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, and the upper part is non-equilibrium zone. However, enhancing molar ratio from 2:1 to 6:1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in **Figure 4b** shows that, when molar ratio of 6:1 is applied, the close-to-equilibrium zone start at N = 0.75 meter downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the non-equilibrium zone inside the column. The larger area of the close-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact of the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force near to zero, the equilibrium condition will be easier to reach. Consequencly, the region of close to equilibrium point is getting larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1:1 with N = 3. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the close-equilibrium-point cannot be reach with this low molar ratio. As shown on the A-N diagram in the **Figure 5b**, all the area in RD column is non-equilibrium zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses due to mixing, phase, and temperature change) along the column. The amount of non-chemical reaction EXL is decreasing from the top to the bottom.

To evaluate the impact of varying the molar ratio on the value of the EXL due to the chemical reaction, both the diagrams in **Figures 4 and 5** are examined. It is exhibited on the Ex-N Diagram in **Figures 4 and 5**, the EXL due to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in **Figure 5**, when the molar ratio of 1:1 is employed, the Ex-N profile is almost similar to that resulted by applying molar ratio of 2:1.

However, if molar ratio of the reactants is drastically enhanced to 6:1, the new Ex-N profile seems interesting. EXL due to the chemical reaction is getting higher from the top downward as seen on the Ex-N Diagram in **Figure 4**. In spite of this, at a certain point in the column, EXL due to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL due to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase is easier. An excellent dispersion of methanol in the organic phase leads the reactants to reacts easily. Consequently, from the top downward, there is a severe increase on the mole number of reactants involving in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction which results in the decreasing of the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL due to chemical reaction in the column. It can be observed that EXL due to the chemical reaction increases significantly at each increment on the upper part of the column, but at a certain point it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. **Figure 6** presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit both for the RD performance and the thermodynamic aspect.

4. 3. Effect of the Height of the Column

The subsequent important aspect to analyzed is the height of the packed column (N). To study this parameter, N is increased from 3 to 6 meter with the similar reactants molar ratio of 2:1. It is revealed that the reaction conversion is enhanced from 30.76 to 58.52%. On the other hand, the result of the thermodynamic evaluation is presented in **Figure 7**. The Ex-N in **Figure 7a** shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared to the profile of the column with the height of 3 meter (N = 3). The highest value of non-chemical EXL occurs at the top of the column, then it is decreasing downward. Subsequently, starting from the N = 2 meters from the top, EXL of the sub processes which depends on temperature (loss due to temperature and phase changes) are approaching zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N Diagram in **Figure 7b**. It is shown that the energy level difference between gas and liquid is decreasing from the top downward. Then, starting at N = 2 meter downward, the energy level difference values near to zero. Thus, the area in the column can be separated into two regions, *i.e*. the non-equilibrium zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to N = 2, while the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the non equilibrium zone area, it just prolong the close-to-equlibrium zone. The existing of non equilibrium region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flowrate will provide more influence on it than the variation on the column height.

Effect of the column height (N) on the EXL due to the chemical reaction is also evaluated. The Ex-N Diagram in **Figure 7** presents the profile of EXL due to the chemical reaction. It is exposed that EXL due to the chemical reaction increases from the top downward. When it reaches the increment of N = 2, EXL due to the chemical reaction values almost constant, and finally it decreases at N = 4 to bottom. EXL due to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column is increasing from the top downward. However, at a certain height from the top, the remaining moles of the unreacted oleic acid does not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared to the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. **Figure 8** discloses that the increasing on the column height leads to the higher reaction conversion and the larger total EXL. Thus, the best point yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Conclusively, there are some finding obtained by analyzing the influence of the reactant molar ratio and the height of the column. Based on the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at the different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen the EXL. It probably facilitates to decrease the driving force and enlarge the close-to-equilibrium region inside the column. This suggestion agrees with the study on exergy analysis using MUD on distillation column proposed by Budiman *et al.* (2011). Besides this way, the optimum efficiency of the RD can be achieved by determining the best height of the column which result in low EXL but high reaction conversion. The other alternative way to improve the reaction performance and reduce EXL loss is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto *et al.* (2011), or by introducing higher fresh feed stream.

Conclusions

A graphical methods called Ex-N-A Diagram has been applied to assess the performance and efficiency of a packed RD column. This technique can display the reaction performance, EXL and energy level characteristic on each increment over the whole packed RD column. This graphical technique also capable to present the exergy characteristic feature in a simple way, easy to understand, even when one of the sub-process has a much larger EXL than the other. In this study, EXL due to the chemical reaction gives the dominant contribution to the total EXL compared to the other sub-process. In this work, a parametric analysis of the effect of column height and the molar ratio of methanol to oleic acid feed on the performance of the system has been conducted in order to find the optimal conditions both from the exergy viewpoint and from the oleic acid conversion viewpoint. It is summarized that by increasing the molar ratio of the reactant and determining the optimum column height, the high reaction conversion and low EXL can be achieved. Conclusively, the graphical Ex-N-A method is an effective tool to analyze the thermodynamic and reaction performance of a packed RD column. This method is also designed to display the graph in a simple way, which is easy to understand even supposing in the condition when one sub-process EXL is much higher than the other. By means of this method, a designer can judge the process feasibility and perform the optimization graphically and intuitively.

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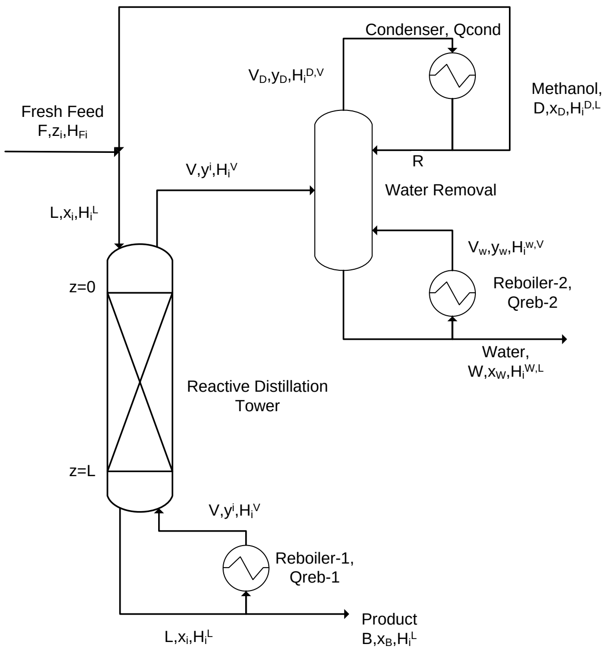


Figure 1. The Configuration of Packed RD Column for Biodiesel Production

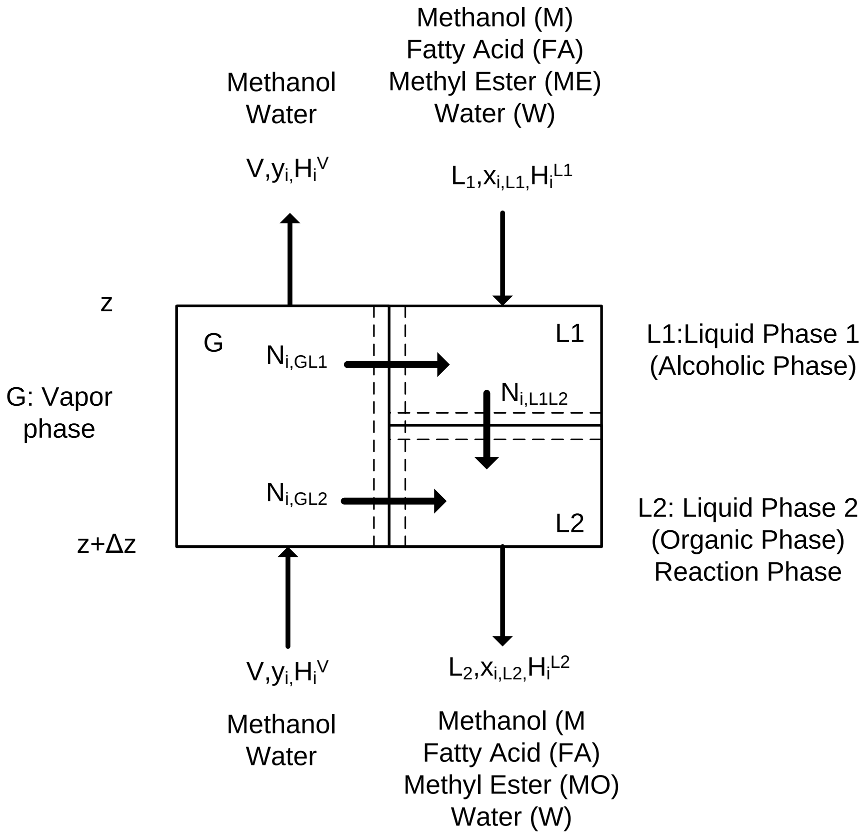
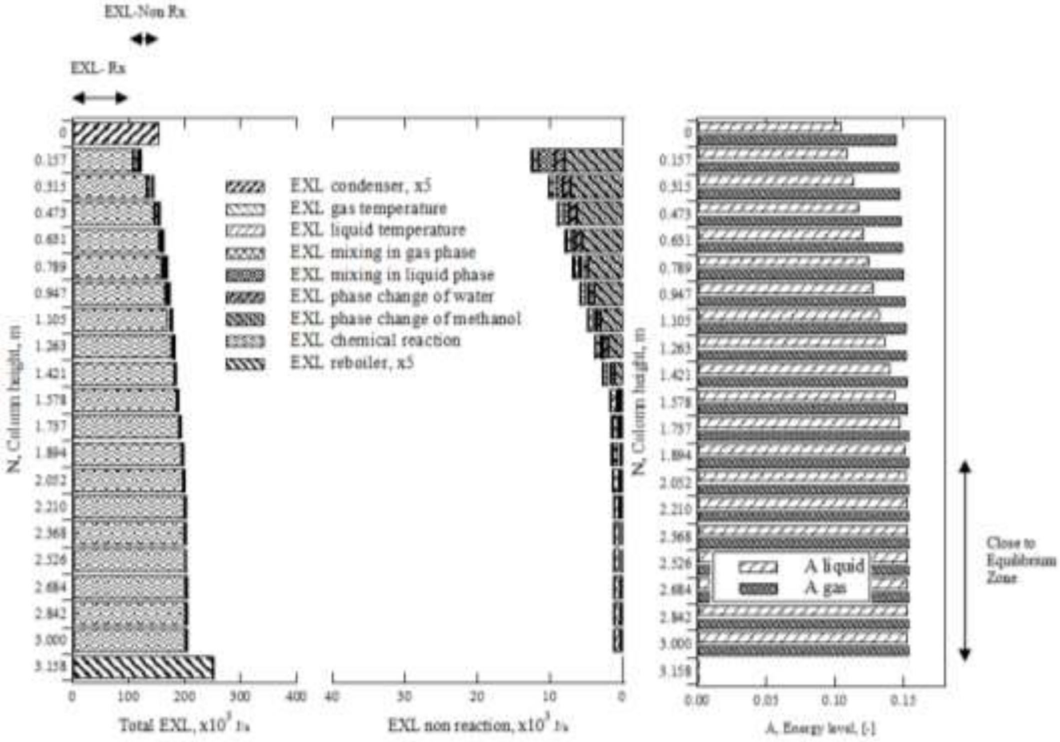
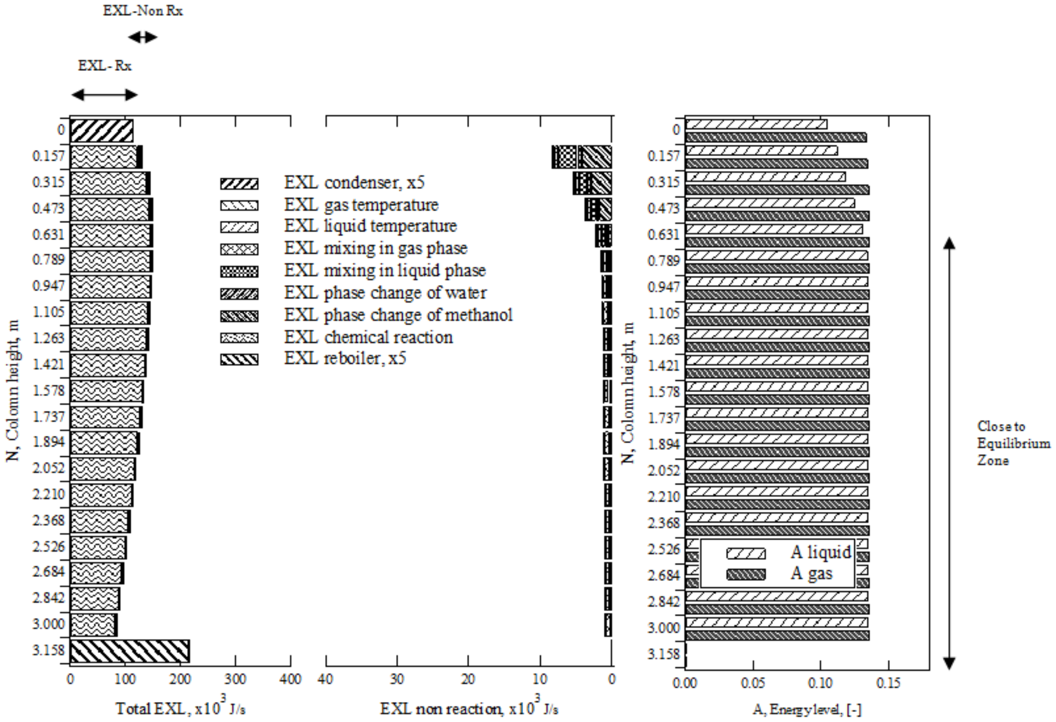


Figure 2. Schematic Representation of One Cell of Three-Phase Packed RD Column



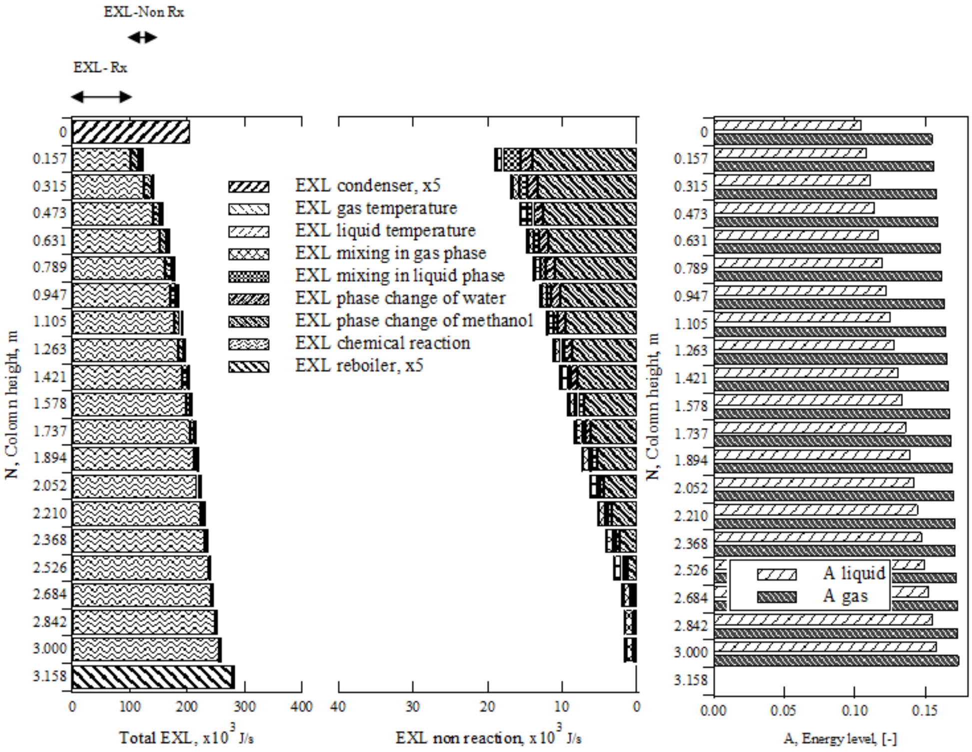
a. Ex-N Diagram **b. A-N Diagram**

Figure 3. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 2:1 at N = 3 m



a. Ex-N Diagram **b. A-N Diagram**

Figure 4. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 6:1 at N = 3 m



a. Ex-N Diagram

b. A-N Diagram

Figure 5. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 1:1 at N = 3 m

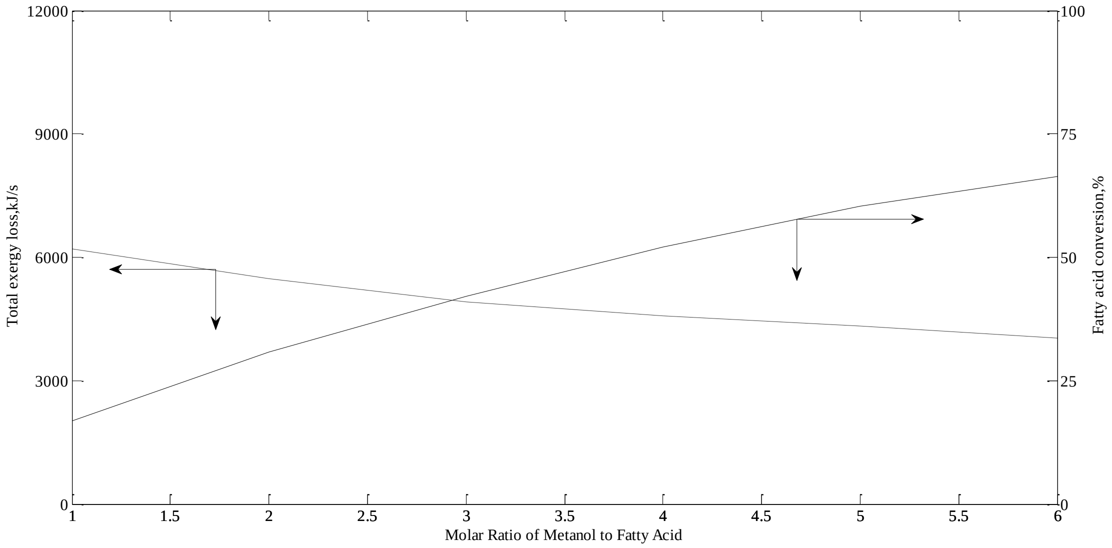
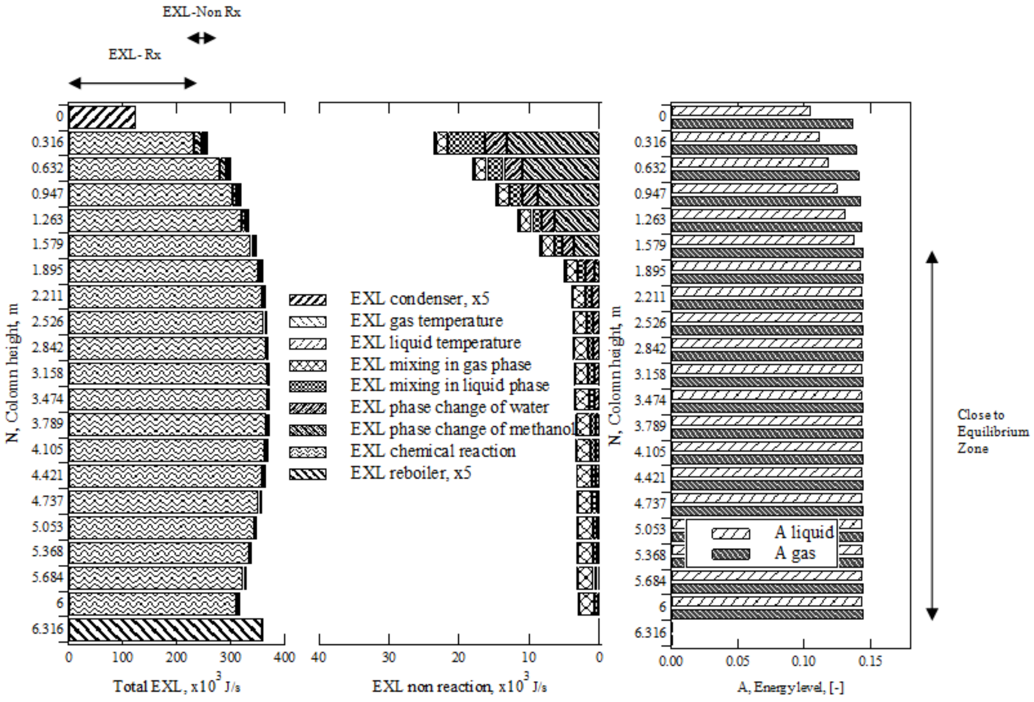


Figure 6. Profile of Total Exergy Loss and Fatty Acid Conversion at Different Reactant Molar Ratio



a. Ex-N Diagram d. A-N Diagram

Figure 7. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 2:1 at N = 6 m

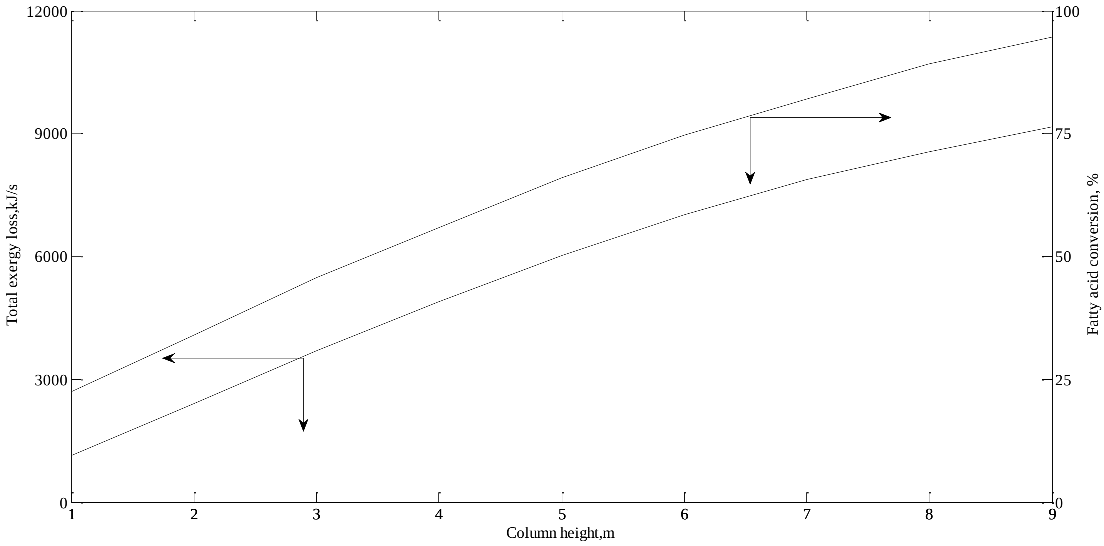


Figure 8. Profile of Total Exergy Loss and Fatty Acid Conversion at Different Column Height

dewinino <dewinino@gmail.com>

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dewinino <dewinino@gmail.com>

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To: Prof Suryo Purwono <spurwono@chemeng.ugm.ac.id>, Ratna Dewi Kusumaningtyas <dewinino@gmail.com>, Prof Rochmadi <rochmadi@chemeng.ugm.ac.id>, Prof Arief Budiman <abudiman@chemeng.ugm.ac.id>, "Prof. Dr. Ibrahim Dincer" <Ibrahim.Dincer@uoit.ca>

Dear Author(s),

We have received the review reports for your paper "GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION".

We require now that you implement in your submission the following recommendations made by the reviewers:

Reviewer A Comments:
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Changes which must be made before publication:
1) Include biographical sketches (75 words for each author).
2) There are many errors in the equations and texts as there must be a careful check and correction needed. All rate symbols must have dots above.
3) List all assumptions in a reasonably manner.
4) Use SI units only.
5) Explain how this paper differs from the literature works.
6) References are incorrect, incomplete and inconsistent.
7) Include related IJEx references as there are several related to this paper.
8) Check all equations, figures, tables, etc. VERY CAREFULLY.
9) Heat transfer cannot be kW unless it is heat transfer rate. Correct and complete all nomenclature items.
10) Omit trivial information and equations.
11) English editing is necessary.

Reviewer B Comments:
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Suggestions which would improve the quality of the paper:
The combined optimization of molar ratio and height may prove to be more relevant from engineering point of view. Further, design of column may be based on optimal molar fluxes rather than purely based on height and molar ratios. Optimization with respect to molar flux may be attempted.
Changes which must be made before publication:
1. Please check the language and the grammar before final publication.
2. whether the column diameter has been kept same or not while varying the molar ratios needs to be clarified.
3. Incorporation of temperature and concentration data at different levels of column for base case is required for calculation of EXL.
4. Conclusions needs to be more focused with quantitative data.

NOTE: Please send an email to the editor to acknowledge the reception of this email notification. The editor needs to make sure that messages reach the authors and don't delay the review process.

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1) To help the reviewer(s) verify that you have made the required corrections, please append a summary of the modifications made at the beginning of your revised manuscript.

2) Append figures, images and tables at the end of your revised manuscript.

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Your prompt attention is much appreciated.

pp. Prof. Dr. Ibrahim Dincer
Int. J. of Exergy (IJEX)
submissions@inderscience.com

Gmail **dewinino <dewinino@gmail.com>**

Revised manuscript IJEX-59470

dewinino . <dewinino@gmail.com> Wed, Nov 27, 2013 at 11:21 AM
To: "Prof. Dr. Ibrahim Dincer" <Ibrahim.Dincer@uoit.ca>, Submissions Manager <submissions@inderscience.com>
Cc: abudiman <abudiman@chemeng.ugm.ac.id>, suryo purwono <spurwono@chemeng.ugm.ac.id>, rochmadi@chemeng.ugm.ac.id

Dear Prof. Dr. Ibrahim Dincer
Int. J. of Exergy (IJEX)

Thank you very much for the review of our paper.
I here with send the revised manuscript of our paper entitled "GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION".
Would you please also find the bibliographical notes and summary of the modification attached?

For your information, the authors of this paper are:
Ratna Dewi Kusumaningtyas, PhD student (First Author)
Suryo Purwono, Professor
Rochmadi, Professor
Arief Budiman, Professor (Corresponding Author)

We have also uploaded the revised manuscript online on the journal's web in the Pdf format. However, we need need a further information about how to upload the file of the Bibliographical Notes and the Summary of the modification because we cannot find it on the web.

Finally, hopefully that our paper will be considered for to be published in your journal
Thank you very much

Sincerely Yours
Ratna
(Graduate student of Prof. Dr. Eng. Arief Budiman)

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6 attachments

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GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed Reactive Distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium model of a three phase packed RD system. The graphical Ex-N-A method was utilized to evaluate exergy features of the internal RD column. This technique is rigorous to demonstrate the value of exergy losses at each increment of the column, *i.e.* losses due to the temperature change, phase change, mixing in liquid and vapour phases, and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Key words: Exergy analysis, reactive distillation, esterification, Ex-N-A, biodiesel

1. Introduction

Reactive Distillation (RD) is a promising alternative process for equilibrium limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gomez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognized as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing, and optimizing an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various method of exergy analysis has been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot factor-specific enthalpy diagram*. This method is easy to utilize for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *Column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications, and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *Energy Utilization Diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXL), namely EXL due to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenience when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called *Integrated Energy Utilization Diagram* (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the *Material-Utilization Diagram* (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub process EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easy to understand diagram for a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared to the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (N) as ordinate while the total EXL, the non-chemical reaction EXL, and A (energy level) as abscissa. This plotting results in a simple diagram which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL due to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation, and chemical reaction incrementally. And it is yet easy to understand even in a case when one of the sub-process EXL is much larger than the other. This diagram can also obviously exhibit the correlation of the exergy losses due to chemical and non-chemical sub-processes with the energy level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A Diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA will be the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, non-equilibrium (NEQ) model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phases and NEQ model has been merely studied for a distillation process which doesn't involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss are also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2. Model and Simulation for Reactive Distillation (RD) Column

A packed RD column was utilized for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the present of solid acid catalyst namely acid ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in a packed RD column was examined. The generic esterification reaction of an FFA and methanol is shown below:

$$\mathrm{RCOOH\ (A)} + \mathrm{CH_3OH\ (B)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCOOCH_3\ (C)} + \mathrm{H_2O\ (D)} \qquad (1)$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1\, x_A\, x_B - k_2\, x_A\, x_B)\ C_{cat} \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with ΔH_r = 11213.12 J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top are condensed, and are subsequently introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the column starts from the top, hence N = 0 meter is the top of the column, while N = n meter is the lowest part of the column. The base case condition employs the packed column with the height of 3 meter with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2:1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and product discharging from the reboiler are 185 mol/s and 69.52 mol/s, respectively.

The simulation of the packed RD column was performed based on the novel NEQ model combined with three phase approach. The unit cell for the NEQ model for three phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester, and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase which contains only methanol and water, alcoholic liquid phase which contains mainly water and methanol, and organic liquid phase which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

The assumptions taken in this modelling and simulation can be written as follows:

1. In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.
2. The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.
3. The RD column operates at the steady state condition
4. There are three phases which occurs in the system, namely: vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).
5. The reaction takes place in the organic phase (liquid-2)
6. Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.
7. The RD column is modelled based on the NEQ approach. Hence the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three phase RD are summarized as follows. The mass balances of each compound in the vapour, Liquid-1, and Liquid-2 phases are formulated in the equations (3), (4), and (5), respectively:

$$\frac{dy_{i,G}}{dz} = \frac{(-\dot{R}_{i,G}) - y_i \frac{dV'}{dz}}{V'} \tag{3}$$

$$\frac{dx_{i,L_1}}{dz} = \frac{-(-\dot{R}_{i,L_1}) - x_{i'} \frac{dL_1'}{dz}}{L_1'} \tag{4}$$

$$\frac{dx_{i,L_2}}{dz} = \frac{-(-\dot{R}_{i,L_2}) - x_i \frac{dL_2'}{dz}}{L_2'} \tag{5}$$

Meanwhile, the total mass balance of the vapour, Liquid-1, and Liquid-2 phase are presented in the equations (6), (7), and (8), respectively:

$$\frac{dV'}{dz} = - \sum \dot{R}_{i,G} \tag{6}$$

$$\frac{dL'_1}{dz} = -(- \sum \dot{R}_{i,L_1}) \tag{7}$$

$$\frac{dL'_2}{dz} = -(- \sum \dot{R}_{i,L_2}) \tag{8}$$

To solve the equations (3) to (8), the rate processes equations are necessary. The rate processes equations for the gas, liquid-1, and liquid-2 phases are equations (9), (10), and (11), respectively.

$$\dot{R}_{i,G} = - \left(\dot{N}_i^{GL_1} + \dot{N}_i^{GL_2} \right) \tag{9}$$

$$\dot{R}_{i,L_1} = \dot{N}_i^{GL_1} - \dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2} = \dot{N}_i^{GL_2} + \dot{N}_i^{L_1L_2} + v_i \, \dot{r} \tag{11}$$

The result outputted from the RD simulation is utilized for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorius method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e. EXL due to the temperature change, phase change, mixing in liquid and vapour phase, and chemical reaction. The loss in reboiler and condenser are also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3. Graphical Ex-N-A Methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, *i.e.* EXL due to changes of the concentration (mixing), phase of the component, and temperature have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL due to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (A) is explained as (Srinophakun et al., 2001):

$$A = \frac{E\dot{X}L}{\Delta H} \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S \tag{13}$$

Hence,

$$A = (1 - T_0 \frac{\Delta s}{\Delta H}) \tag{14}$$

It illustrates the maximum fraction of energy which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{Chem} = (1 - T_0 \frac{\Delta s}{\Delta H}) \tag{15}$$

On the equilibrium condition in which the reaction doesn't occurs, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T} \tag{16}$$

In this condition, energy level A generally can be written as:

$$A = (1 - \frac{T_0}{T}) \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{Liq} = (1 - \frac{T_0}{T}) \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{Gas} = (1 - \frac{T_0}{T}) \tag{19}$$

T in the energy level formula depends on the phase. T is gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL due to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction.

Hence, EXL loss due to the chemical reaction can be written as:

$$E\dot{X}L_{Chem} = (A_{Liq} - A_{Chem})\,\Delta H \tag{20}$$

4. Display of Packed Reactive Distillation Column on Graphical Ex-N-A Diagram

4. 1. Base Case Analysis

Ex-N-A Diagram is an-exergy features based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008), and Budiman et al. (2011) composed the graph for EXL due to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 ln x_j$ as ordinate for the liquid phase and $\Re T_0 ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A Diagram is made by placing the two types of diagram in a single feature. The height of the column (N) is put as ordinate while the total EXL, the non-chemical reaction EXL, and A (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consist of N as ordinate while total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which N was put as ordinate and A is set as abscissa. The two other diagrams exhibiting the correlation between the column height with total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared to the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL due to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub process EXL is much larger than the other. It also can combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy level difference between A_{Gas} and A_{Liq} ($A_{Gas} - A_{Liq}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy level difference and exergy consumption as the shaded area in the diagrams. Hence, it doesn't clearly show the exergy profile at the difference levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (N) is plotted as abscissa against the total EXL, non-chemical reaction EXL, and energy level. Based on this diagram, the graphical correlation between total EXL, non-chemical reaction EXL, and energy level difference between gas and liquid (A_{gas}-A_{liq}) are incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of sub graphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL due to the chemical reaction, and non-chemical EXL (*i.e* losses due to the temperature change, mixing, and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, *i.e*. EXL due to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, temperature change in liquid phase and temperature change in gas phases, are displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses due to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase, and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. Based on this N-A graph, the energy level difference between gas and liquid (A_{gas}-A_{liq}) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (N) was 3 meter, the column diameter was 0.5 meter and the molar ratio of methanol to oleic acid was 2:1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited on Figures 3, 4 and 5, respectively. These data are required for the EXL calculation.

Figure 6 demonstrates the Ex-N-A Diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared to the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s while in condenser it is 769351.3847 J/s. In Figure 6a, EXL of the reboiler and condenser are shown by the scale of 1/5 because of their large values. The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

The incrementally assessment on the RD column using Ex-N-A Diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6a shows that the non-chemical EXL, *i.e.* the summation of EXL due to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, start from N= 2 meter from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the A-N Diagram in Figure 6b, which displays the profile of the energy level difference between gas and liquid (A_{gas}-A_{liq}) inside the column or so-called driving force. Energy level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy level difference.

Based on the A-N diagram in Figure 6b, it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 meter from the top (N=2), the liquid temperature almost reaches the similar temperature to the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses which are influenced by temperature is zero. Hence, simplyput the EXL due to the mixing which exists at N= 2 meter moved downwards. EXL due to mixing was affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL due to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near equilibrium condition has been reached. In this condition, a macro heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium zone, and the second one is the close-to-equilibrium zone.

Two regions, non-equilibrium and close to equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close to equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small difference temperature between gas and liquid, which also results in a very small (near to zero) energy level difference. Pinto et al. (2011) calls the condition where the energy level difference or the driving force is very small (let's say "zero") as the ideal column with minimum thermodynamic condition. This condition has brought about the close-to-equilibrium zone on this lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes referred to as close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011). In their work, CEP has been shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column all feeds are introduced, explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual with the near to equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy level difference (driving force) between gas and liquid at the column top (A-N Diagram in Figure 6b). In addition, the difference energy level decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the Close-to-Equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6a. Thus, it exhibits that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis due to the chemical reaction. However, assessment on the EXL due to chemical reaction incrementally never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N Diagrams in Figure 6b exhibits a different tendency between the profile of the total EXL and EXL due to the chemical reaction on one side, and EXL due to the non-chemical reaction on the other side. The profile of total EXL and EXL due to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL due to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL due to chemical reaction profile.

Based on the Ex-N diagram, it is revealed that the amount of EXL due to chemical reaction increase from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. As the higher mole reacts, it gives rise to a higher EXL In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL due to chemical reaction as well as total EXL increase from the top to the bottom.

Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, in order to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (N). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimization graphically.

4. 2. Effect of the Molar Ratio of the Reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, firstly, the molar ratio of total methanol and oleic acid entering the column is changed from 2:1 to 6:1 at the same column height of 3 meter (N = 3) and column diameter of 0.5 meter. By employing the molar ratio of 6:1, it is shown that the reaction conversion enhances about twice times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7a shows that the profile of non-chemical EXL does not change so much compared to the result given by the molar ratio of 2:1. At molar ratio of 6:1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, and the upper part is non-equilibrium zone. However, enhancing molar ratio from 2:1 to 6:1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7b shows that, when molar ratio of 6:1 is applied, the close-to-equilibrium zone starts at N = 0.75 meter downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the non-equilibrium zone inside the column. The larger area of the close-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of close to equilibrium point gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1:1 with N = 3. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in the Figure 8b, all the areas in RD column are non-equilibrium zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses due to mixing, phase, and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

To evaluate the impact of varying the molar ratio on the value of the EXL due to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N Diagram in Figures 7 and 8 that the EXL due to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1:1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2:1.

However, if molar ratio of the reactants is drastically enhanced to 6:1, the new Ex-N profile seems interesting. It is shown that EXL due to the chemical reaction gets higher from the top downward as seen on the Ex-N Diagram in Figure 7a. In spite of this, at a certain point in the column, EXL due to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL due to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to reacts easily. Consequently, from the top downward, there is a severe increase in the number of mole reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining un-reacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease of the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL due to chemical reaction in the column. It can be observed that EXL due to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

4. 3. Effect of the Height of the Packed Column (N)

The subsequent important aspect to be analysed is the height of the column (N). To study this parameter, N is increased from 3 to 6 meter with the similar reactants molar ratio of 2:1, while the column diameter is kept the same (0.5 meter). Hence, it reveals that the reaction conversion is enhanced from 30.76 to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N Diagram in Figure 10a shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared to the profile of the column with the height of 3 meter (N = 3). The highest value of non-chemical EXL occurs at the top of the column and then decreases downward. Subsequently, starting from the N = 2 meters from the top, EXL of the sub processes which depends on temperature (loss due to temperature and phase changes) are approaching zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N Diagram in Figure 10b. Nevertheless, it is shown that the energy level difference between gas and liquid decreases from the top downward. Then, starting at N = 2 meter downward, the energy level difference values near to zero. Thus, the area in the column can be separated into two regions, *i.e.* the non-equilibrium zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to N = 2, while the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the non-equilibrium area. It just prolongs the close-to-equilibrium zone. The existing of non-equilibrium region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

Effect of the column height (N) on the EXL due to the chemical reaction is evaluated, as well. Ex-N Diagram in Figure 10 presents the profile of EXL due to the chemical reaction. It is observed that EXL due to the chemical reaction increases from the top downward. When it reaches the increment of N = 2, EXL due to the chemical reaction values remain almost constant, and finally decreases at N = 4 to bottom. EXL due to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared to the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Conclusively, there are some finding obtained by analysing the effects of the reactant molar ratio and column height. Based on the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at the different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5. Conclusions

- A graphical method called Ex-N-A Diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-process has a much larger EXL than the others.
- The base case of the RD simulation was studied at N = 3 meter, the column diameter of 0.5 meter and the molar ratio of methanol to oleic acid of 2:1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s while in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2:1 to 6:1 at the similar N of 3 meter and column diameter of 0.5 meter. By employing the molar ratio of 6:1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1:1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, N is increased from 3 to 6 meter, while the reactants molar ratio and column diameter are kept at 2:1 and

0.5 meter, respectively. This reveals that the conversion is enhanced from 30.76 to 58.52%. Thus, the increase in the column height does not change the non-equilibrium area, nevertheless it just prolong the close-to-equilibrium zone.

- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase
C_{cat}	Concentration of the solid catalyst (kg_{cat} /m^3)
E_a	Activation energies (J/mol)
$E\dot{X}L$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant (mol·m^3/kg_{cat}^2/ s)
k_2	Reverse reaction rate constant (mol·m^3/kg_{cat}^2/s)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component i from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component i from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{L_1L_2}$	Mass transfer rate of component i from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference Temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
dz	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase

L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase
Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Figure 1. The Configuration of Packed RD Column for Biodiesel Production

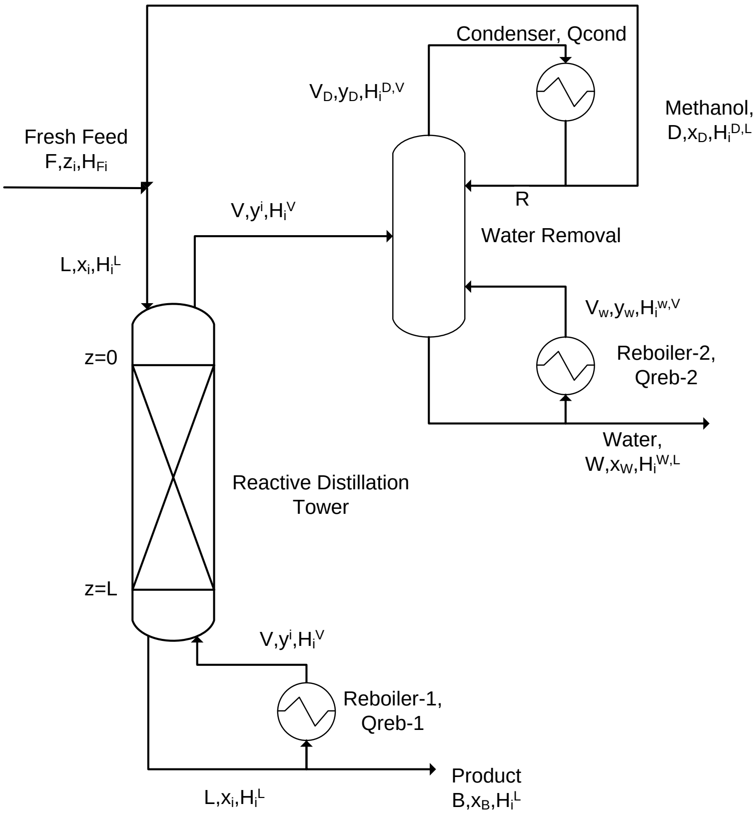


Figure 2. Schematic Representation of One Cell of Three-Phase Packed RD Column

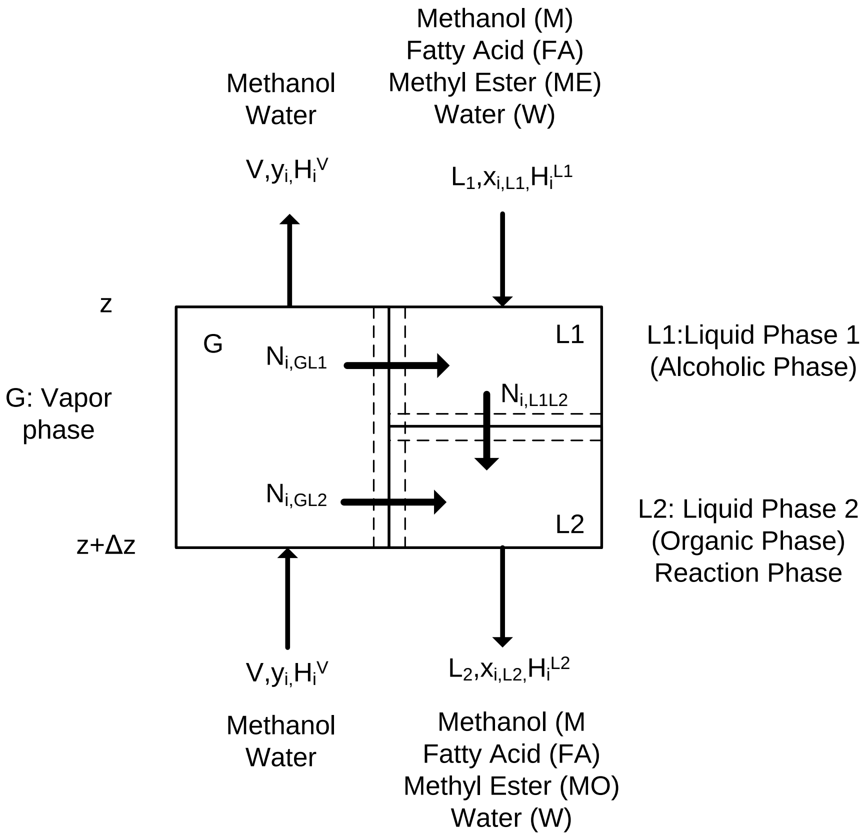


Figure 3. Concentration Profiles of the Compounds in Liquid-1, Liquid-2 and Vapour Phases at Different Column Height

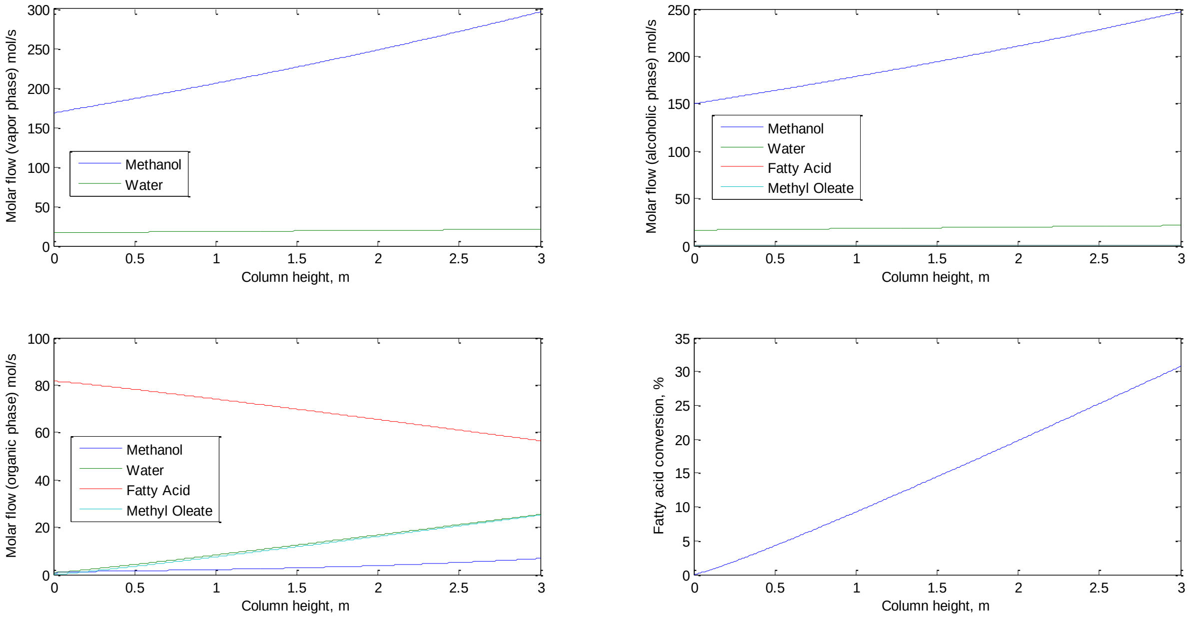


Figure 4. Total Molar Flow of Each Phase at Different Column Height

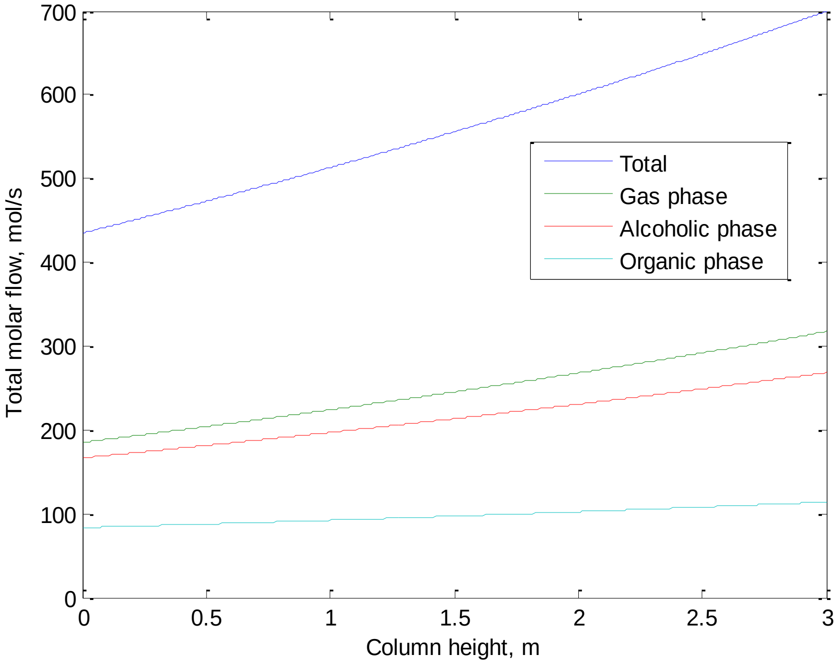


Figure 5. Temperature Profile of Liquid and Vapour Phase at Different Column Height

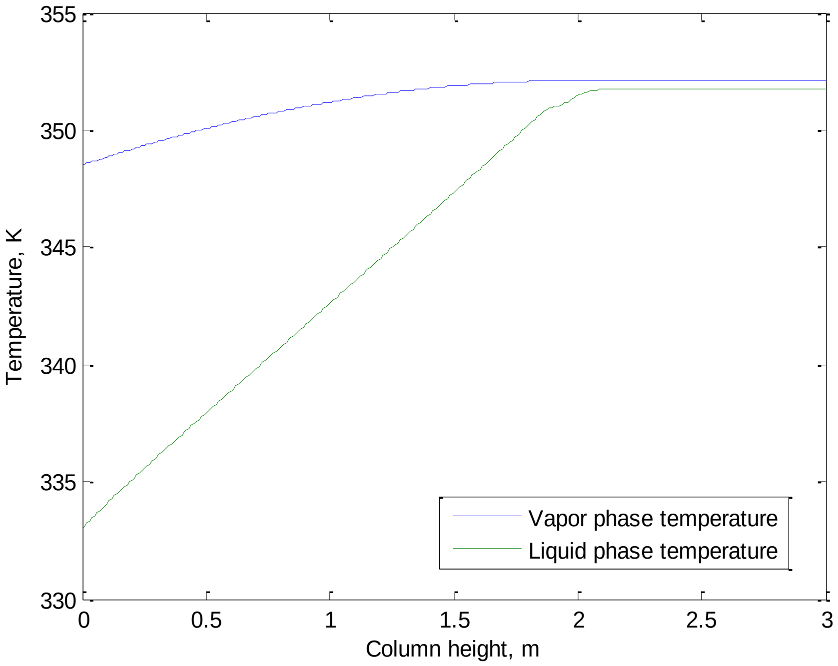
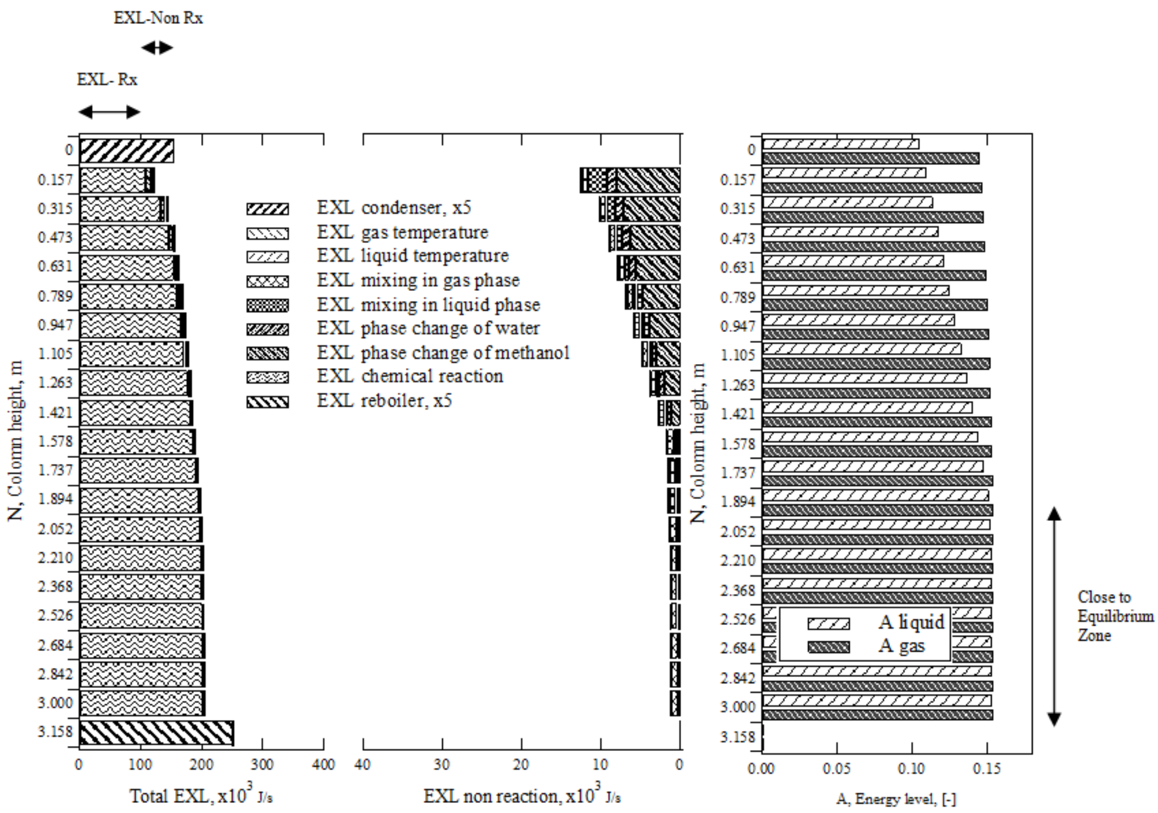
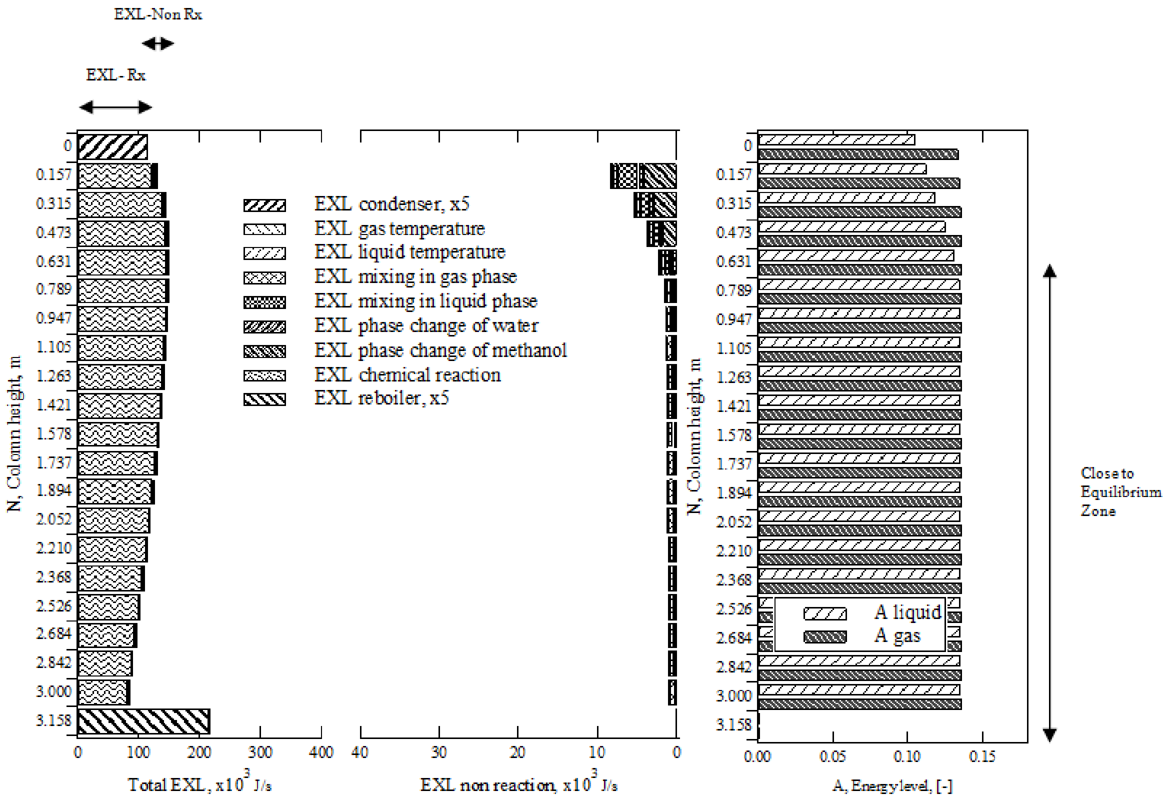


Figure 6. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 2:1 at N = 3 m



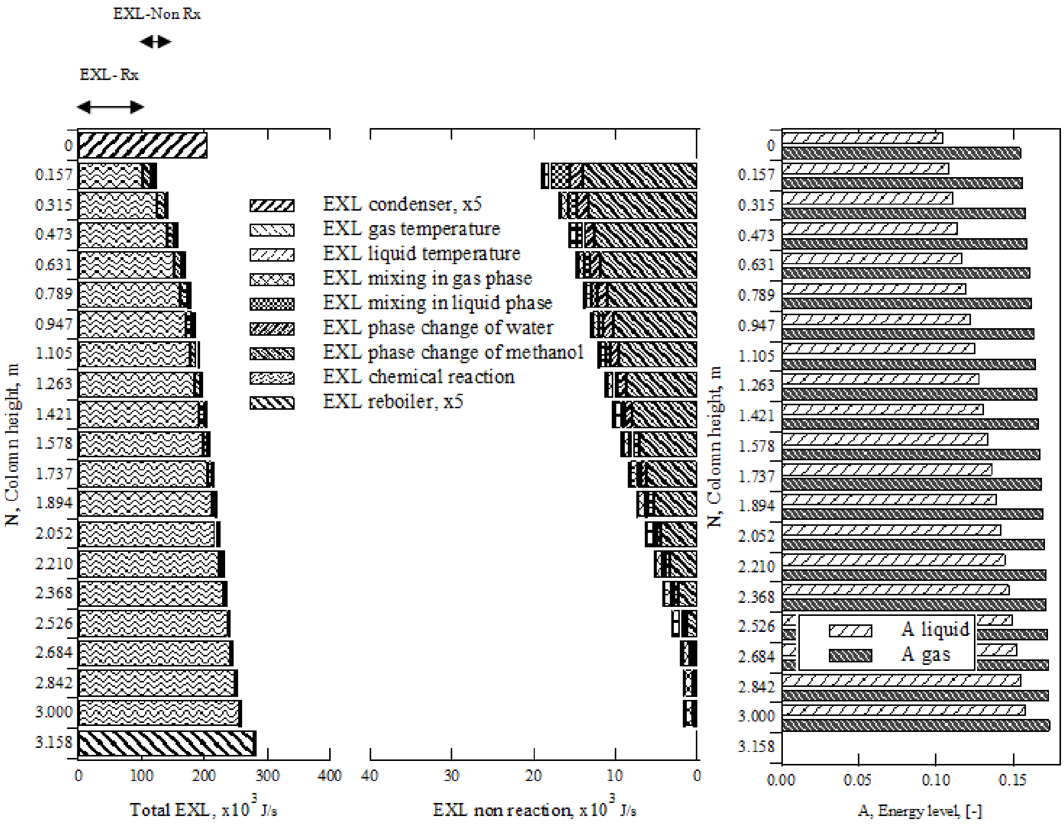
a. Ex-N Diagram **b. A-N Diagram**

Figure 7. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 6:1 at N = 3 m



a. Ex-N Diagram **b. A-N Diagram**

Figure 8. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 1:1 at N = 3 m



a. Ex-N Diagram **b. A-N Diagram**

Figure 9. Profile of Total Exergy Loss and Fatty Acid Conversion at Different Reactant Molar Ratio

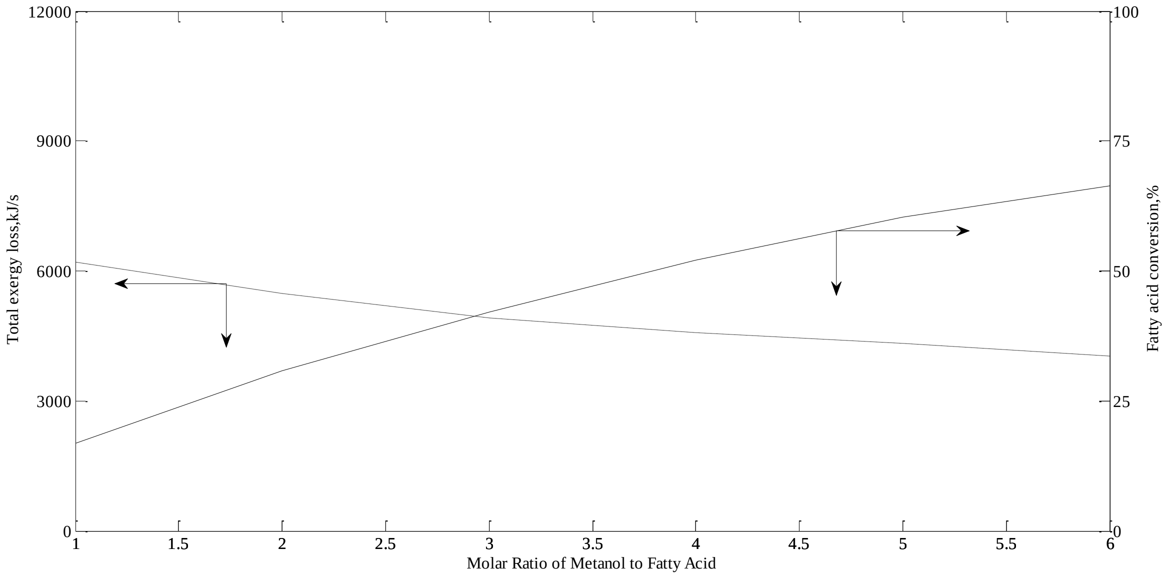
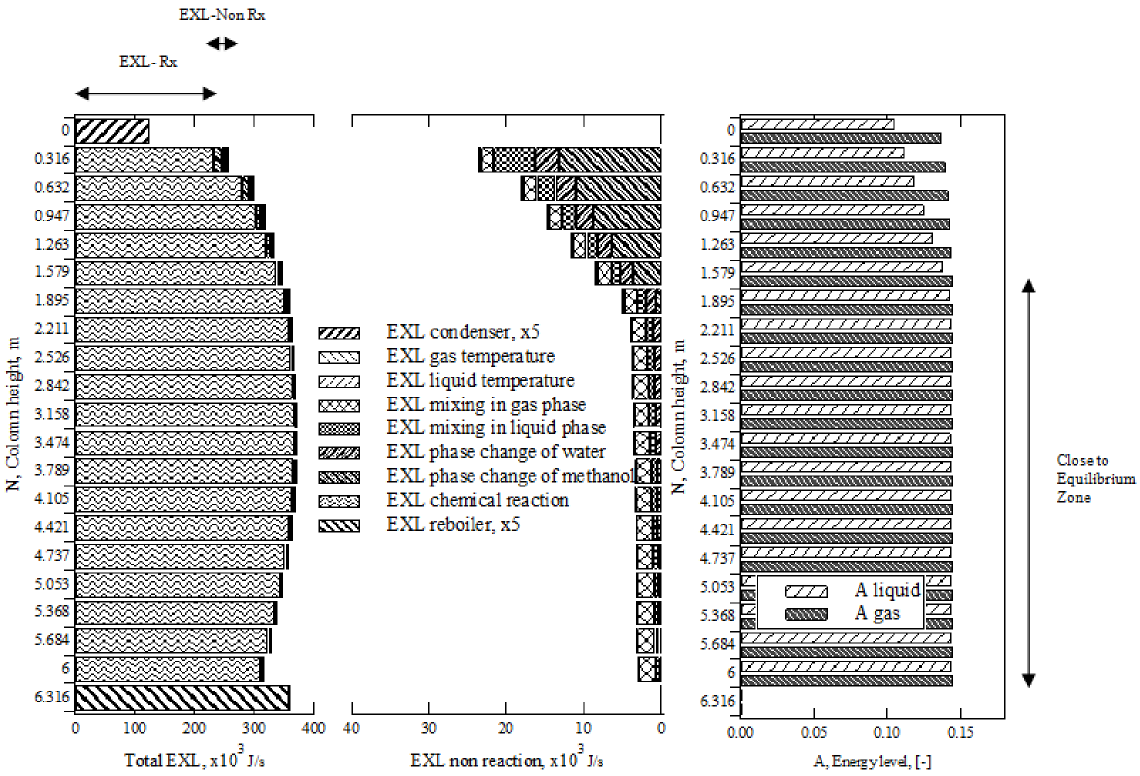


Figure 10. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 2:1 at N = 6 m



a. Ex-N Diagram **d. A-N Diagram**

Figure 11. Profile of Total Exergy Loss and Fatty Acid Conversion at Different Column Height

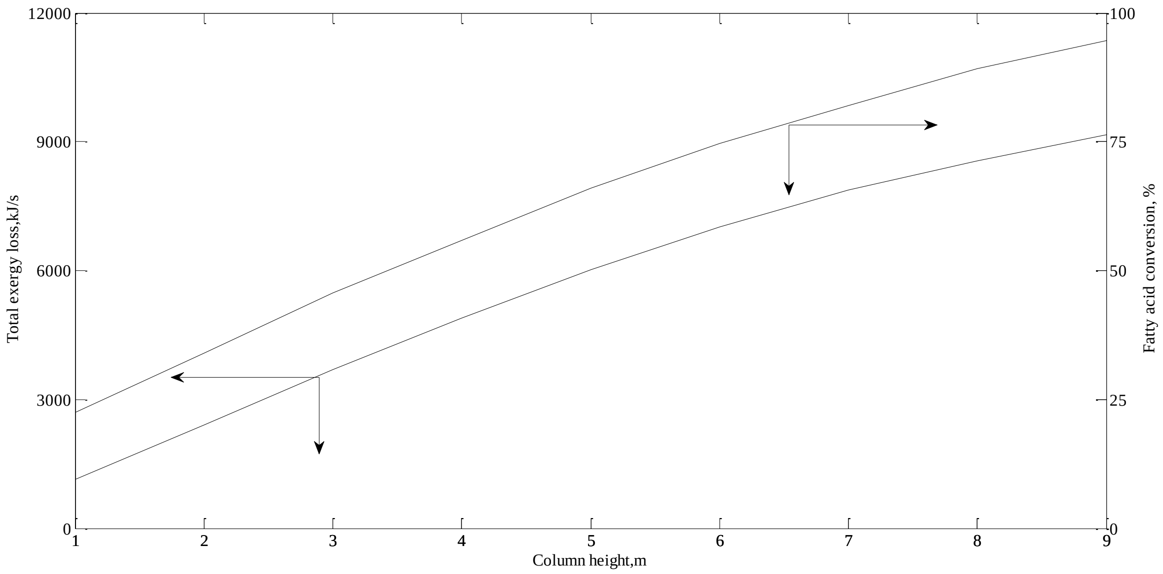


Table 1. Kinetic parameters of the pseudo-homogeneous model

Reaction Rate Constant ($mol \cdot m^3/kg_{cat}^2/s$)	Ln (pre-exponential factor)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

Table 2. Molecular structure and normal boiling points of all the chemical compounds

Compounds	Molecular structure	Boiling point, K
Oleic Acid (A)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	616.85
Water (D)	H_2O	373

SUMMARY OF THE MODIFICATION

Dear Prof. Dr. Ibrahim Dincer,

Thank you very much for the review reports for our paper "GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION". Regarding this review, we have implemented the following recommendations made by the reviewers in our submission. We also put red color on the modification we've made in the revised paper. Herewith we enclose a summary of the modifications and correction in the revised manuscript. For detailed information, we provide an explanation of each point of the review, both those of Reviewer A and B. Thank you very much.

Reviewer A Comments:

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1) Include biographical sketches (75 words for each author).

We have included our biographical sketches separately from the manuscript file in our first submission. Regarding this suggestion, we will send it for the second time.

2) There are many errors in the equations and texts as there must be a careful check and correction needed. All rate symbols must have dots above.

All the equations and texts have been corrected into the proper style according to the Journal's guideline and all rate symbols have been expressed with dots above. Previously, the manuscript has been written in MS Word 2010 version. Hence, to avoid any changes of the text due to the difference of MS Word version, the revised manuscript is now saved in MS Word 1997-2003 version.

3) List all assumptions in a reasonably manner.

We have made an improvement in the paper related to the explanation of the assumption taken on the work. List of assumptions has been inserted in the paper (page 5, paragraph 2). The assumptions taken in this modelling and simulation are:

The assumptions taken in this modelling and simulation can be written as follows:

1. *In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.*
2. *The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.*
3. *The RD column operates at the steady state condition*
4. *There are three phases which occurs in the system, namely: vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).*
5. *The reaction takes place in the organic phase (liquid-2)*
6. *Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.*
7. *The RD column is modelled based on the NEQ approach. Hence the interfacial mass transfer rates play a significant role in the calculation.*

4) Use SI units only.

The units used in this paper have been changed into SI units and, therefore, all the values have been converted into the appropriate ones.

5) Explain how this paper differs from the literature works.

The distinction between this paper from the literature work is described in the introduction (on page 2, paragraph 3).

Compared to the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (N) as ordinate while the total EXL, the non-chemical reaction EXL, and A (energy level) as abscissa. This plotting results in a simple diagram which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL due to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation, and chemical reaction incrementally. And it is yet easy to understand even in a case when one of the sub-process EXL is much larger than the other. This diagram can also obviously exhibit the correlation of the exergy losses due to chemical and non-chemical sub-processes with the energy level difference at various heights of column.

6) References are incorrect, incomplete and inconsistent.

References have been revised for the correctness, completeness and consistency.

7) Include related IJEx references as there are several related to this paper.

IJEx references have been added in this paper, i. e.:

Ao, Y., Wang, Y. and Rosen, M.A. (2012) 'Analysing the effects on the atmosphere of exergy changes due to exhaust-gas emissions', Int. J. Exergy, Vol. 10, No. 1,pp.21–33.
(cited on page 1, paragraph 2)

Budiman, A., Sutijan, and Sawitri, D. R. (2011) 'Graphical exergy analysis of retrofitted distillation column', Int. J. Exergy, Vol. 8, No. 4, pp.477-493.
(cited on page 8, paragraph 1; pages 11, paragraph 2)

Colpan, C.O. (2012) 'Exergy analysis of an integrated two-stage biomass gasifier and Solid Oxide Fuel Cell system', Int. J. Exergy, Vol. 10, No. 1, pp.61–76.
(cited on page 1, paragraph 2)

8) Check all equations, figures, tables, etc. VERY CAREFULLY.

All the equations, figures, and tables have been re-checked, corrected, and displayed in a proper way according to the journal's guidelines. All figures and tables have also been placed at the end of the manuscript

9) Heat transfer cannot be kW unless it is heat transfer rate. Correct and complete all nomenclature items.

In this paper, heat transfer is the heat transfer rate which also denotes the rate of exergy loss ($E\dot{X}L$). Hence, it has the unit of kW (J/s) and it is symbolized with "dot" above. The nomenclature item related to it has been corrected

10) Omit trivial information and equations.

The manuscript has been revised. Thus, the unimportant information and equations have been neglected.

11) English editing is necessary.

Proof–reading by an English native speaker from official proof reader has been managed.

Reviewer B Comments:

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Changes which must be made before publication:

1. Please check the language and the grammar before final publication.

To certify the correctness of the language and grammar, a proof–reading by an English native speaker from official proof reader has been managed.

2. Whether the column diameter has been kept same or not while varying the molar ratios needs to be clarified.

The information concerning the column diameter has been added to the paper. It is briefly stated that the column diameter has been kept same (0.5 meter) while varying the molar ratios and column heights.

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, firstly, the molar ratio of total methanol and oleic acid entering the column is changed from 2:1 to 6:1 at the same column height of 3 meter (N = 3) and column diameter of 0.5 meter. (pages 13, paragraph 1)

The subsequent important aspect to be analysed is the height of the column (N). To study this parameter, N is increased from 3 to 6 meter with the similar reactants molar ratio of 2:1, while the column diameter is kept the same (0.5 meter). (pages 14, paragraph 3).

3. Incorporation of temperature and concentration data at different levels of column for base case is required for calculation of EXL.

The concentration of the compounds, total molar flow rate of each phase and temperature profiles at different levels of column for base case have been added on the paper (Figures 3, 4, and 5). They are also stated on page 9 paragraph 4:

In this work, the base case of the simulation was set up with the following condition: the height of the column (N) was 3 meter, the column diameter was 0.5 meter and the molar ratio of methanol to oleic acid was 2:1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited on Figures 3, 4 and 5, respectively. These data are required for the EXL calculation.

4. Conclusions needs to be more focused with quantitative data.

The conclusion has been modified to be more focused on the quantitative result (page 16-17)

- *The base case of the RD simulation was studied at N = 3 meter, the column diameter of 0.5 meter and the molar ratio of methanol to oleic acid of 2:1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s while in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom which agrees with the A-N profile.*
- *The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2:1 to 6:1 at the similar N of 3 meter and column diameter of 0.5 meter. By employing the molar ratio of 6:1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1:1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.*
- *To study the effect of column height, N is increased from 3 to 6 meter, while the reactants molar ratio and column diameter are kept at 2:1 and 0.5 meter, respectively. This reveals that the conversion is enhanced from 30.76 to 58.52%. Thus, the increase in the column height does not change the non-equilibrium area, nevertheless it just prolong the close-to-equilibrium zone.*
- *The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.*

Dear Editor of the International Journal of Exergy.

Enclosed is a revised article, entitled **"Graphical Exergy Analysis of Reactive Distillation Column for Biodiesel Production"**. Please accept it as a candidate for publication in the International Journal of Exergy. Below are our responses to your submission requirements. We include the abstract of the article and bibliographical notes.

GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi, and Arief Budiman*
Chemical Engineering Department, Faculty of Engineering,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed Reactive Distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium model of a three phase packed RD system. The graphical Ex-N-A method was utilized to evaluate exergy features of the internal RD column. This technique is rigorous to demonstrate the value of exergy losses at each increment of the column, *i.e.* losses due to the temperature change, phase change, mixing in liquid and vapour phases, and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Key words: Exergy analysis, reactive distillation, esterification, Ex-N-A, biodiesel

Biographical notes: Ratna Dewi Kusumaningtyas is a PhD students at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor's and Master's Degree from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange program in Politecnico di Torino, Italy (2010-2012). She is author and co-author of 12 journal and international conference paper during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD Degree from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario, Canada (1993). His research focuses on distillation, petroleum, and renewable energy development. He is author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi is Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK (1991). His research topic is polymer and bio-fuel development. He is author or co-author of 55 scientific papers. He is also the Coordinator of many industrial-university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan (1997). His research focuses on thermodynamics and exergy analysis for system engineering. He is author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009, and 2011) and Visiting Professor at Kyushu University (2012).

Finally, this article is our original unpublished work and it has not been submitted to any other journal for review.

Sincerely,
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Date: 2013.12.06 04:57:52 +07'00'

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GRAPHICAL EXERGY ANALYSIS OF REACTIVE DISTILLATION COLUMN FOR BIODIESEL PRODUCTION

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi, and Arief Budiman*
Chemical Engineering Department, Faculty of Engineering,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed Reactive Distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium model of a three phase packed RD system. The graphical Ex-N-A method was utilized to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, *i.e.* losses due to the temperature change, phase change, mixing in liquid and vapour phases, and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Key words: Exergy analysis, reactive distillation, esterification, Ex-N-A, biodiesel

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Biographical notes: Ratna Dewi Kusumaningtyas is a PhD students at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor’s and Master’s Degree from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange program in Politecnico di Torino, Italy (2010-2012). She is author and co-author of 12 journal and international conference paper during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD Degree from Chemical Engineering

Department, University of Waterloo, Waterloo, Ontario, Canada (1993). His research focuses on distillation, petroleum, and renewable energy development. He is author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi is Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK (1991). His research topic is polymer and bio-fuel development. He is author or co-author of 55 scientific papers. He is also the Coordinator of many industrial-university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan (1997). His research focuses on thermodynamics and exergy analysis for system engineering. He is author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009, and 2011) and Visiting Professor at Kyushu University (2012).

1. Introduction

Reactive Distillation (RD) is a promising alternative process for equilibrium limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gomez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognized as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing, and optimizing an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various method of exergy analysis has been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot factor-specific enthalpy diagram*. This method is easy to utilize for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *Column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications, and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *Energy Utilization Diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXL), namely EXL due to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenience when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called *Integrated Energy Utilization Diagram* (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the *Material-Utilization Diagram* (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub process EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier to understand diagram for a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared to the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (N) as ordinate while the total EXL, the non-chemical reaction EXL, and A (energy level) as abscissa. This plotting results in a simple diagram which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL due to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation, and chemical reaction incrementally. And it is yet easy to understand even in a case when one of the sub-process EXL is much larger than the other. This diagram can also obviously exhibit the correlation of the exergy losses due to chemical and non-chemical sub-processes with the energy level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A Diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, non-equilibrium (NEQ) model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phases and NEQ model has been merely studied for a distillation process which doesn’t involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss are also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2. Model and Simulation for Reactive Distillation (RD) Column

A packed RD column was utilized for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the present of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown below:

$$\mathrm{RCOOH\ (A)} + \mathrm{CH_3OH\ (B)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCOOCH_3\ (C)} + \mathrm{H_2O\ (D)} \qquad (1)$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1\, x_A\, x_B - k_2\, x_A\, x_B)\ C_{cat} \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with ΔH_r = 11213.12 J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top are condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the column starts from the top, hence N = 0 meter is the top of the column, while N = n meter is the lowest part of the column. The base case condition employs the packed column with the height of 3 meter with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2:1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 mol/s and 69.52 mol/s, respectively.

The simulation of the packed RD column was performed based on the novel NEQ model combined with three phase approach. The unit cell for the NEQ model for three phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester, and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase which contains only methanol and water, alcoholic liquid phase which contains mainly water and methanol, and organic liquid phase which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

The assumptions taken in this modelling and simulation can be written as follows:

1. In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.
2. The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.
3. The RD column operates at the steady state condition
4. There are three phases which occur in the system, namely: vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).
5. The reaction takes place in the organic phase (liquid-2)
6. Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.
7. The RD column is modelled based on the NEQ approach. Hence the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three phase RD are summarized as follows. The mass balances of each compound in the vapour, Liquid-1, and Liquid-2 phases are formulated in the equations (3), (4), and (5), respectively:

$$\frac{dy_{i,G}}{dz} = \frac{\left(-\dot{R}_{i,G}\right) - y_i \frac{dV'}{dz}}{V'} \tag{3}$$

$$\frac{dx_{i,L_1}}{dz} = \frac{-\left(-\dot{R}_{i,L_1}\right) - x_{i,} \frac{dL_1'}{dz}}{L_1'} \tag{4}$$

$$\frac{dx_{i,L_2}}{dz} = \frac{-\left(-\dot{R}_{i,L_2}\right) - x_i \frac{dL_2'}{dz}}{L_2'} \tag{5}$$

Meanwhile, the total mass balance of the vapour, Liquid-1, and Liquid-2 phase are presented in the equations (6), (7), and (8), respectively:

$$\frac{dV'}{dz} = -\sum \dot{R}_{i,G} \tag{6}$$

$$\frac{dL_1'}{dz} = -(-\sum \dot{R}_{i,L_1}) \tag{7}$$

$$\frac{dL_2'}{dz} = -(-\sum \dot{R}_{i,L_2}) \tag{8}$$

To solve the equations (3) to (8), the rate processes equations are necessary. The rate processes equations for the gas, liquid-1, and liquid-2 phases are equations (9), (10), and (11), respectively.

$$\dot{R}_{i,G} = -\left(\dot{N}_i^{GL_1} + \dot{N}_i^{GL_2}\right) \tag{9}$$

$$\dot{R}_{i,L_1} = \dot{N}_i^{GL_1} - \dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2} = \dot{N}_i^{GL_2} + \dot{N}_i^{L_1L_2} + v_i\,\dot{r} \tag{11}$$

The result outputted from the RD simulation is utilized for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorius method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e. EXL due to the temperature change, phase change, mixing in liquid and vapour phase, and chemical reaction. The loss in reboiler and condenser are also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3. Graphical Ex-N-A Methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, *i.e.* EXL due to changes of the concentration (mixing), phase of the component, and temperature have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL due to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (A) is explained as (Srinophakun et al., 2001):

$$A = \frac{E\dot{X}L}{\Delta H} \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S \tag{13}$$

Hence,

$$A = (1 - T_0 \, \frac{\Delta s}{\Delta H}) \tag{14}$$

It illustrates the maximum fraction of energy which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{Chem} = (1 - T_0 \, \frac{\Delta s}{\Delta H}) \tag{15}$$

On the equilibrium condition in which the reaction doesn't occurs, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T} \tag{16}$$

In this condition, energy level A generally can be written as:

$$A = (1 - \frac{T_0}{T}) \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{Liq} = (1 - \frac{T_0}{T}) \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{Gas} = (1 - \frac{T_0}{T}) \tag{19}$$

T in the energy level formula depends on the phase. T is gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL due to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL loss due to the chemical reaction can be written as:

$$E\dot{X}L_{Chem} = (A_{Liq} - A_{Chem})\,\Delta H \tag{20}$$

4. Display of Packed Reactive Distillation Column on Graphical Ex-N-A Diagram

4. 1. Base Case Analysis

Ex-N-A Diagram is an-exergy features based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008), and Budiman et al. (2011) composed the graph for EXL due to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 ln x_j$ as ordinate for the liquid phase and $\Re T_0 ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A Diagram is made by placing the two types of diagram in a single feature. The height of the column (N) is put as ordinate while the total EXL, the non-chemical reaction EXL, and A (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of N as ordinate while total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which N was put as ordinate and A is set as abscissa. The two other diagrams exhibiting the correlation between the column height with total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared to the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL due to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub process EXL is much larger than the other. It also can combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy level difference between A_{Gas} and A_{Liq} ($A_{Gas} - A_{Liq}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy level difference and exergy consumption as the shaded area in the diagrams. Hence, it doesn't clearly show the exergy profile at the difference levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (N) is plotted as abscissa against the total EXL, non-chemical reaction EXL, and energy level. Based on this diagram, the graphical correlation between total EXL, non-chemical reaction EXL, and energy level difference between gas and liquid (A_{gas}-A_{liq}) are incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of sub graphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL due to the chemical reaction, and non-chemical EXL (*i.e* losses due to the temperature change, mixing, and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, *i.e*. EXL due to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, temperature change in liquid phase and temperature change in gas phases, are displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses due to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase, and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. Based on this N-A graph, the energy level difference between gas and liquid (A_{gas}-A_{liq}) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (N) was 3 meter, the column diameter was 0.5 meter and the molar ratio of methanol to oleic acid was 2:1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited on Figures 3, 4 and 5, respectively. These data are required for the EXL calculation.

Figure 6 demonstrates the Ex-N-A Diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared to the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s while in condenser it is 769351.3847 J/s. In Figure 6a, EXL of the reboiler and condenser are shown by the scale of 1/5 because of their large values. The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

The incrementally assessment on the RD column using Ex-N-A Diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6a shows that the non-chemical EXL, *i.e.* the summation of EXL due to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, start from N= 2 meter from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the A-N Diagram in Figure 6b, which displays the profile of the energy level difference between gas and liquid (A_{gas}-A_{liq}) inside the column or so-called driving force. Energy level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy level difference.

Based on the A-N diagram in Figure 6b, it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 meter from the top (N=2), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses which are influenced by temperature is zero. Hence, simply the EXL due to the mixing exists at N= 2 meter moved downwards. EXL due to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL due to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near equilibrium condition has been reached. In this condition, a macro heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium zone, and the second one is the close-to-equilibrium zone.

Two regions, non-equilibrium and close to equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close to equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small difference temperature between gas and liquid, which also results in a very small (near to zero) energy level difference. The condition where the energy level difference or the driving force is very small (let's say "zero") is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual with the near to equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy level difference (driving force) between gas and liquid at the column top (A-N Diagram in Figure 6b). In addition, the energy level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the Close-to-Equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6a. Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis due to the chemical reaction. However, assessment on the EXL due to chemical reaction incrementally never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N Diagrams in Figure 6a exposes a different tendency between the profile of the total EXL and EXL due to the chemical reaction on one side, and EXL due to the non-chemical reaction on the other side. The profile of total EXL and EXL due to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL due to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL due to chemical reaction profile.

Based on the Ex-N diagram, it is revealed that the amount of EXL due to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher amount of reactants react, the higher EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL due to chemical reaction as well as total EXL increase from the top to the bottom.

Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, in order to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (N). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimization graphically.

4. 2. Effect of the Molar Ratio of the Reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, firstly, the molar ratio of total methanol and oleic acid entering the column is increased from 2:1 to 6:1 at the same column height of 3 meter (N = 3) and column diameter of 0.5 meter. By employing the molar ratio of 6:1, it is shown that the reaction conversion enhances about twice times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7a shows that the profile of non-chemical EXL does not change so much compared to the result given by the molar ratio of 2:1. At molar ratio of 6:1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, while the upper part is non-equilibrium zone. However, enhancing molar ratio from 2:1 to 6:1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7b shows that, when molar ratio of 6:1 is applied, the close-to-equilibrium zone starts at N = 0.75 meter downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the non-equilibrium zone inside the column. The larger area of the close-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of close to equilibrium point gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1:1 with N = 3. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in the Figure 8b, all the areas in RD column are non-equilibrium zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses due to mixing, phase, and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

To evaluate the impact of varying the molar ratio on the value of the EXL due to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N Diagram in Figures 7 and 8 that the EXL due to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1:1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2:1.

However, if molar ratio of the reactants is drastically enhanced to 6:1, the new Ex-N profile seems interesting. It is shown that EXL due to the chemical reaction gets higher from the top downward as seen on the Ex-N Diagram in Figure 7a. In spite of this, at a certain point in the column, EXL due to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL due to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to reacts easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining un-reacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease of the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL due to chemical reaction in the column. It can be observed that EXL due to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect’s point of view.

4. 3. Effect of the Height of the Packed Column (N)

The subsequent important aspect to be analysed is the height of the column (N). To study this parameter, N is increased from 3 to 6 meter with the similar reactants molar ratio of 2:1, while the column diameter is kept the same (0.5 meter). Hence, it reveals that the reaction conversion is enhanced from 30.76 to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N Diagram in Figure 10a shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared to the profile of the column with the height of 3 meter (N = 3). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the N = 2 meters from the top, EXL of the sub processes which depends on temperature (loss due to temperature and phase changes) approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N Diagram in Figure 10b. Nevertheless, it is shown that the energy level difference between gas and liquid decreases from the top downward. Then, starting at N = 2 meter downward, the energy level difference is near to zero. Thus, the area in the column can be separated into two regions, *i.e.* the non-equilibrium zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to N = 2, while the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the non-equilibrium area. However, it just prolongs the close-to-equilibrium zone. The existing of non-equilibrium region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

Effect of the column height (N) on the EXL due to the chemical reaction is evaluated, as well. Ex-N Diagram in Figure 10 presents the profile of EXL due to the chemical reaction. It is observed that EXL due to the chemical reaction increases from the top downward. When it reaches the increment of N = 2, EXL due to the chemical reaction values remain almost constant, and finally decreases at N = 4 to bottom. EXL due to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared to the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Conclusively, there are some finding obtained by analysing the effects of the reactant molar ratio and column height. Based on the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at the different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5. Conclusions

- A graphical method called Ex-N-A Diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-process has a much larger EXL than the others.
- The base case of the RD simulation was studied at N = 3 meter, the column diameter of 0.5 meter and the molar ratio of methanol to oleic acid of 2:1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s while in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2:1 to 6:1 at the similar N of 3 meter and column diameter of 0.5 meter. By employing the molar ratio of 6:1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1:1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.

- To study the effect of column height, N is increased from 3 to 6 meter, while the reactants molar ratio and column diameter are kept at 2:1 and 0.5 meter, respectively. This reveals that the conversion is enhanced from 30.76 to 58.52%. Thus, the increase in the column height does not change the non-equilibrium area, nevertheless it just prolong the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols

A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase
C_{cat}	Concentration of the solid catalyst (kg_{cat} /m^3)
E_a	Activation energies (J/mol)
$E\dot{X}L$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant (mol·m^3/kg_{cat}^2/ s)
k_2	Reverse reaction rate constant (mol·m^3/kg_{cat}^2/s)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component i from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component i from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{L_1L_2}$	Mass transfer rate of component i from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference Temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
dz	Increment of the column height (m)
v_i	Reaction coefficient

Subscripts

A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase

L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase
Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Figure 1. The Configuration of Packed RD Column for Biodiesel Production

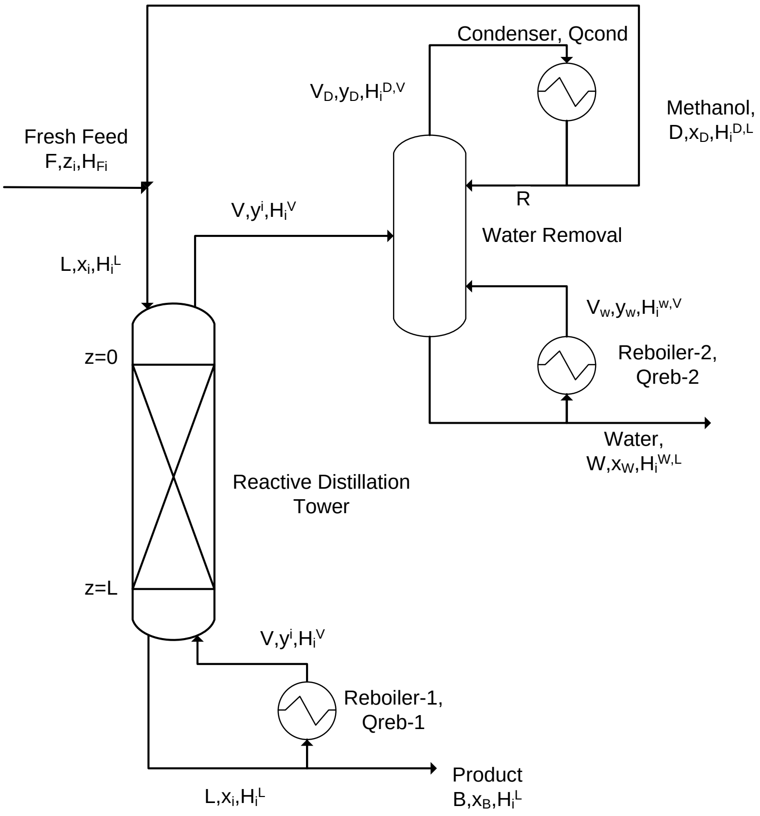


Figure 2. Schematic Representation of One Cell of Three-Phase Packed RD Column

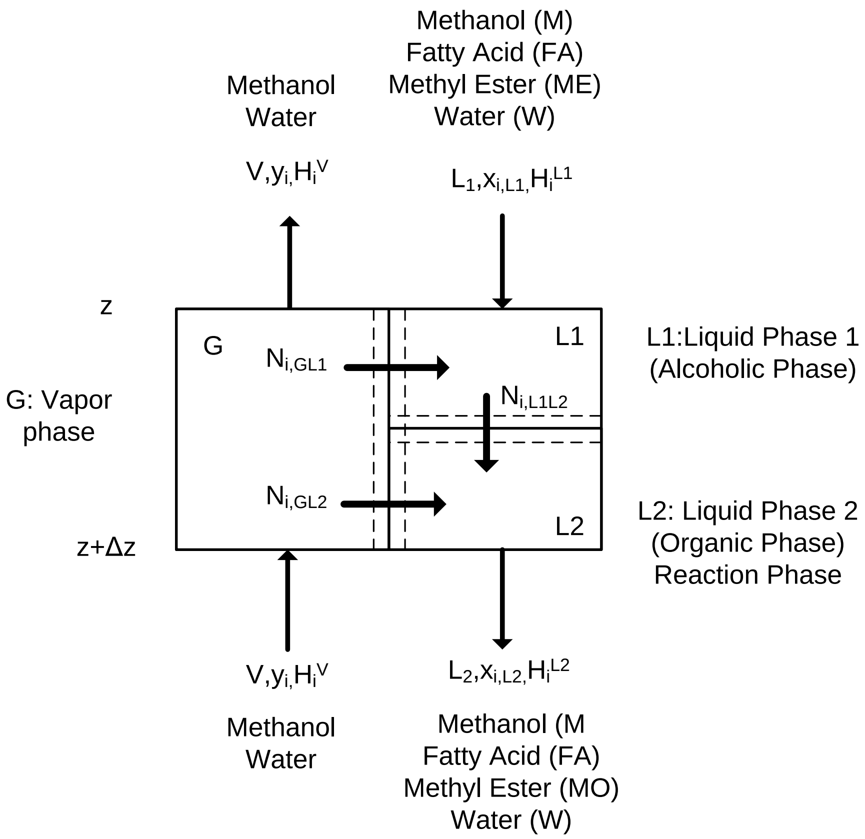


Figure 3. Concentration Profiles of the Compounds in Liquid-1, Liquid-2 and Vapour Phases at Different Column Height

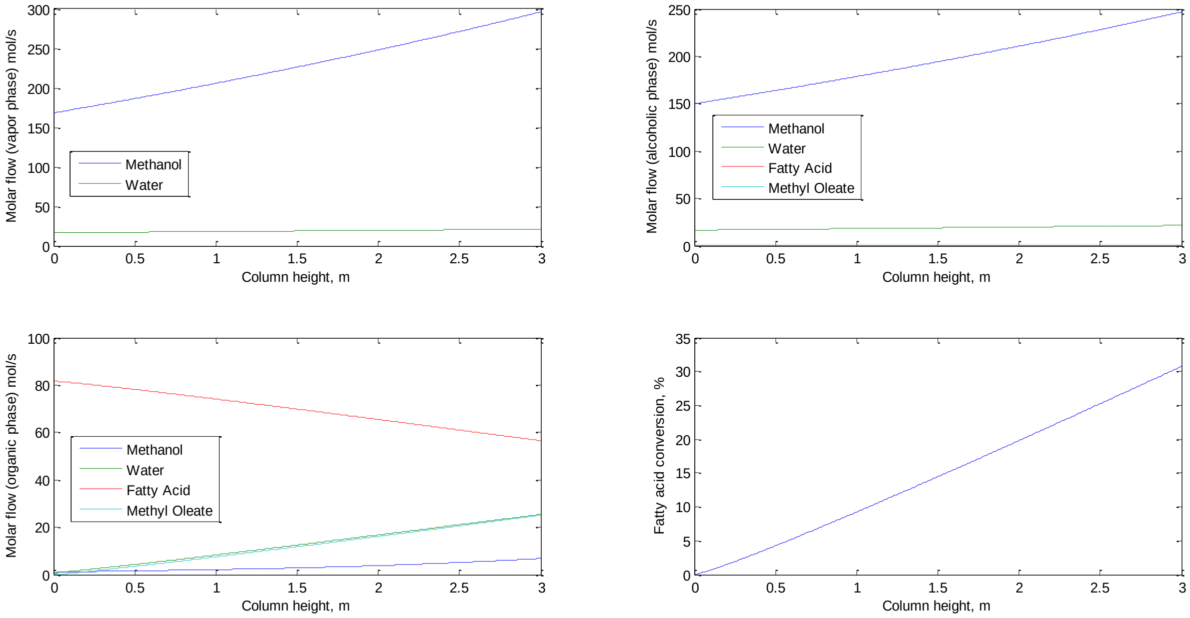


Figure 4. Total Molar Flow of Each Phase at Different Column Height

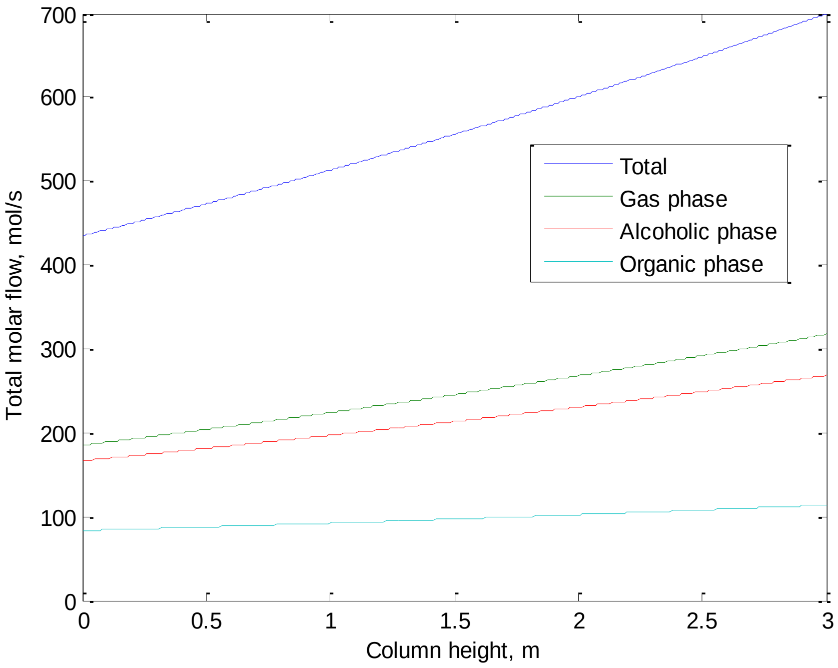


Figure 5. Temperature Profile of Liquid and Vapour Phase at Different Column Height

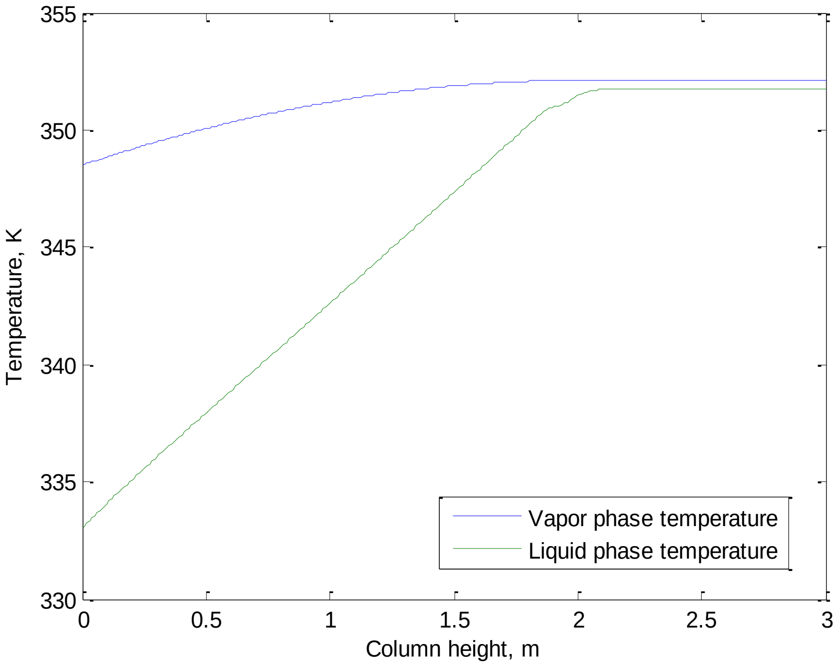
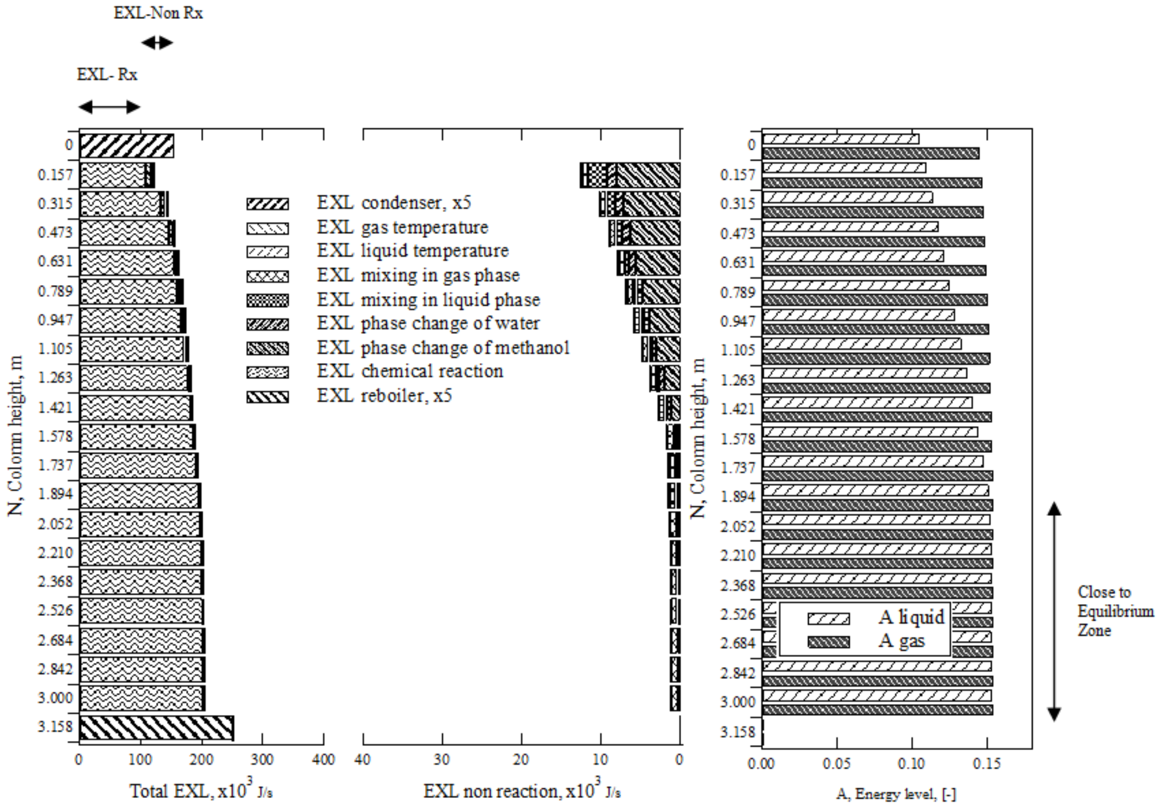
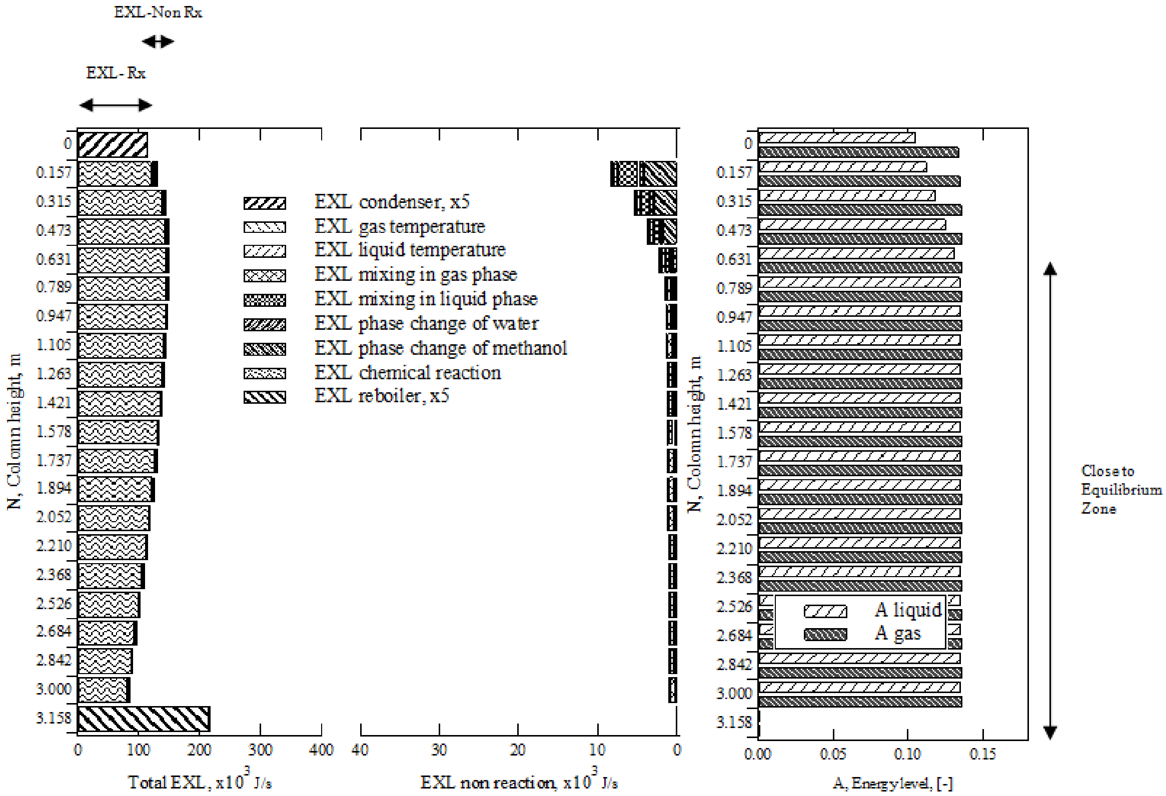


Figure 6. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 2:1 at N = 3 m



a. Ex-N Diagram **b. A-N Diagram**

Figure 7. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 6:1 at N = 3 m



a. Ex-N Diagram **b. A-N Diagram**

Figure 8. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 1:1 at N = 3 m

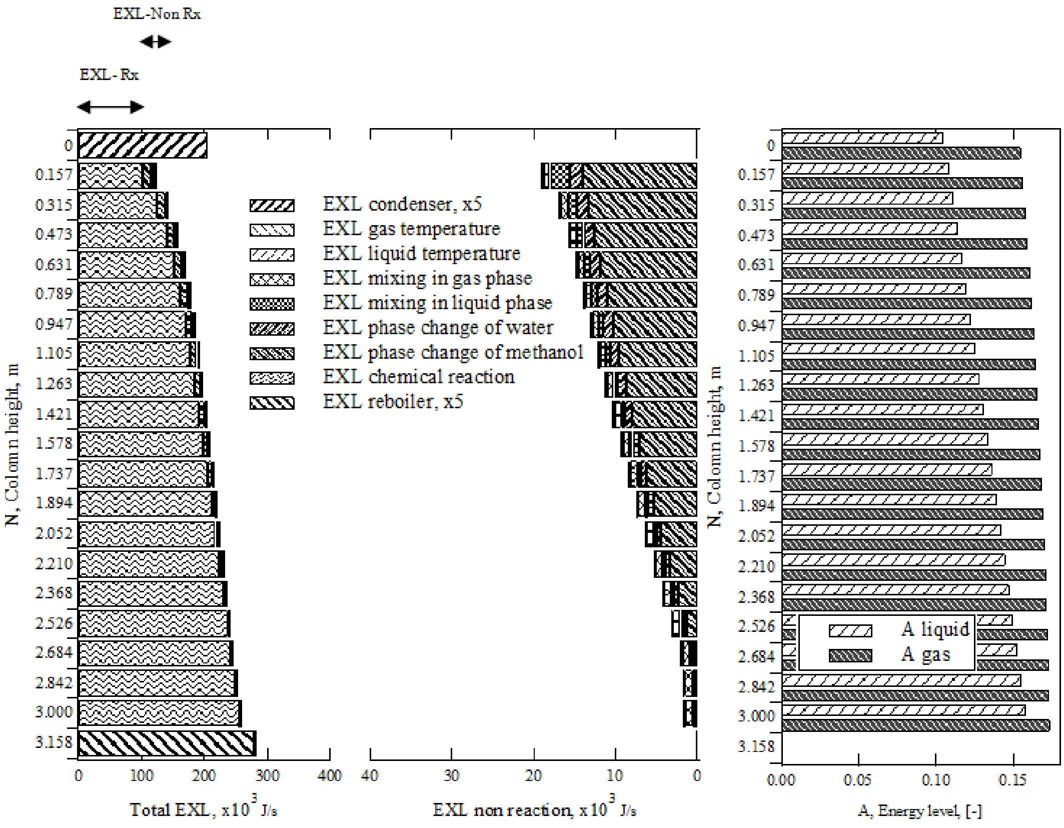


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Figure 9. Profile of Total Exergy Loss and Fatty Acid Conversion at Different Reactant Molar Ratio

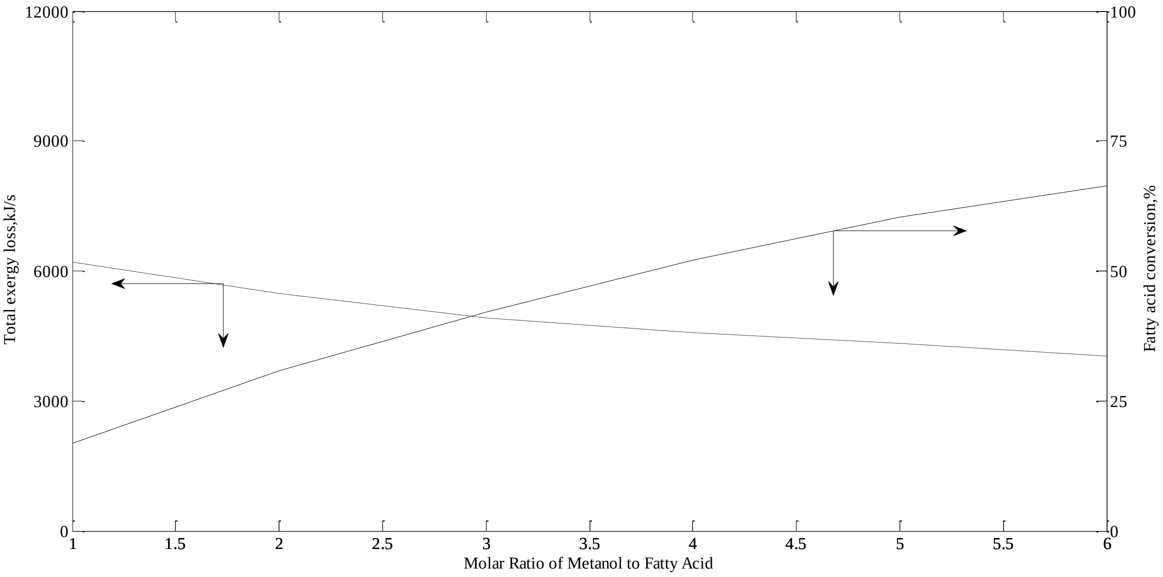
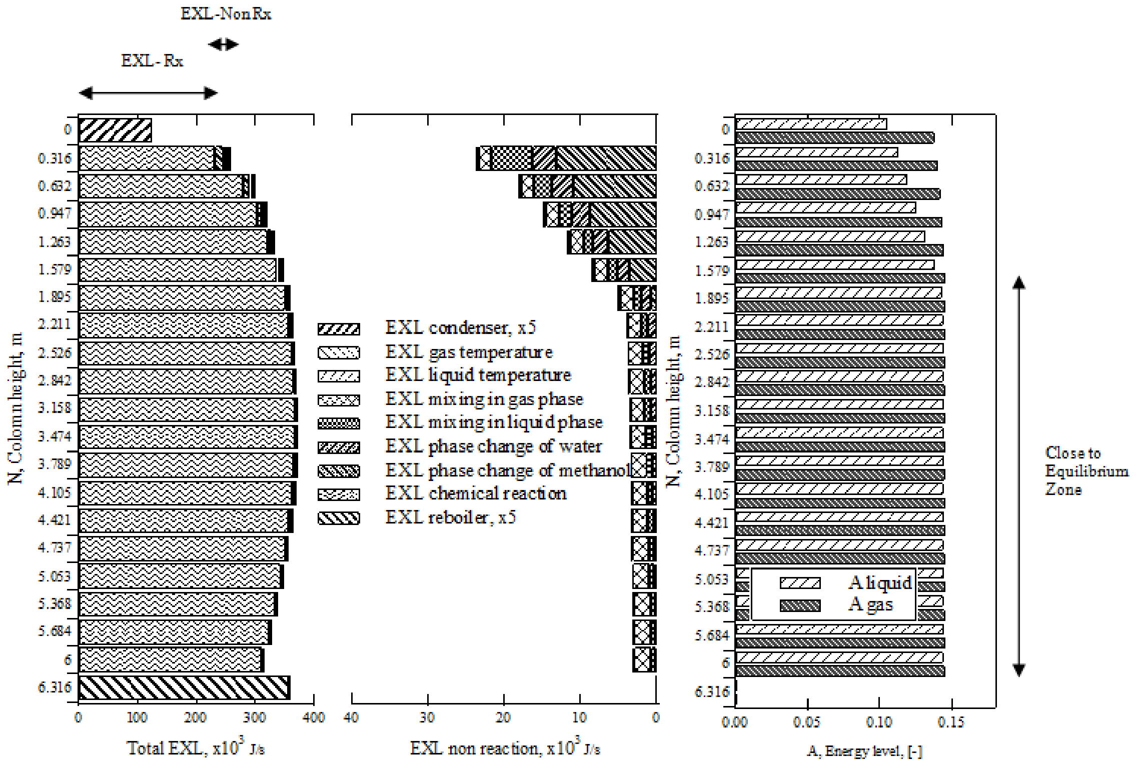


Figure 10. Exergy Loss Profile (Ex-N-A Diagram) for Molar Ratio of Methanol to FFA of 2:1 at N = 6 m



a. Ex-N Diagram **b. A-N Diagram**

Figure 11. Profile of Total Exergy Loss and Fatty Acid Conversion at Different Column Height

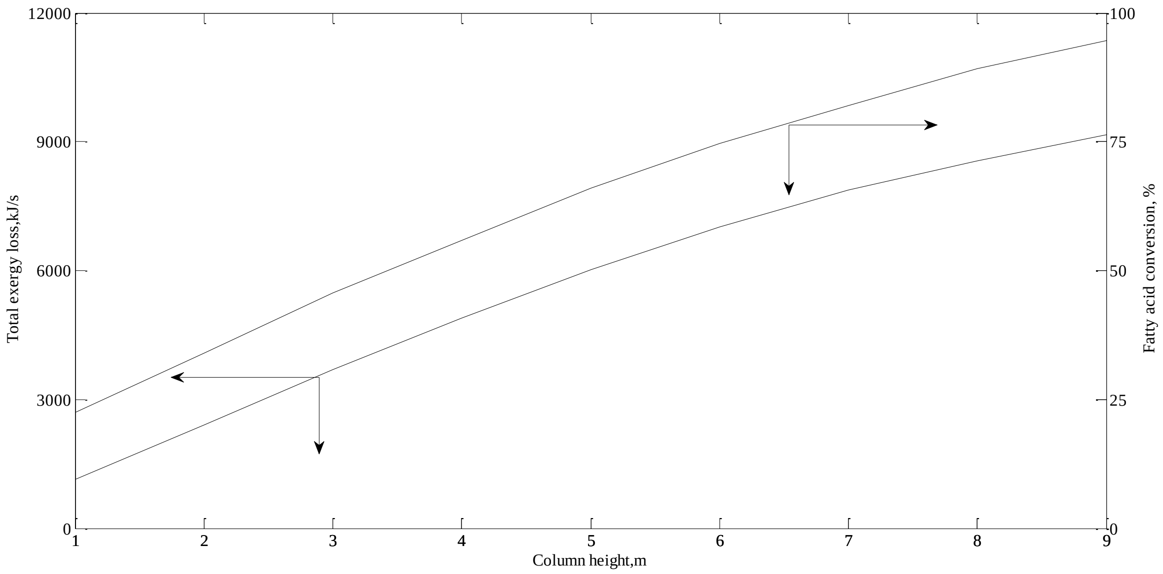


Table 1. Kinetic parameters of the pseudo-homogeneous model

Reaction Rate Constant (mol·m^3/kg$_{cat}$^{2}/s)	Ln (pre-exponential factor)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

Table 2. Molecular structure and normal boiling points of all the chemical compounds

Compounds	Molecular structure	Boiling point, K
Oleic Acid (A)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	616.85
Water (D)	H_2O	373

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Graphical exergy analysis of reactive distillation column for biodiesel production

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi and Arief Budiman*

Faculty of Engineering,
Chemical Engineering Department,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Author: Please supply initial for the highlighted author.

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed reactive distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system. The graphical Ex-N-A method was utilised to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, i.e., losses owing to the temperature change, phase change, mixing in liquid and vapour phases and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Keywords: exergy analysis; RD; reactive distillation; esterification; Ex-N-A; biodiesel.

Reference to this paper should be made as follows: Kusumaningtyas, R.D., Purwono, S., Rochmadi and Budiman, A. (xxxx) 'Graphical exergy analysis of reactive distillation column for biodiesel production', *Int. J. Exergy*, Vol. x, No. x, pp.xxx–xxx.

Biographical notes: Ratna Dewi Kusumaningtyas is a PhD student at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor's and Master's degrees from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange programme in Politecnico di Torino, Italy (2010–2012). She is the author and co-author of 12 journal and international conference papers during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario,

Canada, in 1993. His research focuses on distillation, petroleum and renewable energy development. He is the author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK, in 1991. His research topic is polymer and bio-fuel development. He is the author or co-author of 55 scientific papers. He is also the Coordinator of many industrial–university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan, in 1997. His research focuses on thermodynamics and exergy analysis for system engineering. He is the author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009 and 2011) and Visiting Professor at Kyushu University (2012).

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1 Introduction

Reactive distillation (RD) is a promising alternative process for equilibrium-limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gomez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognised as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing and optimising an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various methods of exergy analysis have been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot-factor-specific enthalpy diagram*. This method is easy to utilise for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *column grand composite curve* (CGCC). Demirel

(2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *energy utilisation diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXLs), namely EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenient when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called integrated energy utilisation diagram (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the material-utilisation diagram (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-processes EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process.

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On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared with the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (*N*) as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) as abscissa. This plotting results in a simple diagram, which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation and chemical reaction incrementally. And, it is yet easy to understand even in a case when one of the sub-processes EXL is much larger than the others. This diagram can also obviously exhibit the correlation of the exergy losses owing to chemical and non-chemical sub-processes with the energy-level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low-grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, NEQ model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phase and NEQ model has been merely studied for a distillation process, which does not involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production.

The effect of some parameters on the reaction conversion and exergy loss is also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2 Model and simulation for reactive distillation (RD) column

A packed RD column was utilised for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the presence of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown here:

Author: Please supply expansion for the highlighted acronym.

$$\mathrm{RCOOH}(\mathrm{A})+\mathrm{CH_3OH}\ (\mathrm{B}) \xrightleftharpoons[k_2]{k_1} \mathrm{RCOOCH_3}(\mathrm{C})+\mathrm{H_2O}\ (\mathrm{D}) \tag{1}$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1 x_A x_B - k_2 x_A x_B) C_{\text{cat}}. \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with $\Delta H_r = 11213.12$ J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 1 Kinetic parameters of the pseudo-homogeneous model

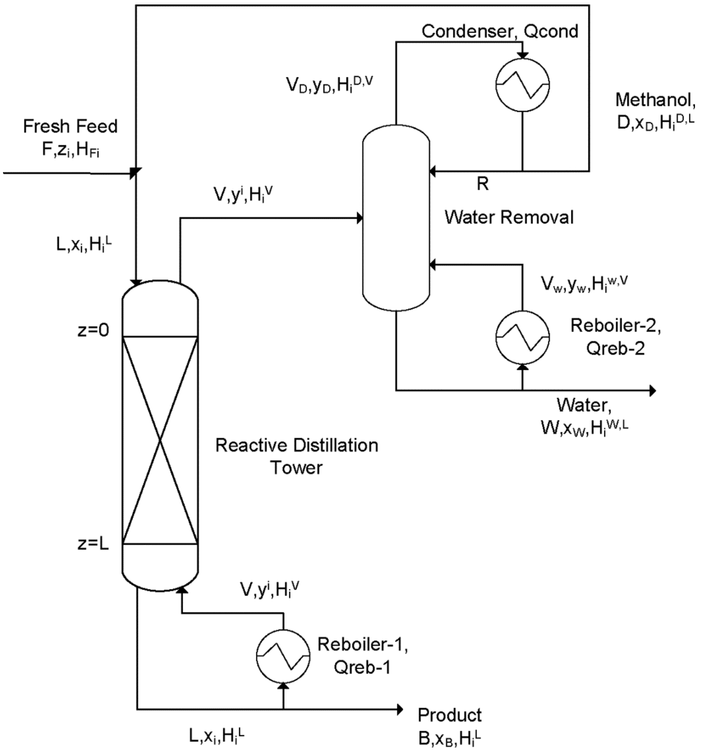
Reaction rate constant (mol $m^3/kg_{cat}^2/s$)	*Ln*(*pre-exponential factor*)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

Table 2 Molecular structure and normal boiling points of all the chemical compounds

Compounds	*Molecular structure*	*Boiling point* (K)
Oleic acid (A)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	616.85
Water (D)	H_2O	373

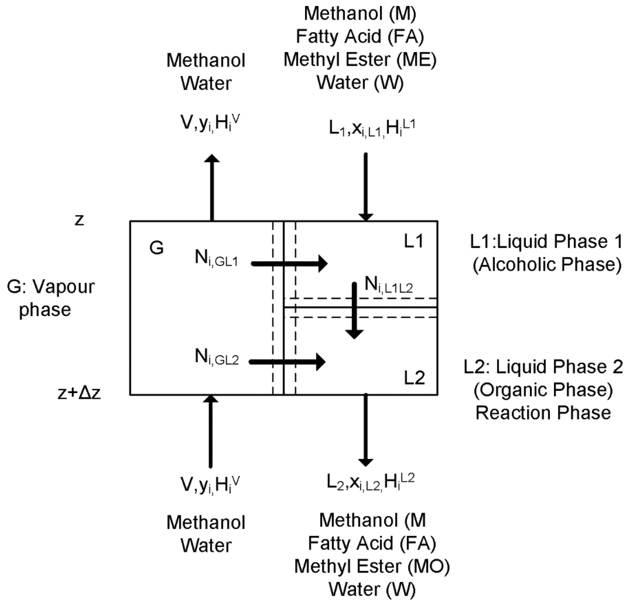
The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top is condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the column starts from the top, hence $N = 0$ m is the top of the column, while $N = n$ m is the lowest part of the column. The base case condition employs the packed column with the height of 3 m with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2 : 1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 and 69.52 mol/s, respectively.

Figure 1 The configuration of packed RD column for biodiesel production



The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase, which contains only methanol and water, alcoholic liquid phase, which contains mainly water and methanol, and organic liquid phase, which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

Figure 2 Schematic representation of one cell of three-phase packed RD column



The assumptions taken in this modelling and simulation can be written as follows:

1. In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.
2. The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.
3. The RD column operates at the steady-state condition.
4. There are three phases that occur in the system, namely vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).
5. The reaction takes place in the organic phase (liquid-2).
6. Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.
7. The RD column is modelled based on the NEQ approach. Hence, the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three-phase RD are summarised as follows. The mass balances of each compound in the vapour, liquid-1 and liquid-2 phases are formulated in equations (3)–(5), respectively:

$$\frac{\mathrm{d}y_{i,G}}{\mathrm{d}z}=\frac{(-\dot{R}_{i,G})-y_i\frac{\mathrm{d}V'}{\mathrm{d}z}}{V'} \tag{3}$$

$$\frac{\mathrm{d}x_{i,L_1}}{\mathrm{d}z}=\frac{(-\dot{R}_{i,L_1})-x_i\frac{\mathrm{d}L_1'}{\mathrm{d}z}}{L_1'} \tag{4}$$

$$\frac{\mathrm{d}x_{i,L_2}}{\mathrm{d}z}=\frac{-(-\dot{R}_{i,L_2})-x_i\frac{\mathrm{d}L_2'}{\mathrm{d}z}}{L_2'}. \tag{5}$$

Meanwhile, the total mass balance of the vapour, liquid-1 and liquid-2 phase is presented in equations (6)–(8), respectively:

$$\frac{\mathrm{d}V'}{\mathrm{d}z}=-\sum\dot{R}_{i,G} \tag{6}$$

$$\frac{\mathrm{d}L_1'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_1}\right) \tag{7}$$

$$\frac{\mathrm{d}L_2'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_2}\right) \tag{8}$$

To solve equations (3)–(8), the rate process equations are necessary. The rate process equations for the gas, liquid-1 and liquid-2 phases are equations (9)–(11), respectively.

$$\dot{R}_{i,G}=-(\dot{N}_i^{GL_1}+\dot{N}_i^{GL_2}) \tag{9}$$

$$\dot{R}_{i,L_1}=\dot{N}_i^{GL_1}-\dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2}=-\dot{N}_i^{GL_2}+\dot{N}_i^{L_1L_2}+v_i\dot{r}. \tag{11}$$

The result outputted from the RD simulation is utilised for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorous method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e., EXL owing to the temperature change, phase change, mixing in liquid and vapour phase and chemical reaction. The loss in reboiler and condenser is also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3 Graphical Ex-N-A methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, i.e., EXL owing to changes of the concentration (mixing), phase of the component and temperature, have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL owing to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (*A*) is explained as (Srinophakun et al., 2001):

$$A = \frac{E\dot{X}L}{\Delta H}. \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S. \tag{13}$$

Hence,

$$A = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{14}$$

It illustrates the maximum fraction of energy, which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{\text{Chem}} = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{15}$$

On the equilibrium condition in which the reaction does not occur, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T}. \tag{16}$$

In this condition, energy level *A* generally can be written as:

$$A = \left(1 - \frac{T_0}{T}\right). \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{\text{Liq}} = \left(1 - \frac{T_0}{T}\right). \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{\text{Gas}} = \left(1 - \frac{T_0}{T}\right). \tag{19}$$

T in the energy-level formula depends on the phase. *T* is the gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL owing to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL owing to the chemical reaction can be written as:

$$E\dot{X}L_{\text{Chem}} = (A_{\text{Liq}} - A_{\text{Chem}})\Delta H. \tag{20}$$

4 Display of packed reactive distillation column on graphical Ex-N-A diagram

4.1 Base case analysis

Ex-N-A diagram is an exergy-feature-based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008) and Budiman et al. (2011) composed the graph for EXL owing to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 \ln x_j$ as ordinate for the liquid phase and $\Re T_0 \ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A diagram is made by placing the two types of diagram in a single feature. The height of the column (N) is put as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of N as ordinate whereas total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which N was put as ordinate and A is set as abscissa. The other two diagrams exhibiting the correlation between the column height and total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared with the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL owing to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub-processes EXL is much larger than the others. It can also combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy-level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy-level difference between A_{gas} and A_{liq} ($A_{\text{gas}} - A_{\text{liq}}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy-level difference and exergy consumption as the shaded area in the diagrams. Hence, it does not clearly show the exergy profile at different levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (N) is plotted as abscissa against the total EXL, non-chemical reaction EXL and energy level. On the basis of this diagram, the graphical correlation between total EXL, non-chemical reaction EXL and energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) is incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph, which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of subgraphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL owing to the chemical reaction and non-chemical EXL (i.e., losses owing to the temperature change, mixing and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, i.e., EXL owing to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, and temperature change in liquid phase and temperature change in gas phases, is displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses owing to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. On the basis of this N-A graph, the energy-level difference between gas and liquid ($A_{gas} - A_{liq}$) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (*N*) was 3 m, the column diameter was 0.5 m and the molar ratio of methanol to oleic acid was 2 : 1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited in Figures 3–5, respectively. These data are required for the EXL calculation.

Figure 3 Concentration profiles of the compounds in liquid-1, liquid-2 and vapour phases at different column height (see online version for colours)

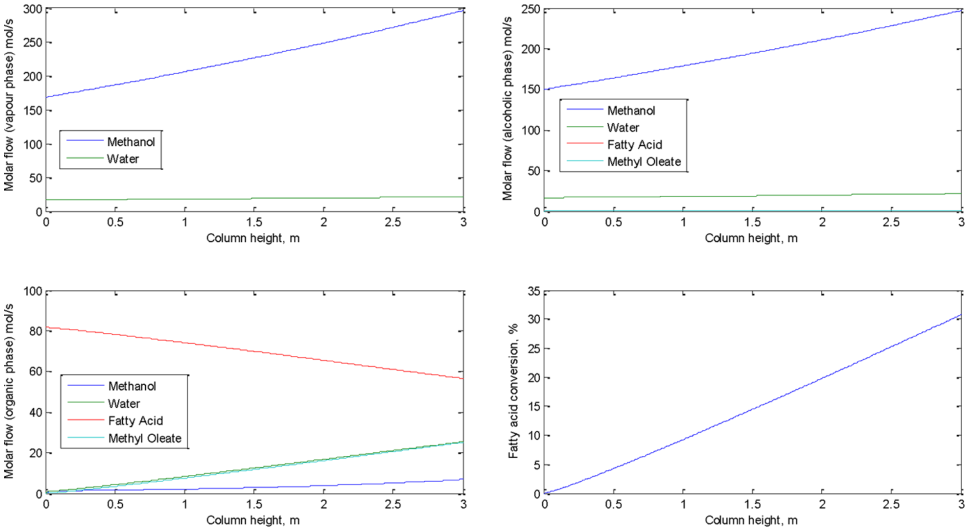


Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. In Figure 6(a), EXL of the reboiler and condenser is shown by the scale of 1/5 because of their large values.

The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

Figure 4 Total molar flow of each phase at different column height (see online version for colours)

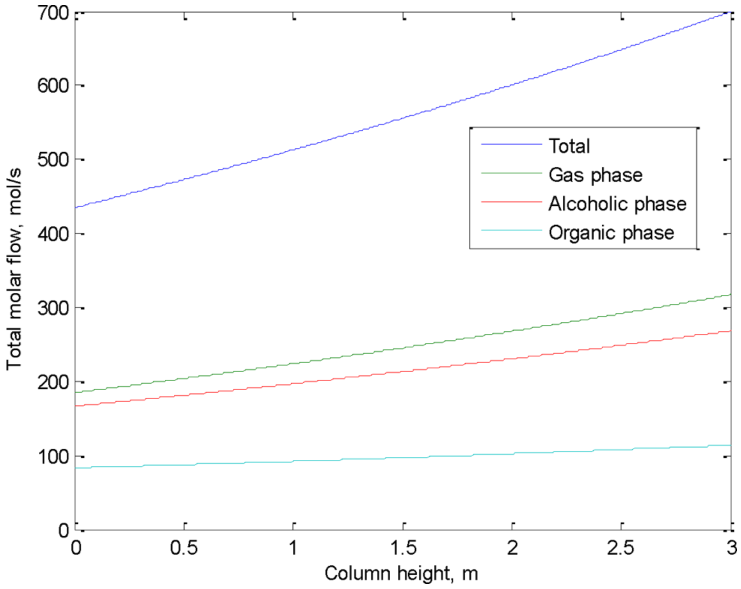


Figure 5 Temperature profile of liquid and vapour phase at different column height (see online version for colours)

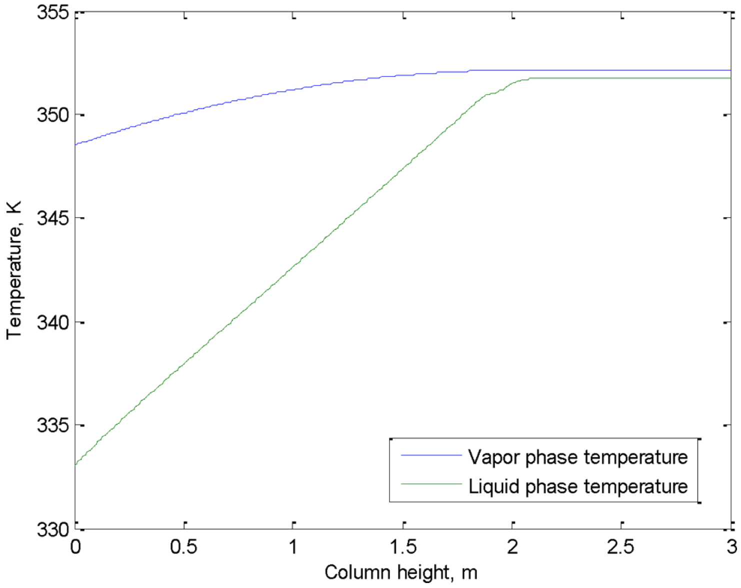
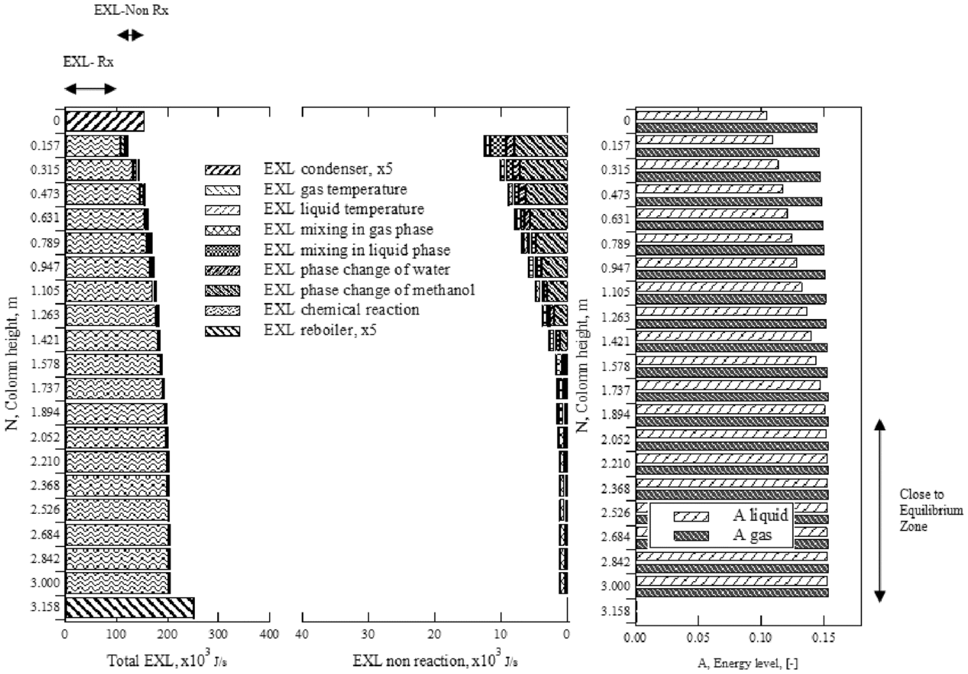


Figure 6 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

The incremental assessment on the RD column using Ex-N-A diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6(a) shows that the non-chemical EXL, i.e., the summation of EXL owing to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, starting from $N = 2$ m from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the A-N diagram in Figure 6(b), which displays the profile of the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) inside the column or the so-called driving force. Energy-level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy-level difference.

On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses that are influenced by temperature are zero. Hence, simply the EXL owing to the mixing exists at $N = 2$ m moved downwards. EXL owing to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL owing to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near-equilibrium condition has been reached. In this condition, a macro-heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium (NEQ) zone, and the second one is the close-to-equilibrium zone.

Two regions, NEQ and close-to-equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close-to-equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small temperature difference between gas and liquid, which also results in a very small (near to zero) energy-level difference. The condition where the energy-level difference or the driving force is very small (let us say ‘zero’) is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column, all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual and the near-to-equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy-level difference (driving force) between gas and liquid at the column top (A-N diagram in Figure 6(b)). In addition, the energy-level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the close-to-equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6(a). Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis owing to the chemical reaction. However, assessment on the EXL owing to chemical reaction incrementally has never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N diagrams in Figure 6(a) expose a different tendency between the profile of the total EXL and EXL owing to the chemical reaction, on the one side, and EXL owing to the non-chemical reaction, on the other side. The profile of total EXL and EXL owing to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL owing to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL owing to chemical reaction profile.

On the basis of the Ex-N diagram, it is revealed that the amount of EXL owing to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher the amount of reactants reacts, the higher the EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL owing to chemical reaction as well as total EXL increase from the top to the bottom.

Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (N). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimisation graphically.

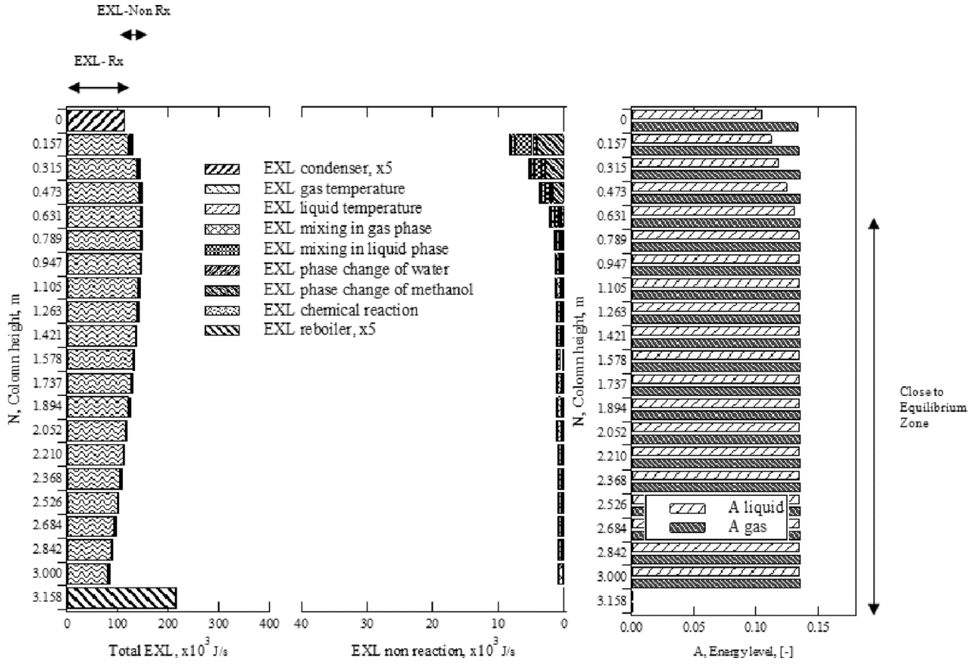
4.2 Effect of the molar ratio of the reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, first, the molar ratio of total methanol and oleic acid entering the column is increased from 2 : 1 to 6 : 1 at the same column height of 3 m ($N = 3$) and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, it is shown that the reaction conversion enhances about two times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7(a) shows that the profile of non-chemical EXL does not change so much compared with the result given by the molar ratio of 2 : 1. At molar ratio of 6 : 1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, whereas the upper part is NEQ zone. However, enhancing molar ratio from 2 : 1 to 6 : 1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7(b) shows that, when molar ratio of 6 : 1 is applied, the close-to-equilibrium zone starts at $N = 0.75$ m downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the NEQ zone inside the column. The larger area of the close-to-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of CEP gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1 : 1 with $N = 3$. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in Figure 8(b), all the areas in RD column are

NEQ zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses owing to mixing, phase and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

Figure 7 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 6 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

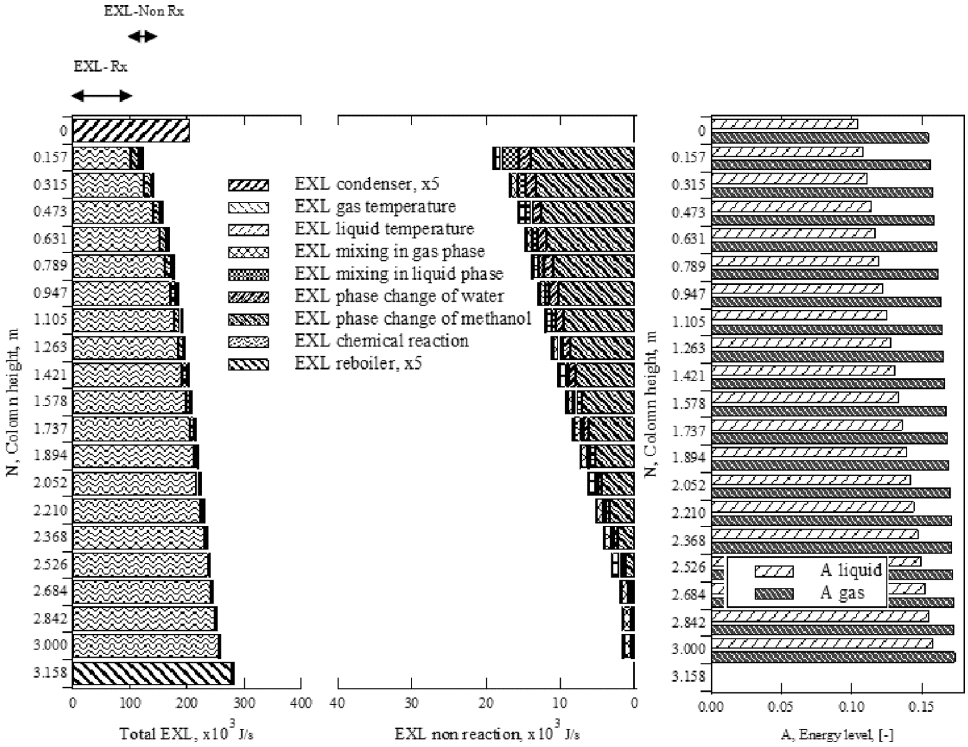
To evaluate the impact of varying the molar ratio on the value of the EXL owing to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1 : 1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2 : 1.

However, if molar ratio of the reactants is drastically enhanced to 6 : 1, the new Ex-N profile seems interesting. It is shown that EXL owing to the chemical reaction gets higher from the top downward as seen on the Ex-N diagram in Figure 7(a). In spite of this, at a certain point in the column, EXL owing to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL owing to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to react easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate.

At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease in the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL owing to chemical reaction in the column. It can be observed that EXL owing to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point, it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

Figure 8 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 1 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram

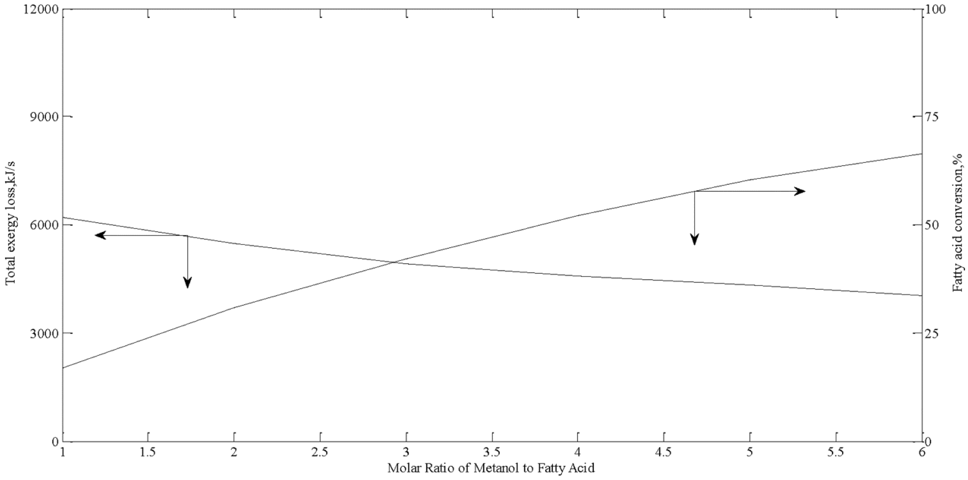


(a) (b)

4.3 *Effect of the height of the packed column (N)*

The subsequent important aspect to be analysed is the height of the column (N). To study this parameter, N is increased from 3 m to 6 m with the similar reactants molar ratio of 2 : 1, whereas the column diameter is kept the same (0.5 m). Hence, it reveals that the reaction conversion is enhanced from 30.76% to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N diagram in Figure 10(a) shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared with the profile of the column with the height of 3 m ($N = 3$). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the $N = 2$ m from the top, EXL of the sub-processes, which depends on temperature (loss owing to temperature and phase changes), approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N diagram in Figure 10(b). Nevertheless, it is shown that the energy-level difference between gas and liquid decreases from the top downward. Then, starting at $N = 2$ m downward, the energy-level difference is near to zero. Thus, the area in the column can be separated into two regions, i.e., the NEQ zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to $N = 2$, whereas the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the NEQ area. However, it just prolongs the close-to-equilibrium zone. The existing of NEQ region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

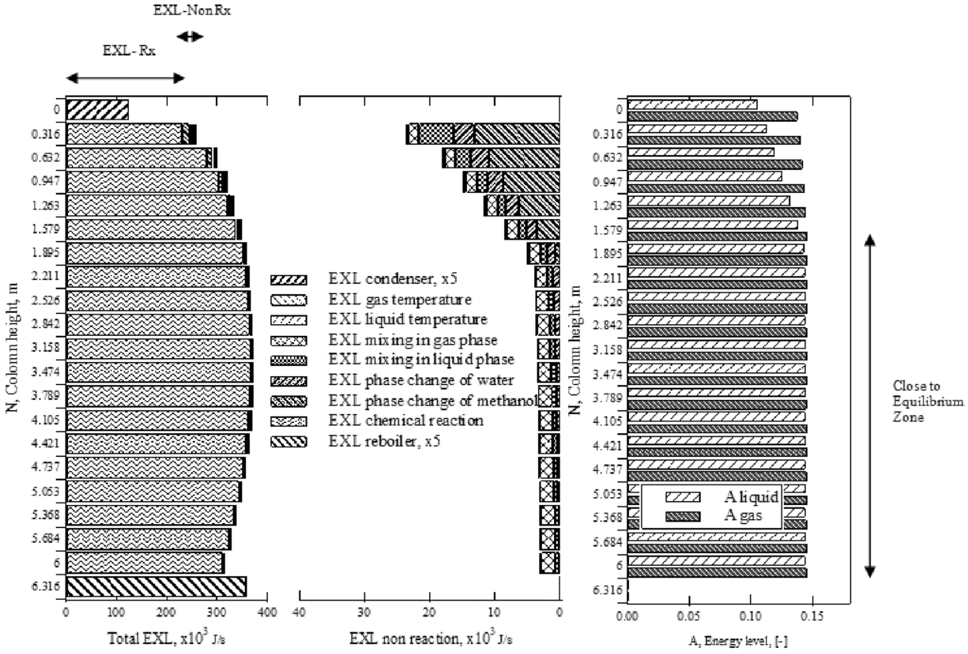
Figure 9 Profile of total exergy loss and fatty acid conversion at different reactant molar ratio



Effect of the column height (N) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment of $N = 2$, EXL owing to the chemical reaction values remains almost constant, and finally decreases at $N = 4$ to bottom. EXL owing to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared with the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

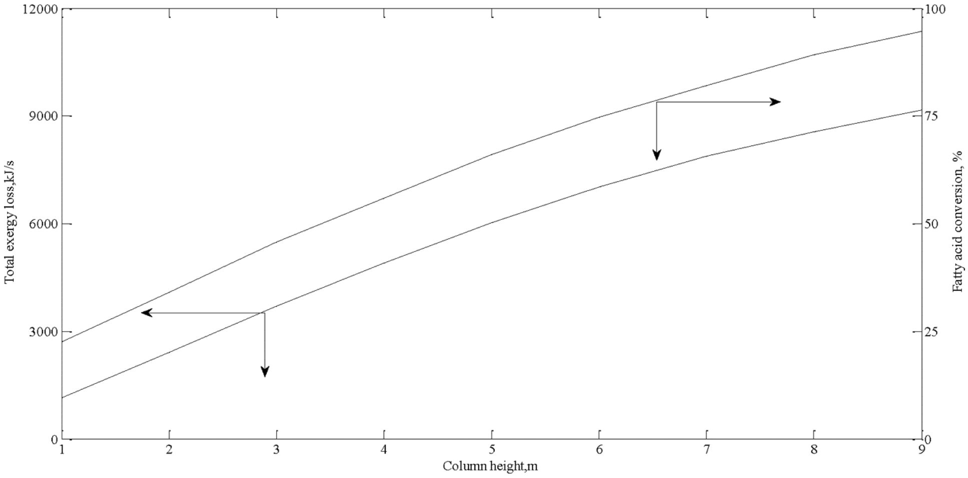
To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Figure 10 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 6$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height



Conclusively, there are some findings obtained by analysing the effects of the reactant molar ratio and column height. On the basis of the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height, which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5 Conclusions

- A graphical method called Ex-N-A diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy-level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-processes has a much larger EXL than the others.
- The base case of the RD simulation was studied at $N = 3$ m, the column diameter of 0.5 m and the molar ratio of methanol to oleic acid of 2 : 1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom, which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2 : 1 to 6 : 1 at the similar N of 3 m and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1 : 1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, N is increased from 3 m to 6 m, whereas the reactants molar ratio and column diameter are kept at 2 : 1 and 0.5 m, respectively. This reveals that the conversion is enhanced from 30.76% to 58.52%. Thus, the increase in the column height does not change the NEQ area; nevertheless, it just prolongs the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase
C_{cat}	Concentration of the solid catalyst ($\mathrm{kg_{cat}/m^3}$)
E_a	Activation energies (J/mol)
$E\dot{X}L$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant ($\mathrm{mol{\cdot}m^3/kg_{cat}^2/s}$)
k_2	Reverse reaction rate constant ($\mathrm{mol{\cdot}m^3/kg_{cat}^2/s}$)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component *i* from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component *i* from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{GL_1L_2}$	Mass transfer rate of component *i* from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
$\mathrm{d}z$	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase
L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase

Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Journal: Int. J. Exergy

Paper title: Graphical exergy analysis of reactive distillation column for biodiesel production

Author: Kusumaningtyas et al.

Page	Section	Paragraph	Line	Amendments/Corrections

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IJEx 16104 Kusumaningtyas et al. (4) - First Proofs

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However, in this list, the first author’s name is written as *Ratna Kusumaningtyas *while it should be* Ratna Dewi Kusumaningtyas. *Thus, we expect that, for the real paper publication, the name should be correctly written as* Ratna Dewi Kusumaningtyas *since the proper name in scientific publication is very important in our institution.

Thank you very much

Sincerely Yours

Arief Budiman
Professor,
Process System Engineering research group
Chemical Engineering Department, Gadjah Mada University, Indonesia
Website : http://pserg.wg.ugm.ac.id
Alternative email: abudiman_id@yahoo.com

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Journal: Int. J. Exergy

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Page	Section	Paragraph	Line	Amendments/Corrections
1	Author	1	4	Rochmadi to be Rochmadi Rochmadi
1	Reference	4	29	Rochmadi to be Rochmadi Rochmadi
2	Biographical notes	2	7	Rochmadi to be Rochmadi Rochmadi
2	Footnote	4	22-23	This paper is a revised and expanded version of a paper entitled **[title]** presented at [ ] To be DELETED (this paper never been published in any forum)
2	Introduction	5	29	Gomez-Castro to be Gómez-Castro
2	Introduction	5	29	2010 to be 2010 (correct) (it doesn't need to be changed)
3	Introduction	2	20-22	Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process. → The change made is OK
4	Model and simulation for reactive distillation (RD) column	2	9	relite CFS is a product name among many types of resin ion exchange, it is not an acronym
20	References	1	9	Sutijan to be Sutijan Sutijan
20	References	1	23	Gómez-Castro to be Gómez-Castro (it is correct)
20	References	1	23	2011 to be 2010

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Title: Graphical exergy analysis of reactive distillation column for biodiesel production

Dear Author

The amendments you requested to your paper have been incorporated and I attach a copy for you to confirm the changes have been made correctly as it may not be possible to make any further amendments at this stage before publication.

To avoid delay to publication it is important that you email confirmation of your acceptance of the proof as soon as possible and certainly within the next seven days. If we do not hear from you again within this time we will process the corrected paper for publication.

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> Dear Mr. Jyothi,

Graphical exergy analysis of reactive distillation column for biodiesel production

Ratna Dewi Kusumaningtyas, Suryo Purwono,
Rochmad Rochmadi and Arief Budiman*

Faculty of Engineering,
Chemical Engineering Department,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed reactive distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system. The graphical Ex-N-A method was utilised to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, i.e., losses owing to the temperature change, phase change, mixing in liquid and vapour phases and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Keywords: exergy analysis; RD; reactive distillation; esterification; Ex-N-A; biodiesel.

Reference to this paper should be made as follows: Kusumaningtyas, R.D., Purwono, S., Rochmadi, R. and Budiman, A. (xxxx) 'Graphical exergy analysis of reactive distillation column for biodiesel production', *Int. J. Exergy*, Vol. x, No. x, pp.xxx–xxx.

Biographical notes: Ratna Dewi Kusumaningtyas is a PhD student at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor's and Master's degrees from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange programme in Politecnico di Torino, Italy (2010–2012). She is the author and co-author of 12 journal and international conference papers during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD from

Chemical Engineering Department, University of Waterloo, Waterloo, Ontario, Canada, in 1993. His research focuses on distillation, petroleum and renewable energy development. He is the author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmad Rochmadi is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK, in 1991. His research topic is polymer and bio-fuel development. He is the author or co-author of 55 scientific papers. He is also the Coordinator of many industrial–university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan, in 1997. His research focuses on thermodynamics and exergy analysis for system engineering. He is the author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009 and 2011) and Visiting Professor at Kyushu University (2012).

1 Introduction

Reactive distillation (RD) is a promising alternative process for equilibrium-limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gómez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognised as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing and optimising an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various methods of exergy analysis have been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot-factor-specific enthalpy diagram*. This method is easy to utilise for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *energy utilisation diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXLs), namely EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenient when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called integrated energy utilisation diagram (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the material-utilisation diagram (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-processes EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared with the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (*N*) as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) as abscissa. This plotting results in a simple diagram, which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation and chemical reaction incrementally. And, it is yet easy to understand even in a case when one of the sub-processes EXL is much larger than the others. This diagram can also obviously exhibit the correlation of the exergy losses owing to chemical and non-chemical sub-processes with the energy-level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low-grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, NEQ model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phase and NEQ model has been merely studied for a distillation process, which does not involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss is also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2 Model and simulation for reactive distillation (RD) column

A packed RD column was utilised for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the presence of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown here:

$$\mathrm{RCOOH}(\mathrm{A})+\mathrm{CH_3OH}\ (\mathrm{B})\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\mathrm{RCOOCH_3}\ (\mathrm{C})+\mathrm{H_2O}\ (\mathrm{D}) \tag{1}$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1 x_A x_B - k_2 x_A x_B)C_{\mathrm{cat}}. \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with $\Delta H_r = 11213.12$ J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 1 Kinetic parameters of the pseudo-homogeneous model

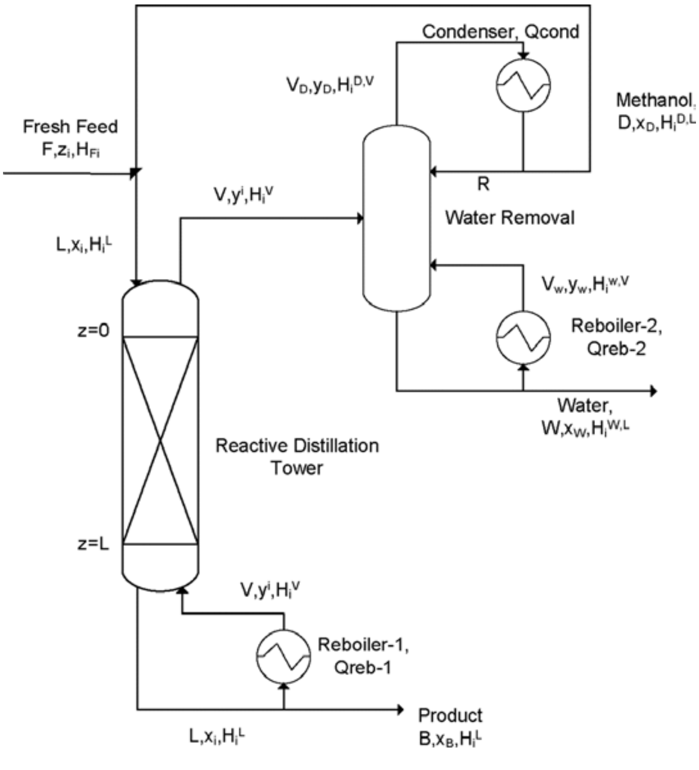
Reaction rate constant (mol m^3/kg$_{\mathrm{cat}}^2$/s)	*Ln*(*pre-exponential factor*)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

Table 2 Molecular structure and normal boiling points of all the chemical compounds

Compounds	*Molecular structure*	*Boiling point* (K)
Oleic acid (A)	$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH}$	632.85
Methanol (B)	$\mathrm{CH_3OH}$	337.7
Methyl-oleate (C)	$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3}$	616.85
Water (D)	$\mathrm{H_2O}$	373

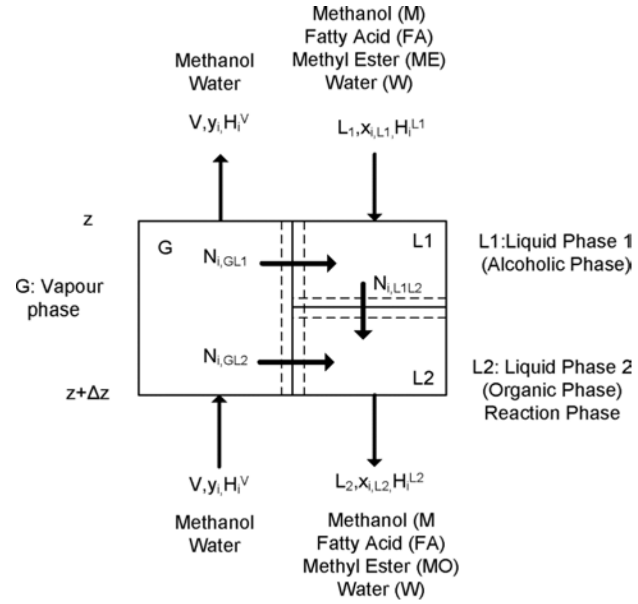
The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top is condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the column starts from the top, hence $N = 0$ m is the top of the column, while $N = n$ m is the lowest part of the column. The base case condition employs the packed column with the height of 3 m with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2 : 1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 and 69.52 mol/s, respectively.

Figure 1 The configuration of packed RD column for biodiesel production



The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase, which contains only methanol and water, alcoholic liquid phase, which contains mainly water and methanol, and organic liquid phase, which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

Figure 2 Schematic representation of one cell of three-phase packed RD column



The assumptions taken in this modelling and simulation can be written as follows:

1. In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.
2. The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.
3. The RD column operates at the steady-state condition.
4. There are three phases that occur in the system, namely vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).
5. The reaction takes place in the organic phase (liquid-2).
6. Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.
7. The RD column is modelled based on the NEQ approach. Hence, the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three-phase RD are summarised as follows. The mass balances of each compound in the vapour, liquid-1 and liquid-2 phases are formulated in equations (3)–(5), respectively:

$$\frac{\mathrm{d}y_{i,G}}{\mathrm{d}z}=\frac{(-\dot{R}_{i,G})-y_i\frac{\mathrm{d}V'}{\mathrm{d}z}}{V'} \tag{3}$$

$$\frac{\mathrm{d}x_{i,L_1}}{\mathrm{d}z}=\frac{(-\dot{R}_{i,L_1})-x_i\frac{\mathrm{d}L_1'}{\mathrm{d}z}}{L_1'} \tag{4}$$

$$\frac{\mathrm{d}x_{i,L_2}}{\mathrm{d}z}=\frac{-(-\dot{R}_{i,L_2})-x_i\frac{\mathrm{d}L_2'}{\mathrm{d}z}}{L_2'}. \tag{5}$$

Meanwhile, the total mass balance of the vapour, liquid-1 and liquid-2 phase is presented in equations (6)–(8), respectively:

$$\frac{\mathrm{d}V'}{\mathrm{d}z}=-\sum\dot{R}_{i,G} \tag{6}$$

$$\frac{\mathrm{d}L_1'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_1}\right) \tag{7}$$

$$\frac{\mathrm{d}L_2'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_2}\right) \tag{8}$$

To solve equations (3)–(8), the rate process equations are necessary. The rate process equations for the gas, liquid-1 and liquid-2 phases are equations (9)–(11), respectively.

$$\dot{R}_{i,G}=-(\dot{N}_i^{GL_1}+\dot{N}_i^{GL_2}) \tag{9}$$

$$\dot{R}_{i,L_1}=\dot{N}_i^{GL_1}-\dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2}=-\dot{N}_i^{GL_2}+\dot{N}_i^{L_1L_2}+v_i\dot{r}. \tag{11}$$

The result outputted from the RD simulation is utilised for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorous method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e., EXL owing to the temperature change, phase change, mixing in liquid and vapour phase and chemical reaction. The loss in reboiler and condenser is also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3 Graphical Ex-N-A methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, i.e., EXL owing to changes of the concentration (mixing), phase of the component and temperature, have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL owing to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (*A*) is explained as (Srinophakun et al., 2001):

$$A = \frac{E\dot{X}L}{\Delta H}. \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S. \tag{13}$$

Hence,

$$A = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{14}$$

It illustrates the maximum fraction of energy, which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{\text{Chem}} = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{15}$$

On the equilibrium condition in which the reaction does not occur, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T}. \tag{16}$$

In this condition, energy level *A* generally can be written as:

$$A = \left(1 - \frac{T_0}{T}\right). \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{\text{Liq}} = \left(1 - \frac{T_0}{T}\right). \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{\text{Gas}} = \left(1 - \frac{T_0}{T}\right). \tag{19}$$

T in the energy-level formula depends on the phase. *T* is the gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL owing to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL owing to the chemical reaction can be written as:

$$E\dot{X}L_{\text{Chem}} = (A_{\text{Liq}} - A_{\text{Chem}})\Delta H. \tag{20}$$

4 Display of packed reactive distillation column on graphical Ex-N-A diagram

4.1 Base case analysis

Ex-N-A diagram is an exergy-feature-based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008) and Budiman et al. (2011) composed the graph for EXL owing to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 \ln x_j$ as ordinate for the liquid phase and $\Re T_0 \ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A diagram is made by placing the two types of diagram in a single feature. The height of the column (N) is put as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of N as ordinate whereas total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which N was put as ordinate and A is set as abscissa. The other two diagrams exhibiting the correlation between the column height and total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared with the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL owing to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub-processes EXL is much larger than the others. It can also combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy-level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy-level difference between A_{gas} and A_{liq} ($A_{\mathrm{gas}} - A_{\mathrm{liq}}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy-level difference and exergy consumption as the shaded area in the diagrams. Hence, it does not clearly show the exergy profile at different levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (N) is plotted as abscissa against the total EXL, non-chemical reaction EXL and energy level. On the basis of this diagram, the graphical correlation between total EXL, non-chemical reaction EXL and energy-level difference between gas and liquid ($A_{\mathrm{gas}} - A_{\mathrm{liq}}$) is incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph, which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of subgraphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL owing to the chemical reaction and non-chemical EXL (i.e., losses owing to the temperature change, mixing and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, i.e., EXL owing to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, and temperature change in liquid phase and temperature change in gas phases, is displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses owing to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. On the basis of this N-A graph, the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (*N*) was 3 m, the column diameter was 0.5 m and the molar ratio of methanol to oleic acid was 2 : 1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited in Figures 3–5, respectively. These data are required for the EXL calculation.

Figure 3 Concentration profiles of the compounds in liquid-1, liquid-2 and vapour phases at different column height (see online version for colours)

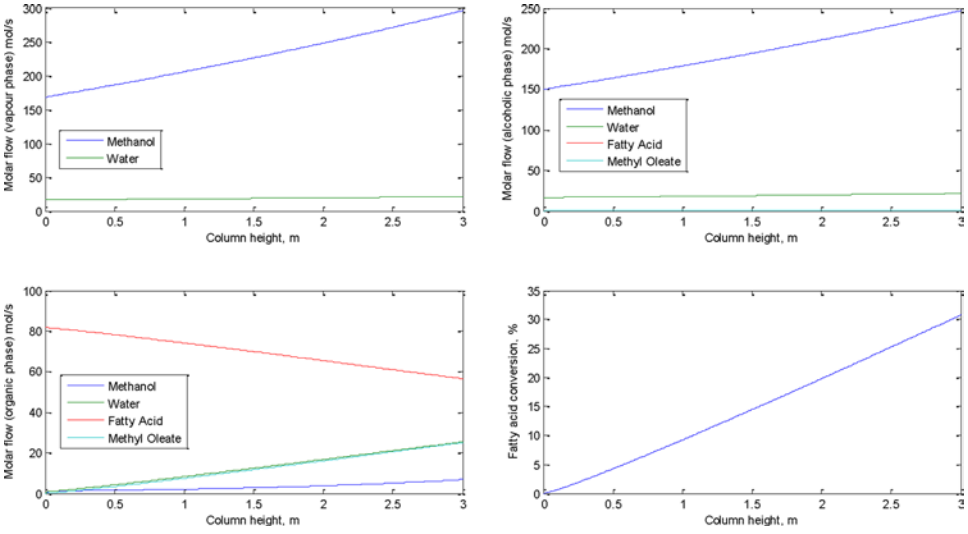


Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. In Figure 6(a), EXL of the reboiler and condenser is shown by the scale of 1/5 because of their large values.

The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

Figure 4 Total molar flow of each phase at different column height (see online version for colours)

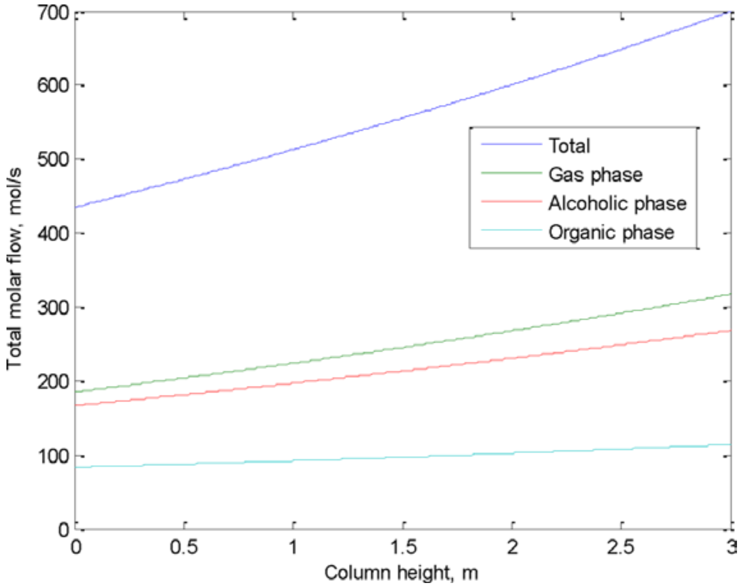


Figure 5 Temperature profile of liquid and vapour phase at different column height (see online version for colours)

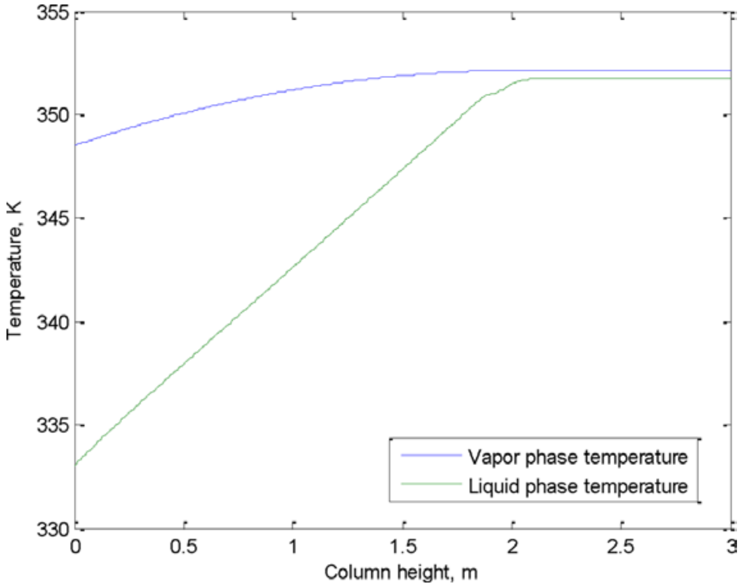
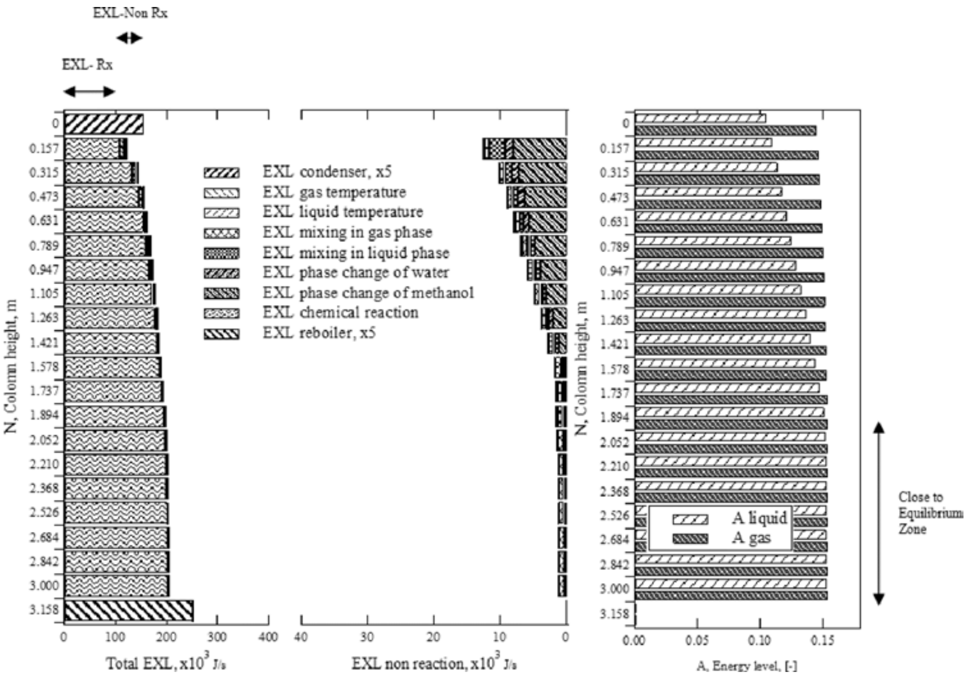


Figure 6 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

The incremental assessment on the RD column using Ex-N-A diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6(a) shows that the non-chemical EXL, i.e., the summation of EXL owing to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, starting from $N = 2$ m from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the A-N diagram in Figure 6(b), which displays the profile of the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) inside the column or the so-called driving force. Energy-level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy-level difference.

On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses that are influenced by temperature are zero. Hence, simply the EXL owing to the mixing exists at $N = 2$ m moved downwards. EXL owing to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL owing to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near-equilibrium condition has been reached. In this condition, a macro-heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium (NEQ) zone, and the second one is the close-to-equilibrium zone.

Two regions, NEQ and close-to-equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close-to-equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small temperature difference between gas and liquid, which also results in a very small (near to zero) energy-level difference. The condition where the energy-level difference or the driving force is very small (let us say 'zero') is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column, all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual and the near-to-equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy-level difference (driving force) between gas and liquid at the column top (A-N diagram in Figure 6(b)). In addition, the energy-level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the close-to-equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6(a). Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis owing to the chemical reaction. However, assessment on the EXL owing to chemical reaction incrementally has never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N diagrams in Figure 6(a) expose a different tendency between the profile of the total EXL and EXL owing to the chemical reaction, on the one side, and EXL owing to the non-chemical reaction, on the other side. The profile of total EXL and EXL owing to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL owing to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL owing to chemical reaction profile.

On the basis of the Ex-N diagram, it is revealed that the amount of EXL owing to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher the amount of reactants reacts, the higher the EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL owing to chemical reaction as well as total EXL increase from the top to the bottom.

Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (*N*). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimisation graphically.

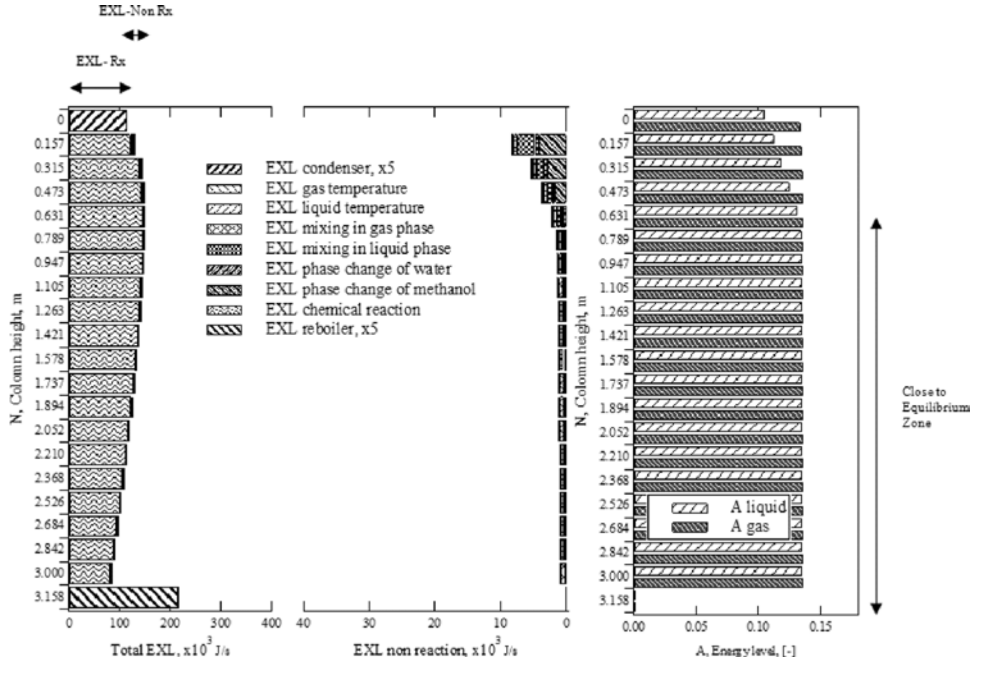
4.2 Effect of the molar ratio of the reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, first, the molar ratio of total methanol and oleic acid entering the column is increased from 2 : 1 to 6 : 1 at the same column height of 3 m ($N = 3$) and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, it is shown that the reaction conversion enhances about two times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7(a) shows that the profile of non-chemical EXL does not change so much compared with the result given by the molar ratio of 2 : 1. At molar ratio of 6 : 1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, whereas the upper part is NEQ zone. However, enhancing molar ratio from 2 : 1 to 6 : 1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7(b) shows that, when molar ratio of 6 : 1 is applied, the close-to-equilibrium zone starts at $N = 0.75$ m downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the NEQ zone inside the column. The larger area of the close-to-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of CEP gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1 : 1 with $N = 3$. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in Figure 8(b), all the areas in RD column are

NEQ zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses owing to mixing, phase and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

Figure 7 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 6 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

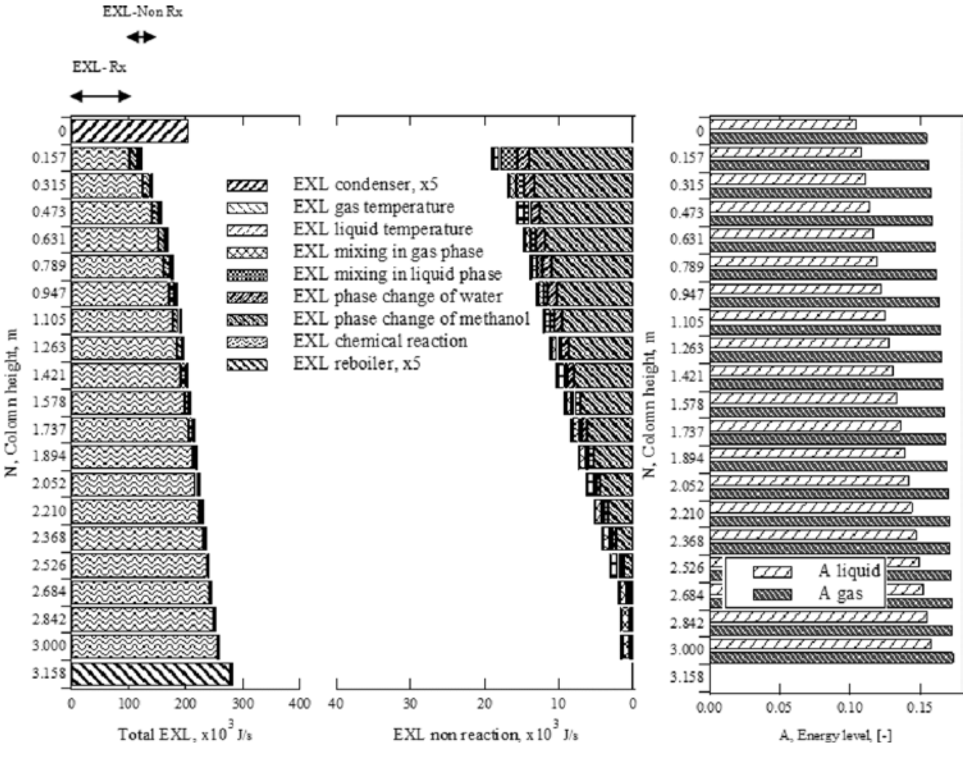
To evaluate the impact of varying the molar ratio on the value of the EXL owing to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1 : 1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2 : 1.

However, if molar ratio of the reactants is drastically enhanced to 6 : 1, the new Ex-N profile seems interesting. It is shown that EXL owing to the chemical reaction gets higher from the top downward as seen on the Ex-N diagram in Figure 7(a). In spite of this, at a certain point in the column, EXL owing to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL owing to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to react easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate.

At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease in the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL owing to chemical reaction in the column. It can be observed that EXL owing to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point, it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

Figure 8 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 1 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram

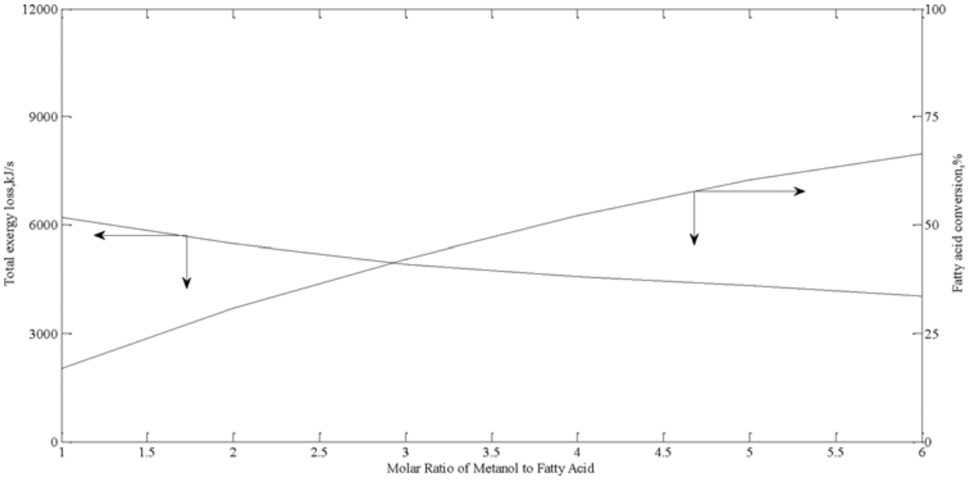


(a) (b)

4.3 *Effect of the height of the packed column (N)*

The subsequent important aspect to be analysed is the height of the column (*N*). To study this parameter, *N* is increased from 3 m to 6 m with the similar reactants molar ratio of 2 : 1, whereas the column diameter is kept the same (0.5 m). Hence, it reveals that the reaction conversion is enhanced from 30.76% to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N diagram in Figure 10(a) shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared with the profile of the column with the height of 3 m ($N = 3$). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the $N = 2$ m from the top, EXL of the sub-processes, which depends on temperature (loss owing to temperature and phase changes), approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N diagram in Figure 10(b). Nevertheless, it is shown that the energy-level difference between gas and liquid decreases from the top downward. Then, starting at $N = 2$ m downward, the energy-level difference is near to zero. Thus, the area in the column can be separated into two regions, i.e., the NEQ zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to $N = 2$, whereas the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the NEQ area. However, it just prolongs the close-to-equilibrium zone. The existing of NEQ region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

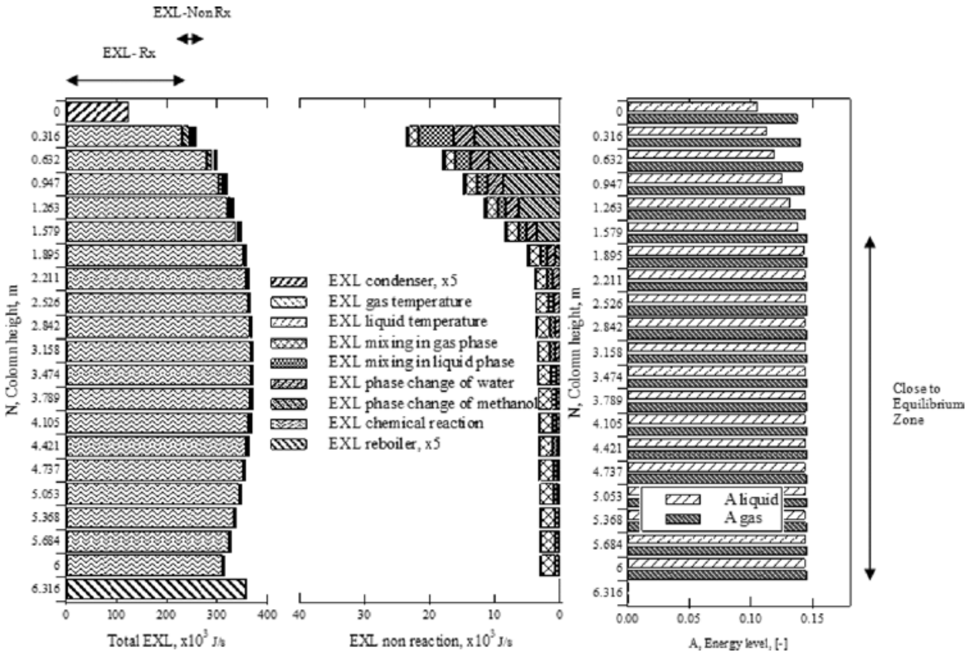
Figure 9 Profile of total exergy loss and fatty acid conversion at different reactant molar ratio



Effect of the column height (N) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment of $N = 2$, EXL owing to the chemical reaction values remains almost constant, and finally decreases at $N = 4$ to bottom. EXL owing to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared with the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

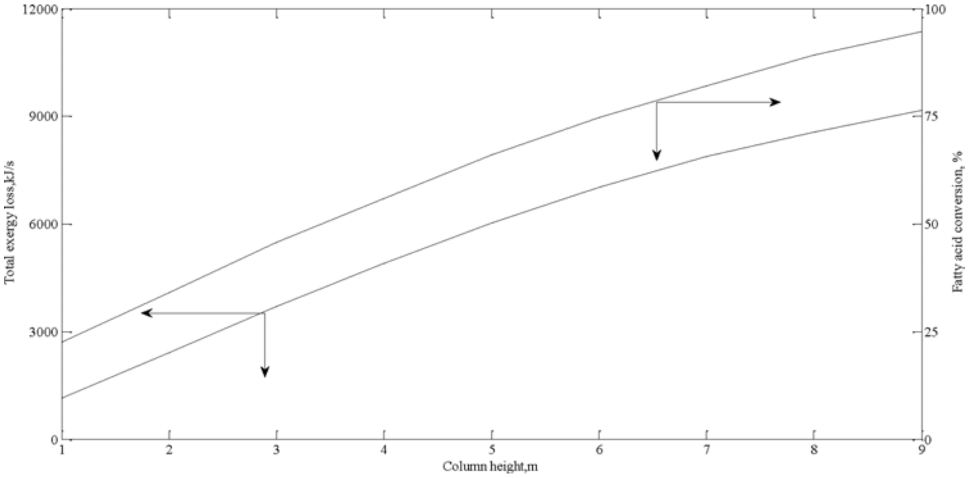
To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Figure 10 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at *N* = 6 m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height



Conclusively, there are some findings obtained by analysing the effects of the reactant molar ratio and column height. On the basis of the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height, which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5 Conclusions

- A graphical method called Ex-N-A diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy-level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-processes has a much larger EXL than the others.
- The base case of the RD simulation was studied at $N = 3$ m, the column diameter of 0.5 m and the molar ratio of methanol to oleic acid of 2 : 1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom, which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2 : 1 to 6 : 1 at the similar N of 3 m and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1 : 1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, N is increased from 3 m to 6 m, whereas the reactants molar ratio and column diameter are kept at 2 : 1 and 0.5 m, respectively. This reveals that the conversion is enhanced from 30.76% to 58.52%. Thus, the increase in the column height does not change the NEQ area; nevertheless, it just prolongs the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase
C_{cat}	Concentration of the solid catalyst ($\mathrm{kg_{cat}/m^3}$)
E_a	Activation energies (J/mol)
$E\dot{X}L$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant ($\mathrm{mol{\cdot}m^3/kg_{cat}{}^2/s}$)
k_2	Reverse reaction rate constant ($\mathrm{mol{\cdot}m^3/kg_{cat}{}^2/s}$)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component *i* from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component *i* from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{GL_1L_2}$	Mass transfer rate of component *i* from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
$\mathrm{d}z$	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase
L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase

Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Gmail

dewinino <dewinino@gmail.com>

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1. Page 1, author name

The third author's name is written Rochmad Rochmadi, while it should be: Rochmadi Rochmadi

2. Page 1, Keywords

"Keywords" is written as:

Keywords: exergy analysis; RD; reactive distillation; esterification; Ex-N-A; biodiesel.

While it should be written as:

Keywords: exergy analysis; reactive distillation (RD); esterification; Ex-N-A; biodiesel.

3. Page 2, Biographical notes:

It is written as Rochmad Rochmadi, while it should be: Rochmadi Rochmadi

Thank you very much for your attention and willingness for correction before publication

Sincerely Yours

Arief Budiman
Professor,
Process System Engineering research group
Chemical Engineering Department, Gadjah Mada University, Indonesia
Website : http://pserg.wg.ugm.ac.id
Alternative email: abudiman_id@yahoo.com

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Graphical exergy analysis of reactive distillation column for biodiesel production

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi Rochmadi and Arief Budiman*

Faculty of Engineering,
Chemical Engineering Department,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed reactive distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system. The graphical Ex-N-A method was utilised to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, i.e., losses owing to the temperature change, phase change, mixing in liquid and vapour phases and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Keywords: exergy analysis; reactive distillation; esterification; Ex-N-A; biodiesel.

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Biographical notes: Ratna Dewi Kusumaningtyas is a PhD student at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor's and Master's degrees from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange programme in Politecnico di Torino, Italy (2010–2012). She is the author and co-author of 12 journal and international conference papers during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario,

Canada, in 1993. His research focuses on distillation, petroleum and renewable energy development. He is the author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi Rochmadi is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK, in 1991. His research topic is polymer and bio-fuel development. He is the author or co-author of 55 scientific papers. He is also the Coordinator of many industrial–university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan, in 1997. His research focuses on thermodynamics and exergy analysis for system engineering. He is the author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009 and 2011) and Visiting Professor at Kyushu University (2012).

1 Introduction

Reactive distillation (RD) is a promising alternative process for equilibrium-limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gómez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognised as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing and optimising an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various methods of exergy analysis have been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot-factor-specific enthalpy diagram*. This method is easy to utilise for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *energy utilisation diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXLs), namely EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenient when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called integrated energy utilisation diagram (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the material-utilisation diagram (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-processes EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared with the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (N) as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) as abscissa. This plotting results in a simple diagram, which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation and chemical reaction incrementally. And, it is yet easy to understand even in a case when one of the sub-processes EXL is much larger than the others. This diagram can also obviously exhibit the correlation of the exergy losses owing to chemical and non-chemical sub-processes with the energy-level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low-grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, NEQ model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phase and NEQ model has been merely studied for a distillation process, which does not involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss is also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2 Model and simulation for reactive distillation (RD) column

A packed RD column was utilised for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the presence of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown here:

$$\text{RCOOH}(\text{A})+\text{CH}_3\text{OH}\ (\text{B}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{RCOOCH}_3\,(\text{C})+\text{H}_2\text{O}\ (\text{D}) \tag{1}$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1 x_A x_B - k_2 x_A x_B) C_{\text{cat}}. \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with $\Delta H_r = 11213.12$ J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 1 Kinetic parameters of the pseudo-homogeneous model

Reaction rate constant (mol $m^3/kg_{cat}^2/s$)	*Ln*(*pre-exponential factor*)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

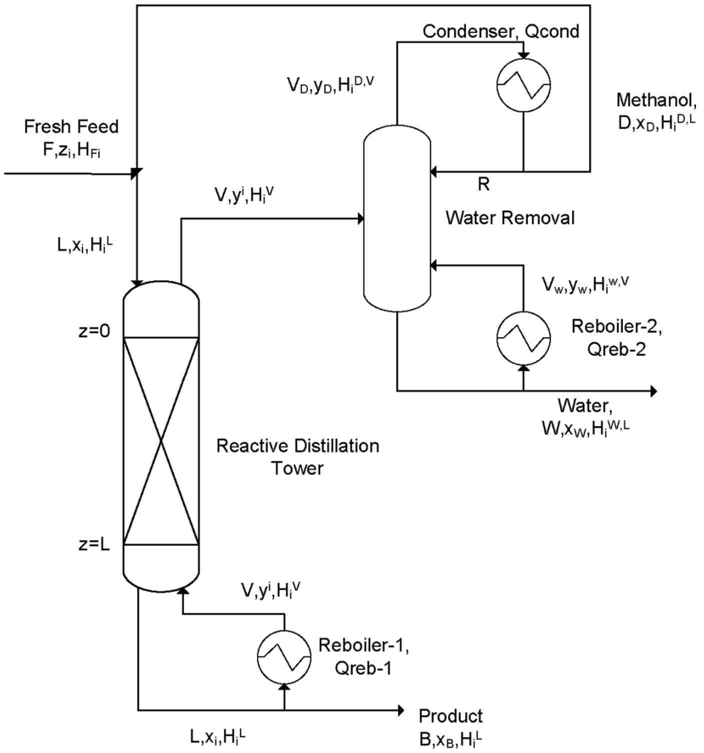
Table 2 Molecular structure and normal boiling points of all the chemical compounds

Compounds	*Molecular structure*	*Boiling point* (K)
Oleic acid (A)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	616.85
Water (D)	H_2O	373

The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top is condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the

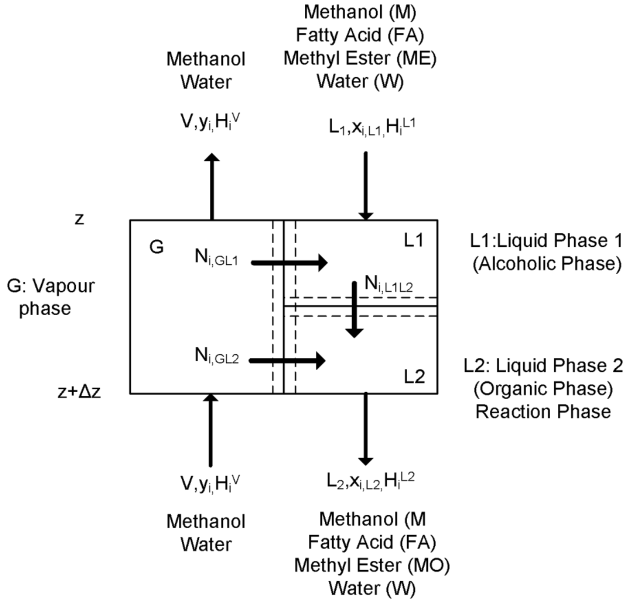
column starts from the top, hence $N = 0$ m is the top of the column, while $N = n$ m is the lowest part of the column. The base case condition employs the packed column with the height of 3 m with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2 : 1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 and 69.52 mol/s, respectively.

Figure 1 The configuration of packed RD column for biodiesel production



The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase, which contains only methanol and water, alcoholic liquid phase, which contains mainly water and methanol, and organic liquid phase, which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

Figure 2 Schematic representation of one cell of three-phase packed RD column



The assumptions taken in this modelling and simulation can be written as follows:

1. In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.
2. The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.
3. The RD column operates at the steady-state condition.
4. There are three phases that occur in the system, namely vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).
5. The reaction takes place in the organic phase (liquid-2).
6. Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.
7. The RD column is modelled based on the NEQ approach. Hence, the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three-phase RD are summarised as follows. The mass balances of each compound in the vapour, liquid-1 and liquid-2 phases are formulated in equations (3)–(5), respectively:

$$\frac{\mathrm{d}y_{i,G}}{\mathrm{d}z} = \frac{(-\dot{R}_{i,G}) - y_i \frac{\mathrm{d}V'}{\mathrm{d}z}}{V'} \tag{3}$$

$$\frac{\mathrm{d}x_{i,L_1}}{\mathrm{d}z} = \frac{(-\dot{R}_{i,L_1}) - x_i \frac{\mathrm{d}L_1'}{\mathrm{d}z}}{L_1'} \tag{4}$$

$$\frac{\mathrm{d}x_{i,L_2}}{\mathrm{d}z} = \frac{-(-\dot{R}_{i,L_2}) - x_i \frac{\mathrm{d}L_2'}{\mathrm{d}z}}{L_2'}. \tag{5}$$

Meanwhile, the total mass balance of the vapour, liquid-1 and liquid-2 phase is presented in equations (6)–(8), respectively:

$$\frac{\mathrm{d}V'}{\mathrm{d}z} = -\sum \dot{R}_{i,G} \tag{6}$$

$$\frac{\mathrm{d}L_1'}{\mathrm{d}z} = -\left(-\sum \dot{R}_{i,L_1}\right) \tag{7}$$

$$\frac{\mathrm{d}L_2'}{\mathrm{d}z} = -\left(-\sum \dot{R}_{i,L_2}\right) \tag{8}$$

To solve equations (3)–(8), the rate process equations are necessary. The rate process equations for the gas, liquid-1 and liquid-2 phases are equations (9)–(11), respectively.

$$\dot{R}_{i,G} = -(\dot{N}_i^{GL_1} + \dot{N}_i^{GL_2}) \tag{9}$$

$$\dot{R}_{i,L_1} = \dot{N}_i^{GL_1} - \dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2} = -\dot{N}_i^{GL_2} + \dot{N}_i^{L_1L_2} + v_i\dot{r}. \tag{11}$$

The result outputted from the RD simulation is utilised for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorous method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e., EXL owing to the temperature change, phase change, mixing in liquid and vapour phase and chemical reaction. The loss in reboiler and condenser is also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3 Graphical Ex-N-A methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, i.e., EXL owing to changes of the concentration (mixing), phase of the component and temperature, have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL owing to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (*A*) is explained as (Srinophakun et al., 2001):

$$A = \frac{E\dot{X}L}{\Delta H}. \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S. \tag{13}$$

Hence,

$$A = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{14}$$

It illustrates the maximum fraction of energy, which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{\text{Chem}} = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{15}$$

On the equilibrium condition in which the reaction does not occur, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T}. \tag{16}$$

In this condition, energy level A generally can be written as:

$$A = \left(1 - \frac{T_0}{T}\right). \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{\text{Liq}} = \left(1 - \frac{T_0}{T}\right). \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{\text{Gas}} = \left(1 - \frac{T_0}{T}\right). \tag{19}$$

T in the energy-level formula depends on the phase. T is the gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL owing to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL owing to the chemical reaction can be written as:

$$E\dot{X}L_{\text{Chem}} = (A_{\text{Liq}} - A_{\text{Chem}})\Delta H. \tag{20}$$

4 Display of packed reactive distillation column on graphical Ex-N-A diagram

4.1 Base case analysis

Ex-N-A diagram is an exergy-feature-based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous

graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008) and Budiman et al. (2011) composed the graph for EXL owing to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 \ln x_j$ as ordinate for the liquid phase and $\Re T_0 \ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A diagram is made by placing the two types of diagram in a single feature. The height of the column (N) is put as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of N as ordinate whereas total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which N was put as ordinate and A is set as abscissa. The other two diagrams exhibiting the correlation between the column height and total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared with the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL owing to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub-processes EXL is much larger than the others. It can also combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy-level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy-level difference between A_{gas} and A_{liq} ($A_{\text{gas}} - A_{\text{liq}}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy-level difference and exergy consumption as the shaded area in the diagrams. Hence, it does not clearly show the exergy profile at different levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (N) is plotted as abscissa against the total EXL, non-chemical reaction EXL and energy level. On the basis of this diagram, the graphical correlation between total EXL, non-chemical reaction EXL and energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) is incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph, which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of subgraphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL owing to the chemical reaction and non-chemical EXL (i.e., losses owing to the temperature change, mixing and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, i.e., EXL owing to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, and temperature change in liquid phase and temperature change in gas phases, is displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses owing to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. On the basis of this N-A graph, the energy-level difference between gas and liquid ($A_{gas} - A_{liq}$) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (N) was 3 m, the column diameter was 0.5 m and the molar ratio of methanol to oleic acid was 2 : 1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited in Figures 3–5, respectively. These data are required for the EXL calculation.

Figure 3 Concentration profiles of the compounds in liquid-1, liquid-2 and vapour phases at different column height (see online version for colours)

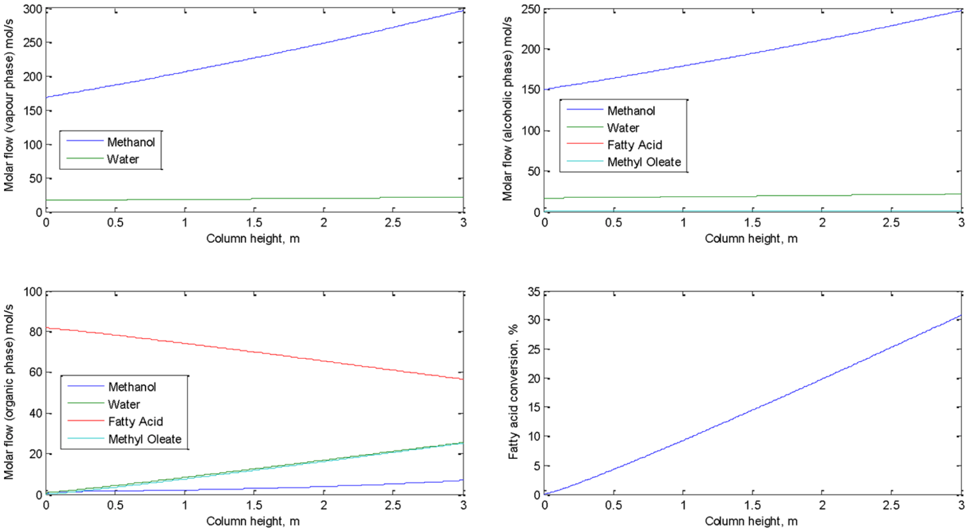


Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. In Figure 6(a), EXL of the reboiler and condenser is shown by the scale of 1/5 because of their large values.

The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

Figure 4 Total molar flow of each phase at different column height (see online version for colours)

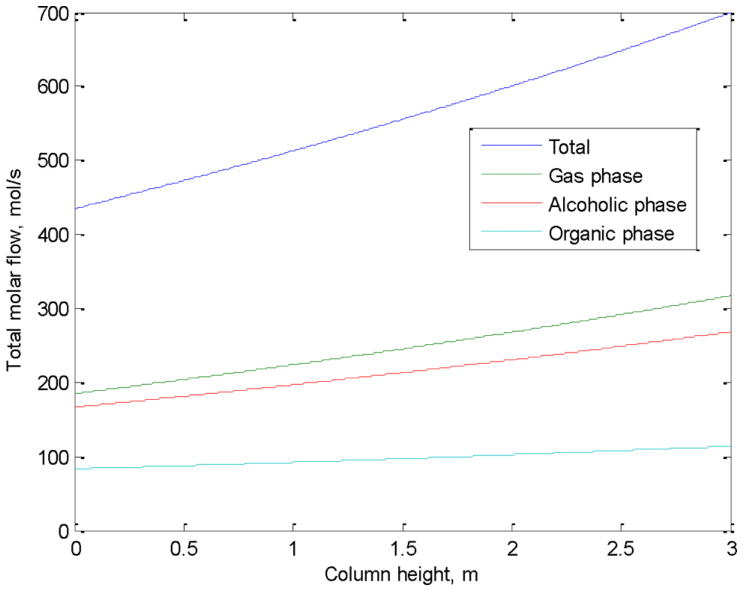


Figure 5 Temperature profile of liquid and vapour phase at different column height (see online version for colours)

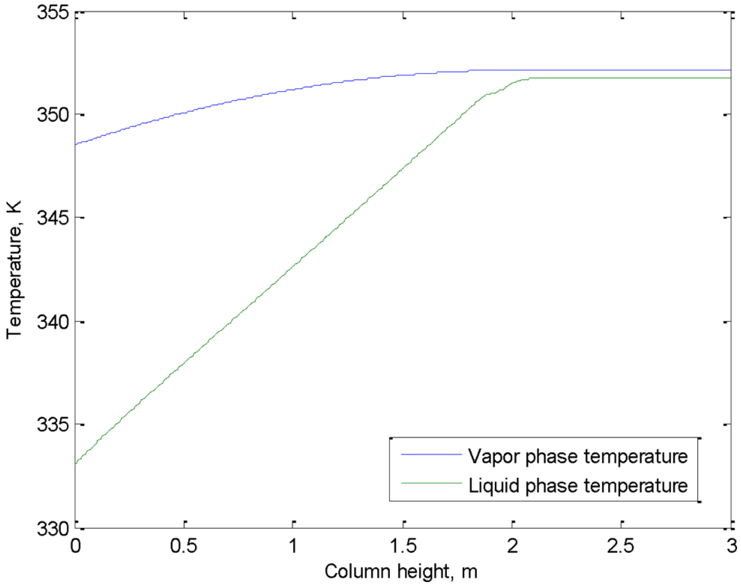
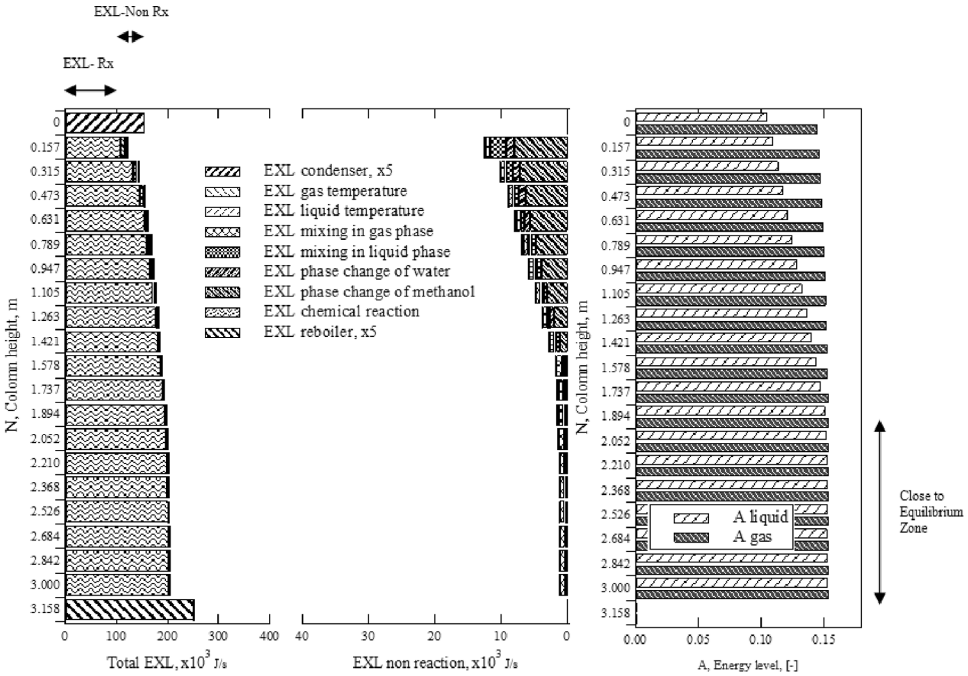


Figure 6 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

The incremental assessment on the RD column using Ex-N-A diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6(a) shows that the non-chemical EXL, i.e., the summation of EXL owing to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, starting from $N = 2$ m from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the A-N diagram in Figure 6(b), which displays the profile of the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) inside the column or the so-called driving force. Energy-level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy-level difference.

On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses that are influenced by temperature are zero. Hence, simply the EXL owing to the mixing exists at $N = 2$ m moved downwards. EXL owing to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL owing to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near-equilibrium condition has been reached. In this condition, a macro-heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium (NEQ) zone, and the second one is the close-to-equilibrium zone.

Two regions, NEQ and close-to-equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close-to-equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small temperature difference between gas and liquid, which also results in a very small (near to zero) energy-level difference. The condition where the energy-level difference or the driving force is very small (let us say 'zero') is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column, all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual and the near-to-equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy-level difference (driving force) between gas and liquid at the column top (A-N diagram in Figure 6(b)). In addition, the energy-level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the close-to-equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6(a). Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis owing to the chemical reaction. However, assessment on the EXL owing to chemical reaction incrementally has never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N diagrams in Figure 6(a) expose a different tendency between the profile of the total EXL and EXL owing to the chemical reaction, on the one side, and EXL owing to the non-chemical reaction, on the other side. The profile of total EXL and EXL owing to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL owing to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL owing to chemical reaction profile.

On the basis of the Ex-N diagram, it is revealed that the amount of EXL owing to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher the amount of reactants reacts, the higher the EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL owing to chemical reaction as well as total EXL increase from the top to the bottom.

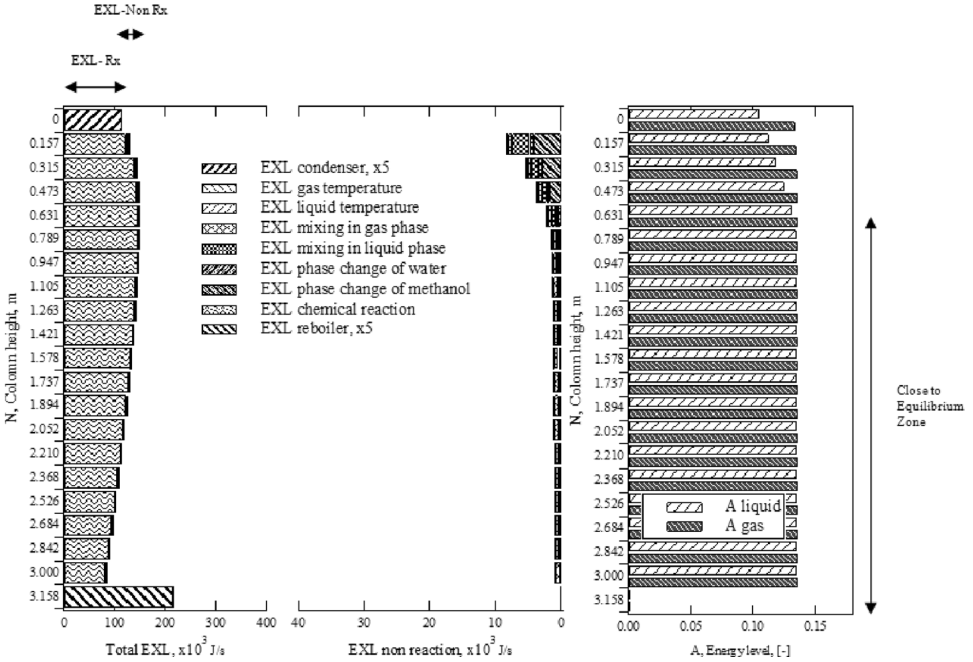
Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (N). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimisation graphically.

4.2 Effect of the molar ratio of the reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, first, the molar ratio of total methanol and oleic acid entering the column is increased from 2 : 1 to 6 : 1 at the same column height of 3 m ($N = 3$) and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, it is shown that the reaction conversion enhances about two times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7(a) shows that the profile of non-chemical EXL does not change so much compared with the result given by the molar ratio of 2 : 1. At molar ratio of 6 : 1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, whereas the upper part is NEQ zone. However, enhancing molar ratio from 2 : 1 to 6 : 1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7(b) shows that, when molar ratio of 6 : 1 is applied, the close-to-equilibrium zone starts at $N = 0.75$ m downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the NEQ zone inside the column. The larger area of the close-to-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of CEP gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1 : 1 with $N = 3$. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in Figure 8(b), all the areas in RD column are NEQ zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses owing to mixing, phase and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

Figure 7 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 6 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram



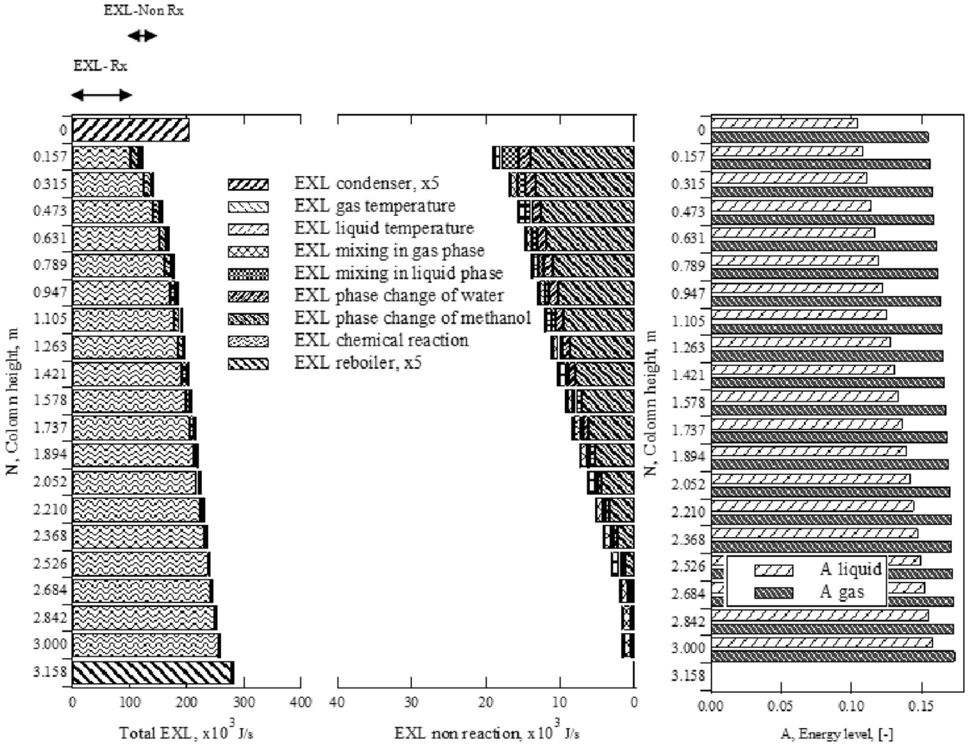
(a) (b)

To evaluate the impact of varying the molar ratio on the value of the EXL owing to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1 : 1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2 : 1.

However, if molar ratio of the reactants is drastically enhanced to 6 : 1, the new Ex-N profile seems interesting. It is shown that EXL owing to the chemical reaction gets higher from the top downward as seen on the Ex-N diagram in Figure 7(a). In spite of this, at a certain point in the column, EXL owing to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL owing to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to react easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease in the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL owing to chemical reaction in the column. It can be observed that EXL owing to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point, it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

Figure 8 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 1 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram



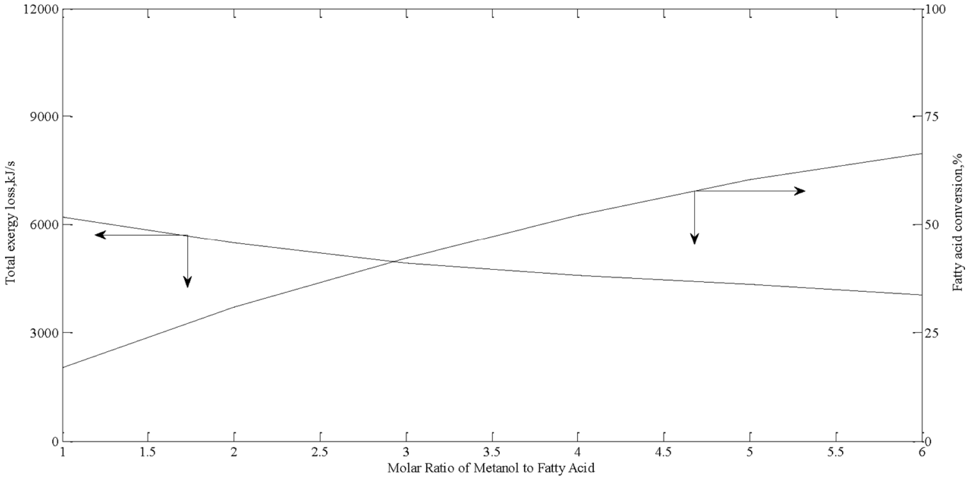
(a) (b)

4.3 *Effect of the height of the packed column (N)*

The subsequent important aspect to be analysed is the height of the column (*N*). To study this parameter, *N* is increased from 3 m to 6 m with the similar reactants molar ratio of 2 : 1, whereas the column diameter is kept the same (0.5 m). Hence, it reveals that the reaction conversion is enhanced from 30.76% to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N diagram in

Figure 10(a) shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared with the profile of the column with the height of 3 m (*N* = 3). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the *N* = 2 m from the top, EXL of the sub-processes, which depends on temperature (loss owing to temperature and phase changes), approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N diagram in Figure 10(b). Nevertheless, it is shown that the energy-level difference between gas and liquid decreases from the top downward. Then, starting at *N* = 2 m downward, the energy-level difference is near to zero. Thus, the area in the column can be separated into two regions, i.e., the NEQ zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to *N* = 2, whereas the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the NEQ area. However, it just prolongs the close-to-equilibrium zone. The existing of NEQ region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

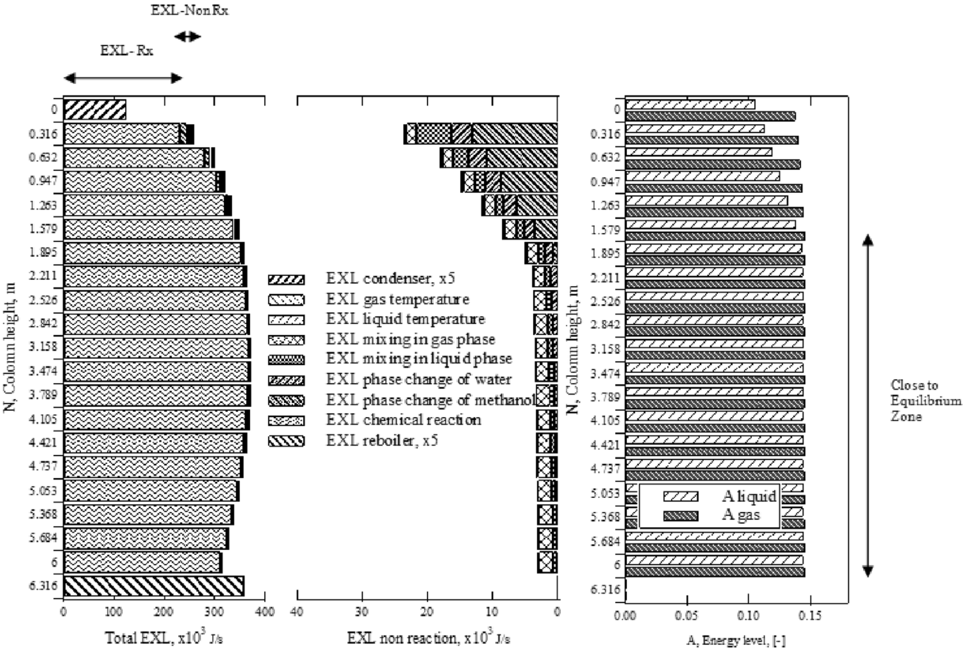
Figure 9 Profile of total exergy loss and fatty acid conversion at different reactant molar ratio



Effect of the column height (*N*) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment of *N* = 2, EXL owing to the chemical reaction values remains almost constant, and finally decreases at *N* = 4 to bottom. EXL owing to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared with the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

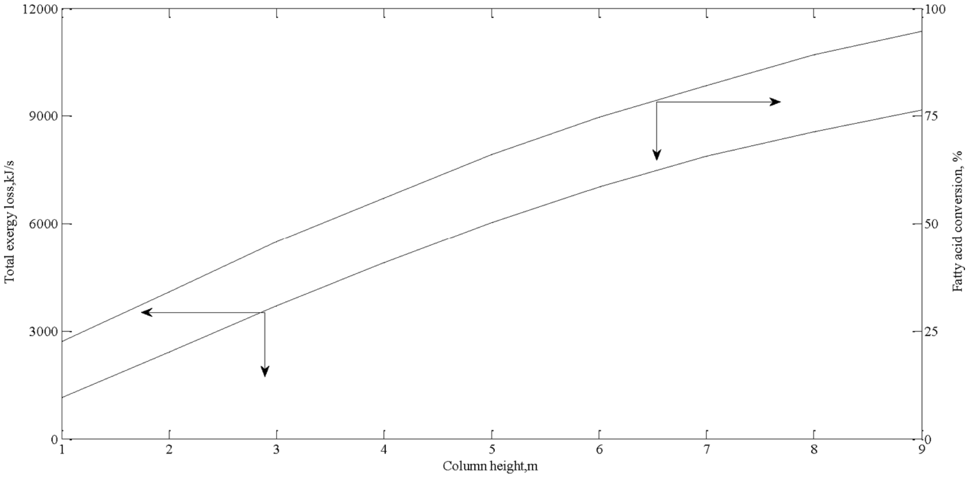
To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Figure 10 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 6$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height



Conclusively, there are some findings obtained by analysing the effects of the reactant molar ratio and column height. On the basis of the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height, which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5 Conclusions

- A graphical method called Ex-N-A diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy-level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-processes has a much larger EXL than the others.
- The base case of the RD simulation was studied at $N = 3$ m, the column diameter of 0.5 m and the molar ratio of methanol to oleic acid of 2 : 1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom, which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2 : 1 to 6 : 1 at the similar N of 3 m and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1 : 1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, N is increased from 3 m to 6 m, whereas the reactants molar ratio and column diameter are kept at 2 : 1 and 0.5 m, respectively. This reveals that the conversion is enhanced from 30.76% to 58.52%. Thus, the increase in the column height does not change the NEQ area; nevertheless, it just prolongs the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase
C_{cat}	Concentration of the solid catalyst ($\mathrm{kg_{cat}/m^3}$)
E_a	Activation energies (J/mol)
$\dot{EXL}$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant ($\mathrm{mol \cdot m^3/kg_{cat}^2/s}$)
k_2	Reverse reaction rate constant ($\mathrm{mol \cdot m^3/kg_{cat}^2/s}$)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component *i* from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component *i* from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{GL_1L_2}$	Mass transfer rate of component *i* from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
$\mathrm{d}z$	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase
L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase

Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Gmail **dewinino <dewinino@gmail.com>**

Re: REPLY - IJEx 16104 Kusumaningtyas et al. (4) - Revises

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abudiman@chemeng.ugm.ac.id <abudiman@chemeng.ugm.ac.id> Wed, Jan 29, 2014 at 8:58 AM
To: Galaxy <inderscience@galaxyeservices.com>
Cc: dewinino@gmail.com, spurwono@chemeng.ugm.ac.id

Dear Mr. Jyothi

Thank you very much for sending us the corrected paper for publication

We confirm that we agree with the content, language, and writing of this corrected paper.

However, we have some question regarding the layout of the figures.

1. We found that some figures are put on the different pages from the figures' title (we marked it with yellow colour)

Figure 4 is put on page 11, while the figure's title (Fig 4. *Total molar flow of each phase at different column height*) is placed on page 10

Figure 6 is placed on page 12, while the figure's title (Fig 6. *Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at N = 3 m: (a) Ex-N diagram and (b) A-N diagram*) is put on page 11

Would you please check them before publishing?

2. Figure 9 (Profile of total exergy loss and fatty acid conversion at different reactant molar ratio)

The phenomenon occurs in Figure 9 is discussed in sub-chapter 4.2 (4.2 *Effect of the molar ratio of the reactants*). However, in this figure layout, we found that Figure 9 is placed among the discussion of sub-chapter 4.3 (4.3 *Effect of the height of the packed column (N)*)

Therefore, is it technically possible to put Figure 9 in sub-chapter 4.2?

Thank you very much

Sincerely Yours

Arief Budiman
Professor,
Process System Engineering research group
Chemical Engineering Department, Gadjah Mada University, Indonesia
Website : http://pserg.wg.ugm.ac.id
Alternative email: abudiman_id@yahoo.com

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Graphical exergy analysis of reactive distillation column for biodiesel production

Ratna Dewi Kusumaningtyas, Suryo Purwono,
Rochmadi Rochmadi and Arief Budiman*

Faculty of Engineering,
Chemical Engineering Department,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed reactive distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system. The graphical Ex-N-A method was utilised to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, i.e., losses owing to the temperature change, phase change, mixing in liquid and vapour phases and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Keywords: exergy analysis; reactive distillation; esterification; Ex-N-A; biodiesel.

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Biographical notes: Ratna Dewi Kusumaningtyas is a PhD student at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor's and Master's degrees from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange programme in Politecnico di Torino, Italy (2010–2012). She is the author and co-author of 12 journal and international conference papers during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario,

Canada, in 1993. His research focuses on distillation, petroleum and renewable energy development. He is the author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi Rochmadi is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK, in 1991. His research topic is polymer and bio-fuel development. He is the author or co-author of 55 scientific papers. He is also the Coordinator of many industrial–university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan, in 1997. His research focuses on thermodynamics and exergy analysis for system engineering. He is the author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009 and 2011) and Visiting Professor at Kyushu University (2012).

1 Introduction

Reactive distillation (RD) is a promising alternative process for equilibrium-limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gómez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognised as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing and optimising an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various methods of exergy analysis have been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot-factor-specific enthalpy diagram*. This method is easy to utilise for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *energy utilisation diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXLs), namely EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenient when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called integrated energy utilisation diagram (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the material-utilisation diagram (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-processes EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared with the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (N) as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) as abscissa. This plotting results in a simple diagram, which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation and chemical reaction incrementally. And, it is yet easy to understand even in a case when one of the sub-processes EXL is much larger than the others. This diagram can also obviously exhibit the correlation of the exergy losses owing to chemical and non-chemical sub-processes with the energy-level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low-grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, NEQ model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phase and NEQ model has been merely studied for a distillation process, which does not involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss is also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2 Model and simulation for reactive distillation (RD) column

A packed RD column was utilised for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the presence of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown here:

$$\mathrm{RCOOH}(\mathrm{A})+\mathrm{CH_3OH}\ (\mathrm{B}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCOOCH_3}\ (\mathrm{C})+\mathrm{H_2O}\ (\mathrm{D}) \tag{1}$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1 x_A x_B - k_2 x_A x_B) C_{\text{cat}}. \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with $\Delta H_r = 11213.12$ J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 1 Kinetic parameters of the pseudo-homogeneous model

Reaction rate constant (mol m^3/kg$_{\text{cat}}^2$/s)	*Ln*(*pre-exponential factor*)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

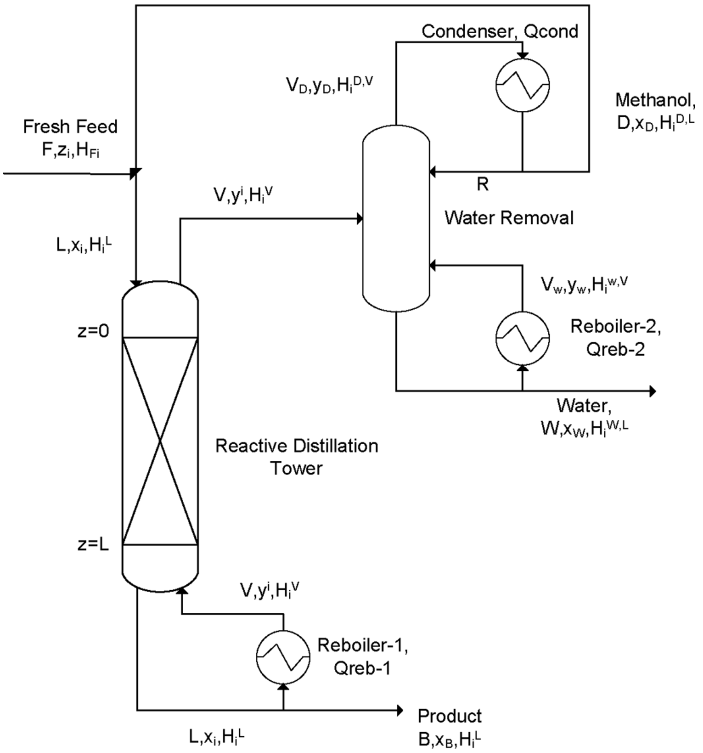
Table 2 Molecular structure and normal boiling points of all the chemical compounds

Compounds	*Molecular structure*	*Boiling point* (K)
Oleic acid (A)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$	616.85
Water (D)	H_2O	373

The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top is condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the

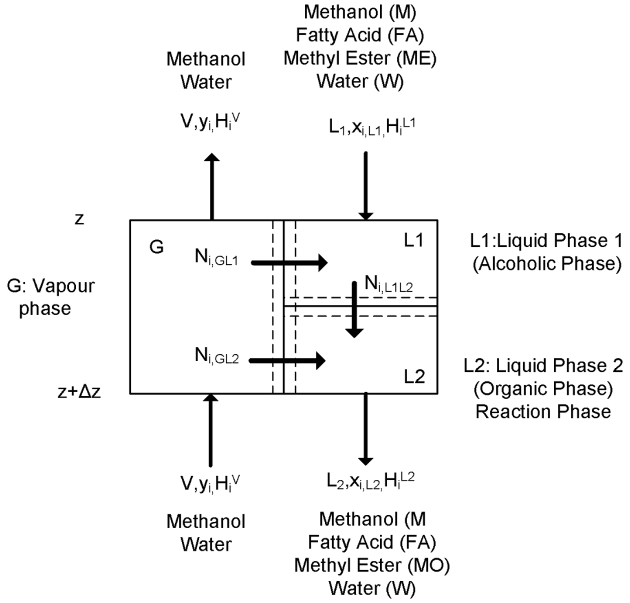
column starts from the top, hence *N* = 0 m is the top of the column, while *N* = *n* m is the lowest part of the column. The base case condition employs the packed column with the height of 3 m with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2 : 1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 and 69.52 mol/s, respectively.

Figure 1 The configuration of packed RD column for biodiesel production



The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase, which contains only methanol and water, alcoholic liquid phase, which contains mainly water and methanol, and organic liquid phase, which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

Figure 2 Schematic representation of one cell of three-phase packed RD column



The assumptions taken in this modelling and simulation can be written as follows:

1 In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.

2 The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.

3 The RD column operates at the steady-state condition.

4 There are three phases that occur in the system, namely vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).

5 The reaction takes place in the organic phase (liquid-2).

6 Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.

7 The RD column is modelled based on the NEQ approach. Hence, the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three-phase RD are summarised as follows. The mass balances of each compound in the vapour, liquid-1 and liquid-2 phases are formulated in equations (3)–(5), respectively:

$$\frac{\mathrm{d}y_{i,G}}{\mathrm{d}z} = \frac{(-\dot{R}_{i,G}) - y_i \frac{\mathrm{d}V'}{\mathrm{d}z}}{V'} \tag{3}$$

$$\frac{\mathrm{d}x_{i,L_1}}{\mathrm{d}z} = \frac{(-\dot{R}_{i,L_1}) - x_i \frac{\mathrm{d}L_1'}{\mathrm{d}z}}{L_1'} \tag{4}$$

$$\frac{\mathrm{d}x_{i,L_2}}{\mathrm{d}z}=\frac{-(-\dot{R}_{i,L_2})-x_i\frac{\mathrm{d}L_2'}{\mathrm{d}z}}{L_2'}. \tag{5}$$

Meanwhile, the total mass balance of the vapour, liquid-1 and liquid-2 phase is presented in equations (6)–(8), respectively:

$$\frac{\mathrm{d}V'}{\mathrm{d}z}=-\sum\dot{R}_{i,G} \tag{6}$$

$$\frac{\mathrm{d}L_1'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_1}\right) \tag{7}$$

$$\frac{\mathrm{d}L_2'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_2}\right) \tag{8}$$

To solve equations (3)–(8), the rate process equations are necessary. The rate process equations for the gas, liquid-1 and liquid-2 phases are equations (9)–(11), respectively.

$$\dot{R}_{i,G}=-(\dot{N}_i^{GL_1}+\dot{N}_i^{GL_2}) \tag{9}$$

$$\dot{R}_{i,L_1}=\dot{N}_i^{GL_1}-\dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2}=-\dot{N}_i^{GL_2}+\dot{N}_i^{L_1L_2}+v_i\dot{r}. \tag{11}$$

The result outputted from the RD simulation is utilised for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorous method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e., EXL owing to the temperature change, phase change, mixing in liquid and vapour phase and chemical reaction. The loss in reboiler and condenser is also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3 Graphical Ex-N-A methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, i.e., EXL owing to changes of the concentration (mixing), phase of the component and temperature, have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL owing to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (A) is explained as (Srinophakun et al., 2001):

$$A=\frac{E\dot{X}L}{\Delta H}. \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S. \tag{13}$$

Hence,

$$A = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{14}$$

It illustrates the maximum fraction of energy, which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{\text{Chem}} = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{15}$$

On the equilibrium condition in which the reaction does not occur, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T}. \tag{16}$$

In this condition, energy level *A* generally can be written as:

$$A = \left(1 - \frac{T_0}{T}\right). \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{\text{Liq}} = \left(1 - \frac{T_0}{T}\right). \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{\text{Gas}} = \left(1 - \frac{T_0}{T}\right). \tag{19}$$

T in the energy-level formula depends on the phase. *T* is the gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL owing to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL owing to the chemical reaction can be written as:

$$E\dot{X}L_{\text{Chem}} = (A_{\text{Liq}} - A_{\text{Chem}})\Delta H. \tag{20}$$

4 Display of packed reactive distillation column on graphical Ex-N-A diagram

4.1 Base case analysis

Ex-N-A diagram is an exergy-feature-based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous

graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008) and Budiman et al. (2011) composed the graph for EXL owing to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 \ln x_j$ as ordinate for the liquid phase and $\Re T_0 \ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A diagram is made by placing the two types of diagram in a single feature. The height of the column (*N*) is put as ordinate whereas the total EXL, the non-chemical reaction EXL and *A* (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of *N* as ordinate whereas total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which *N* was put as ordinate and *A* is set as abscissa. The other two diagrams exhibiting the correlation between the column height and total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared with the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL owing to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub-processes EXL is much larger than the others. It can also combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy-level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy-level difference between A_{gas} and A_{liq} ($A_{\text{gas}} - A_{\text{liq}}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy-level difference and exergy consumption as the shaded area in the diagrams. Hence, it does not clearly show the exergy profile at different levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (*N*) is plotted as abscissa against the total EXL, non-chemical reaction EXL and energy level. On the basis of this diagram, the graphical correlation between total EXL, non-chemical reaction EXL and energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) is incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph, which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of subgraphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL owing to the chemical reaction and non-chemical EXL (i.e., losses owing to the temperature change, mixing and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, i.e., EXL owing to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, and temperature change in liquid phase and temperature change in gas phases, is displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses owing to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. On the basis of this N-A graph, the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (N) was 3 m, the column diameter was 0.5 m and the molar ratio of methanol to oleic acid was 2 : 1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited in Figures 3–5, respectively. These data are required for the EXL calculation.

Figure 3 Concentration profiles of the compounds in liquid-1, liquid-2 and vapour phases at different column height (see online version for colours)

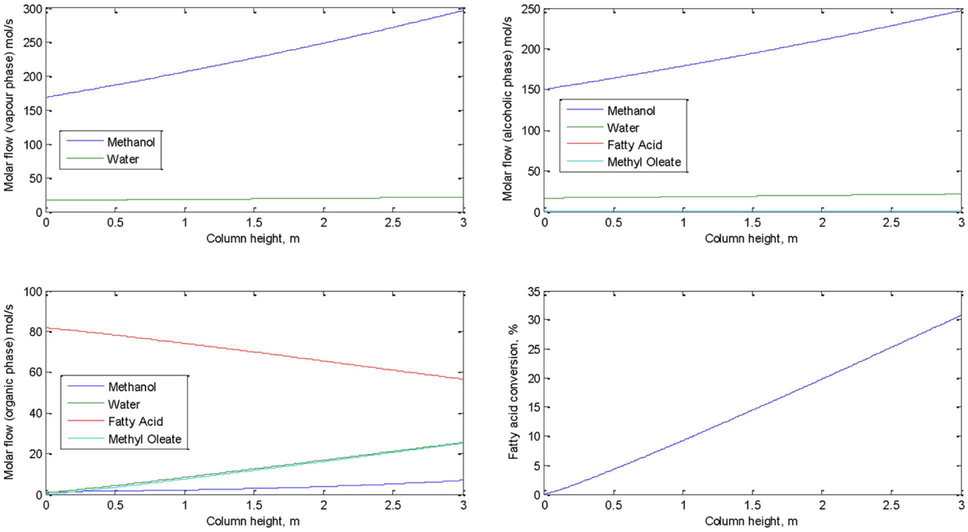


Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. In Figure 6(a), EXL of the reboiler and condenser is shown by the scale of 1/5 because of their large values.

The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

Figure 4 Total molar flow of each phase at different column height (see online version for colours)

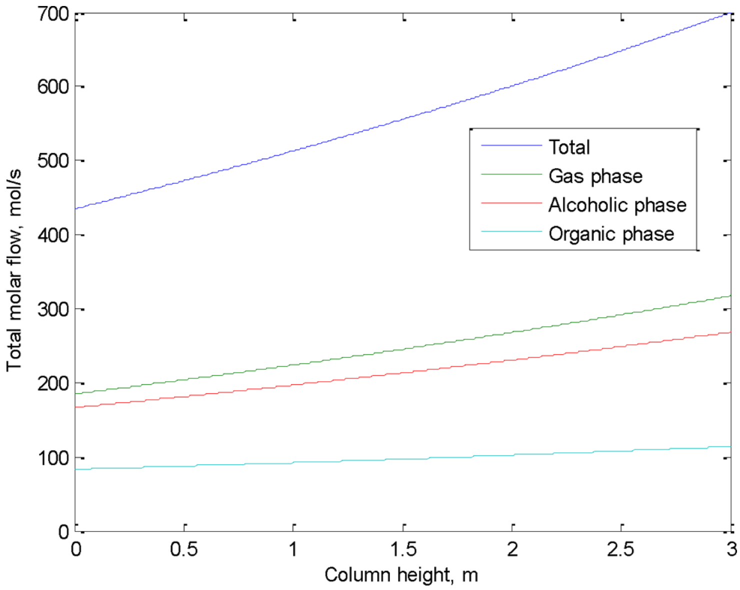


Figure 5 Temperature profile of liquid and vapour phase at different column height (see online version for colours)

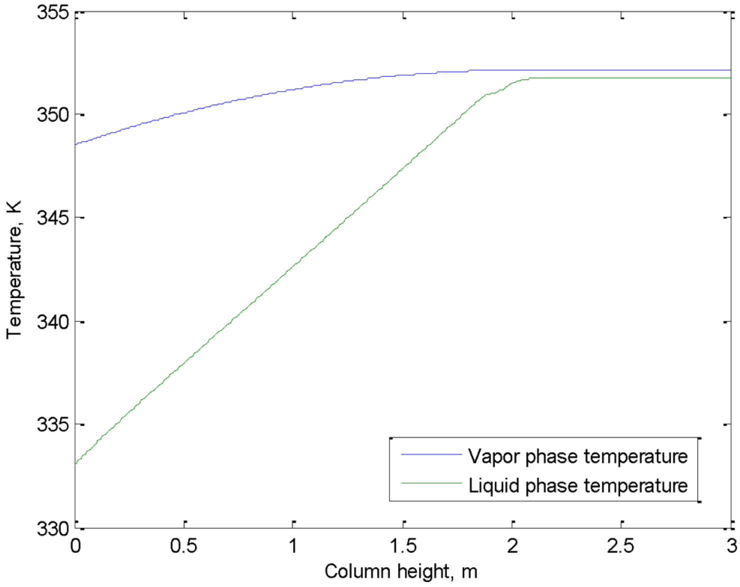
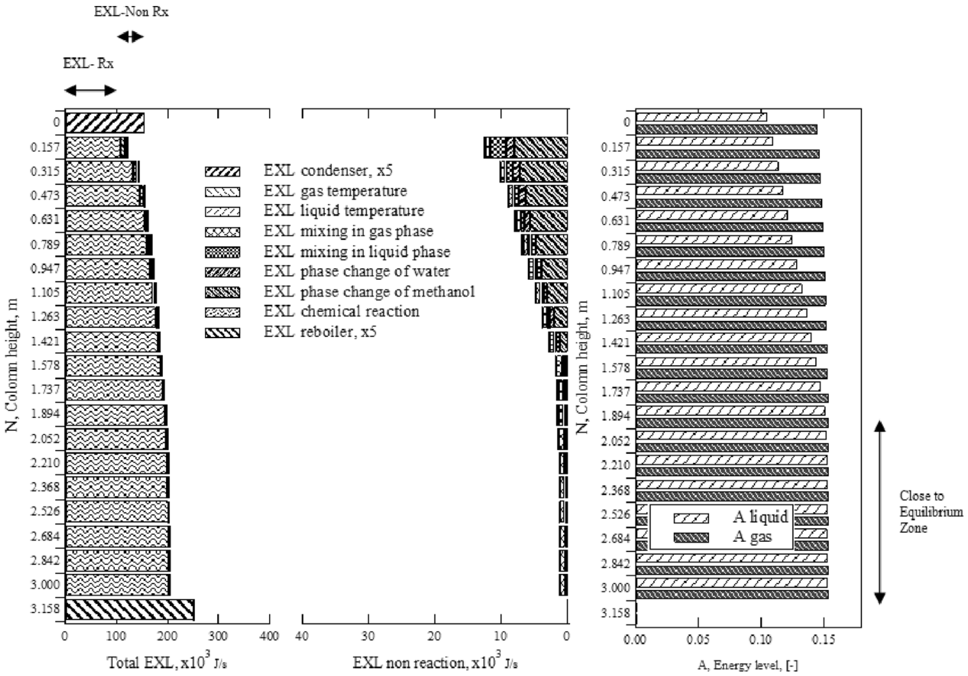


Figure 6 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

The incremental assessment on the RD column using Ex-N-A diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6(a) shows that the non-chemical EXL, i.e., the summation of EXL owing to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, starting from $N = 2$ m from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the A-N diagram in Figure 6(b), which displays the profile of the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) inside the column or the so-called driving force. Energy-level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy-level difference.

On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses that are influenced by temperature are zero. Hence, simply the EXL owing to the mixing exists at $N = 2$ m moved downwards. EXL owing to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL owing to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near-equilibrium condition has been reached. In this condition, a macro-heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium (NEQ) zone, and the second one is the close-to-equilibrium zone.

Two regions, NEQ and close-to-equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close-to-equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small temperature difference between gas and liquid, which also results in a very small (near to zero) energy-level difference. The condition where the energy-level difference or the driving force is very small (let us say 'zero') is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column, all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual and the near-to-equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy-level difference (driving force) between gas and liquid at the column top (A-N diagram in Figure 6(b)). In addition, the energy-level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the close-to-equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6(a). Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis owing to the chemical reaction. However, assessment on the EXL owing to chemical reaction incrementally has never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N diagrams in Figure 6(a) expose a different tendency between the profile of the total EXL and EXL owing to the chemical reaction, on the one side, and EXL owing to the non-chemical reaction, on the other side. The profile of total EXL and EXL owing to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL owing to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL owing to chemical reaction profile.

On the basis of the Ex-N diagram, it is revealed that the amount of EXL owing to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher the amount of reactants reacts, the higher the EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL owing to chemical reaction as well as total EXL increase from the top to the bottom.

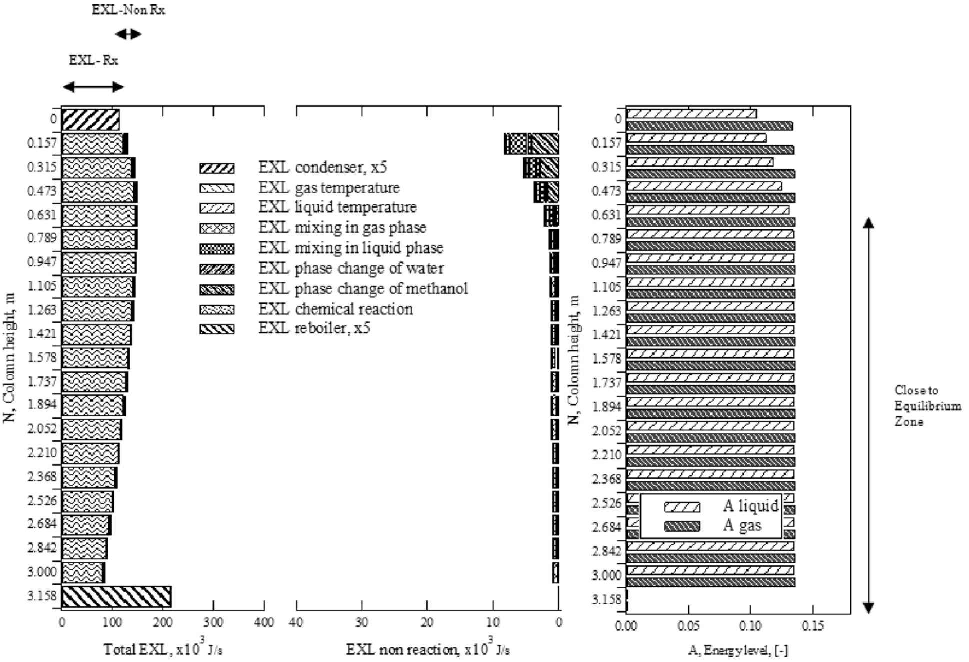
Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (N). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimisation graphically.

4.2 *Effect of the molar ratio of the reactants*

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, first, the molar ratio of total methanol and oleic acid entering the column is increased from 2 : 1 to 6 : 1 at the same column height of 3 m ($N = 3$) and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, it is shown that the reaction conversion enhances about two times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7(a) shows that the profile of non-chemical EXL does not change so much compared with the result given by the molar ratio of 2 : 1. At molar ratio of 6 : 1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, whereas the upper part is NEQ zone. However, enhancing molar ratio from 2 : 1 to 6 : 1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7(b) shows that, when molar ratio of 6 : 1 is applied, the close-to-equilibrium zone starts at $N = 0.75$ m downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the NEQ zone inside the column. The larger area of the close-to-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of CEP gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1 : 1 with $N = 3$. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in Figure 8(b), all the areas in RD column are NEQ zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses owing to mixing, phase and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

Figure 7 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 6 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram



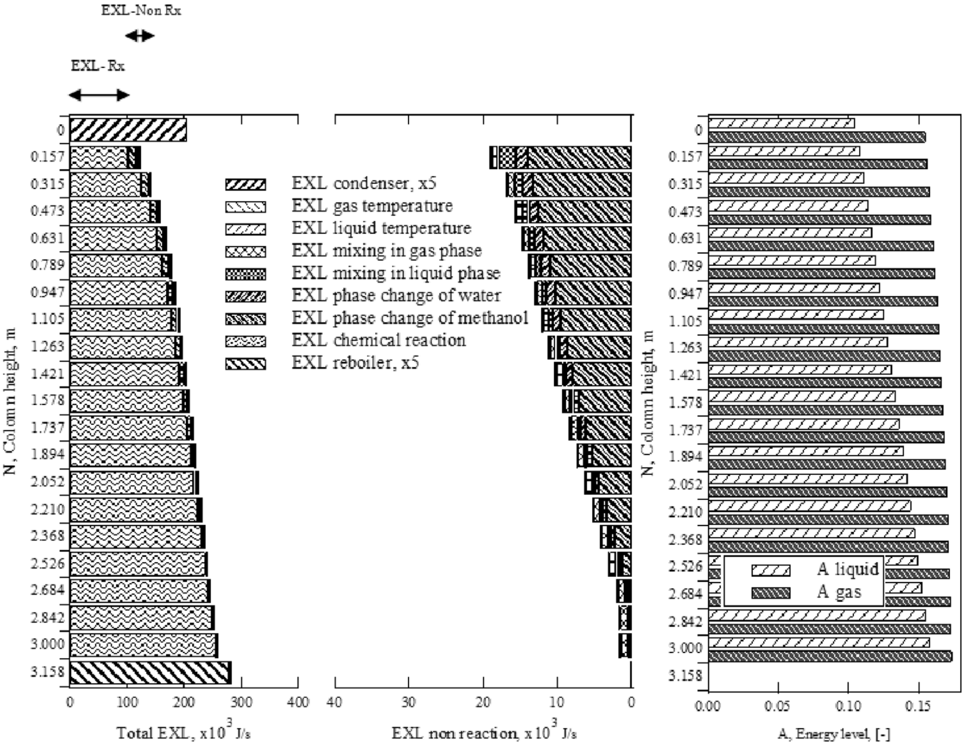
(a) (b)

To evaluate the impact of varying the molar ratio on the value of the EXL owing to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1 : 1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2 : 1.

However, if molar ratio of the reactants is drastically enhanced to 6 : 1, the new Ex-N profile seems interesting. It is shown that EXL owing to the chemical reaction gets higher from the top downward as seen on the Ex-N diagram in Figure 7(a). In spite of this, at a certain point in the column, EXL owing to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL owing to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to react easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease in the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL owing to chemical reaction in the column. It can be observed that EXL owing to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point, it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

Figure 8 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 1 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



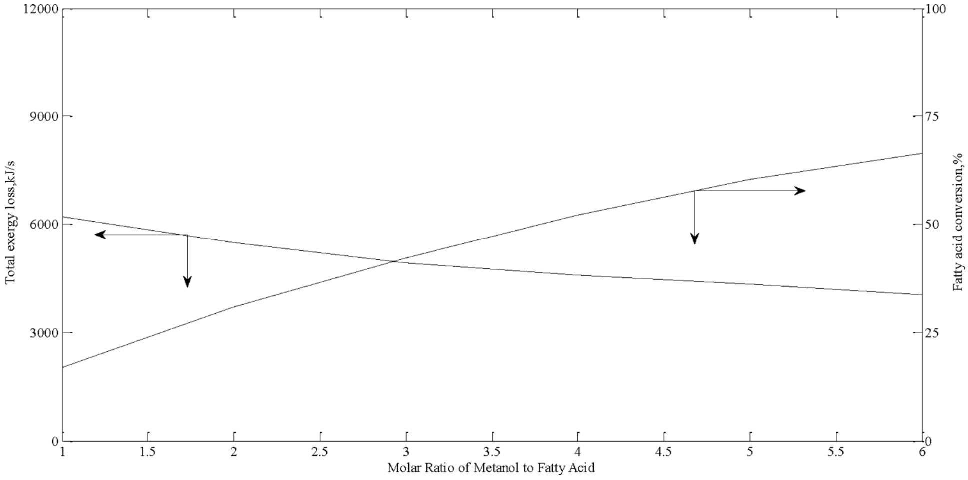
(a) (b)

4.3 *Effect of the height of the packed column (N)*

The subsequent important aspect to be analysed is the height of the column (*N*). To study this parameter, *N* is increased from 3 m to 6 m with the similar reactants molar ratio of 2 : 1, whereas the column diameter is kept the same (0.5 m). Hence, it reveals that the reaction conversion is enhanced from 30.76% to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N diagram in

Figure 10(a) shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared with the profile of the column with the height of 3 m ($N = 3$). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the $N = 2$ m from the top, EXL of the sub-processes, which depends on temperature (loss owing to temperature and phase changes), approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N diagram in Figure 10(b). Nevertheless, it is shown that the energy-level difference between gas and liquid decreases from the top downward. Then, starting at $N = 2$ m downward, the energy-level difference is near to zero. Thus, the area in the column can be separated into two regions, i.e., the NEQ zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to $N = 2$, whereas the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the NEQ area. However, it just prolongs the close-to-equilibrium zone. The existing of NEQ region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

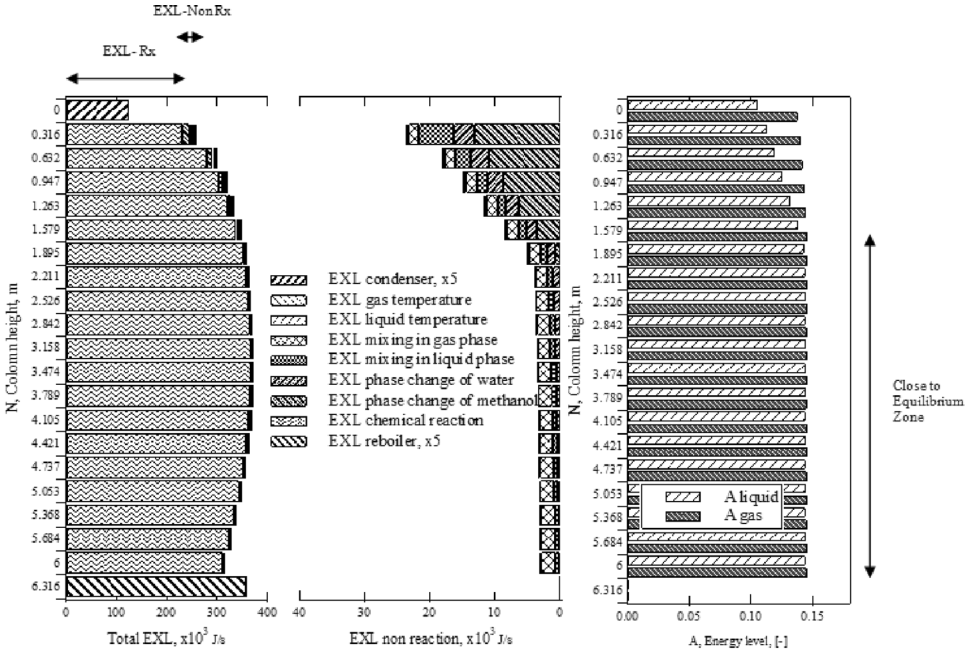
Figure 9 Profile of total exergy loss and fatty acid conversion at different reactant molar ratio



Effect of the column height (N) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment of $N = 2$, EXL owing to the chemical reaction values remains almost constant, and finally decreases at $N = 4$ to bottom. EXL owing to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared with the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

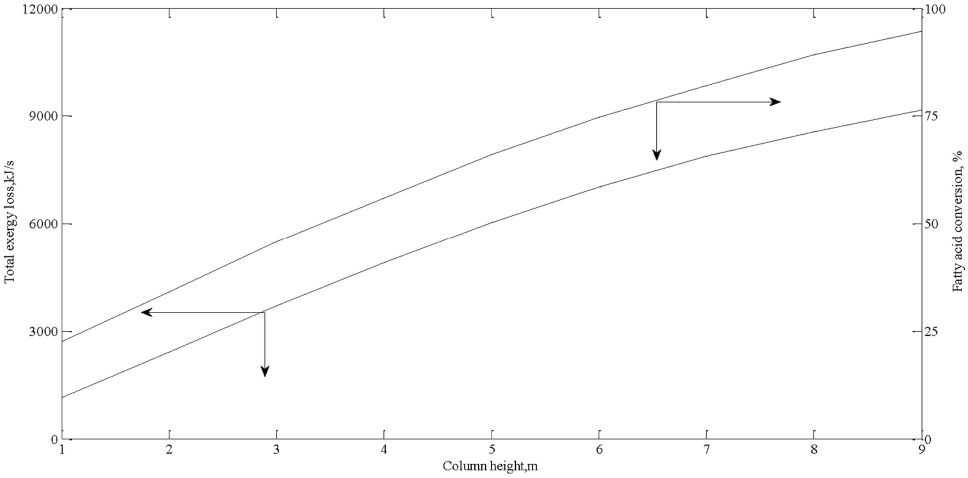
To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Figure 10 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 6$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height



Conclusively, there are some findings obtained by analysing the effects of the reactant molar ratio and column height. On the basis of the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height, which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5 Conclusions

- A graphical method called Ex-N-A diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy-level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-processes has a much larger EXL than the others.
- The base case of the RD simulation was studied at $N = 3$ m, the column diameter of 0.5 m and the molar ratio of methanol to oleic acid of 2 : 1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom, which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2 : 1 to 6 : 1 at the similar N of 3 m and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1 : 1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, N is increased from 3 m to 6 m, whereas the reactants molar ratio and column diameter are kept at 2 : 1 and 0.5 m, respectively. This reveals that the conversion is enhanced from 30.76% to 58.52%. Thus, the increase in the column height does not change the NEQ area; nevertheless, it just prolongs the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase
C_{cat}	Concentration of the solid catalyst ($\mathrm{kg_{cat}/m^3}$)
E_a	Activation energies (J/mol)
$E\dot{X}L$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant ($\mathrm{mol{\cdot}m^3/kg_{cat}^2/s}$)
k_2	Reverse reaction rate constant ($\mathrm{mol{\cdot}m^3/kg_{cat}^2/s}$)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component *i* from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component *i* from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{GL_1L_2}$	Mass transfer rate of component *i* from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
dz	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase
L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase

Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Gmail **dewinino <dewinino@gmail.com>**

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Graphical exergy analysis of reactive distillation column for biodiesel production

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi Rochmadi and Arief Budiman*

Faculty of Engineering,
Chemical Engineering Department,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed reactive distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system. The graphical Ex-N-A method was utilised to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, i.e., losses owing to the temperature change, phase change, mixing in liquid and vapour phases and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Keywords: exergy analysis; reactive distillation; esterification; Ex-N-A; biodiesel.

Reference to this paper should be made as follows: Kusumaningtyas, R.D., Purwono, S., Rochmadi, R. and Budiman, A. (xxxx) ‘Graphical exergy analysis of reactive distillation column for biodiesel production’, *Int. J. Exergy*, Vol. x, No. x, pp.xxx–xxx.

Biographical notes: Ratna Dewi Kusumaningtyas is a PhD student at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor’s and Master’s degrees from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange programme in Politecnico di Torino, Italy (2010–2012). She is the author and co-author of 12 journal and international conference papers during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario,

Canada, in 1993. His research focuses on distillation, petroleum and renewable energy development. He is the author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi Rochmadi is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK, in 1991. His research topic is polymer and bio-fuel development. He is the author or co-author of 55 scientific papers. He is also the Coordinator of many industrial–university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan, in 1997. His research focuses on thermodynamics and exergy analysis for system engineering. He is the author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009 and 2011) and Visiting Professor at Kyushu University (2012).

1 Introduction

Reactive distillation (RD) is a promising alternative process for equilibrium-limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gómez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognised as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing and optimising an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various methods of exergy analysis have been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot-factor-specific enthalpy diagram*. This method is easy to utilise for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *energy utilisation diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXLs), namely EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenient when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called integrated energy utilisation diagram (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the material-utilisation diagram (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-processes EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared with the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (*N*) as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) as abscissa. This plotting results in a simple diagram, which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation and chemical reaction incrementally. And, it is yet easy to understand even in a case when one of the sub-processes EXL is much larger than the others. This diagram can also obviously exhibit the correlation of the exergy losses owing to chemical and non-chemical sub-processes with the energy-level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low-grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, NEQ model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phase and NEQ model has been merely studied for a distillation process, which does not involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss is also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2 Model and simulation for reactive distillation (RD) column

A packed RD column was utilised for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the presence of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown here:

$$\mathrm{RCOOH}(\mathrm{A}) + \mathrm{CH_3OH}\ (\mathrm{B}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{RCOOCH_3}\ (\mathrm{C}) + \mathrm{H_2O}\ (\mathrm{D}) \tag{1}$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1 x_A x_B - k_2 x_A x_B) C_{\text{cat}}. \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with $\Delta H_r = 11213.12$ J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 1 Kinetic parameters of the pseudo-homogeneous model

Reaction rate constant (mol m^3/kg$_{\text{cat}}^2$/s)	*Ln*(*pre-exponential factor*)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

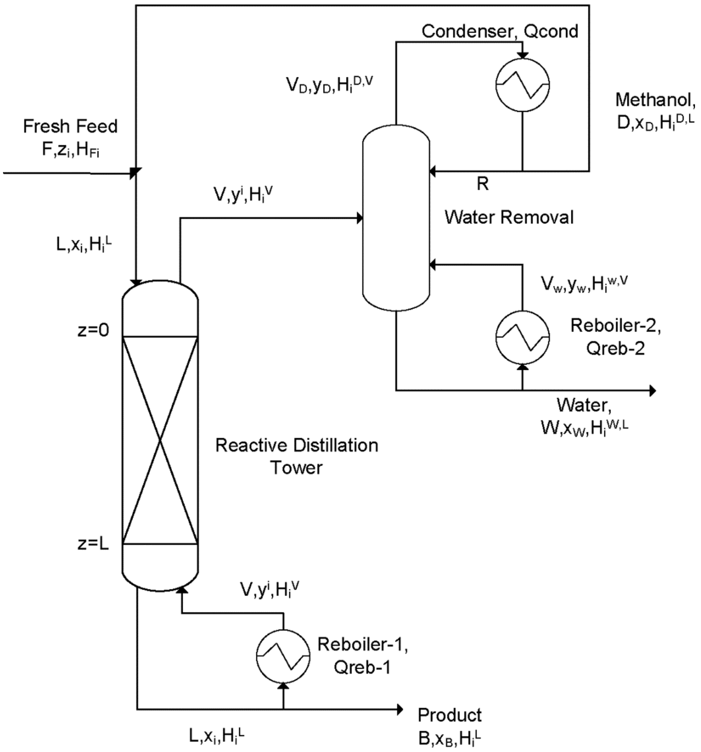
Table 2 Molecular structure and normal boiling points of all the chemical compounds

Compounds	*Molecular structure*	*Boiling point* (K)
Oleic acid (A)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	616.85
Water (D)	H_2O	373

The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top is condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the

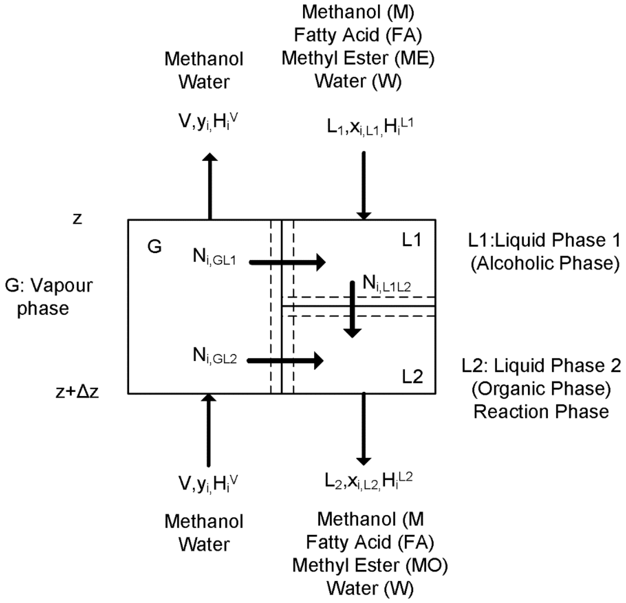
column starts from the top, hence $N = 0$ m is the top of the column, while $N = n$ m is the lowest part of the column. The base case condition employs the packed column with the height of 3 m with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2 : 1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 and 69.52 mol/s, respectively.

Figure 1 The configuration of packed RD column for biodiesel production



The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase, which contains only methanol and water, alcoholic liquid phase, which contains mainly water and methanol, and organic liquid phase, which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

Figure 2 Schematic representation of one cell of three-phase packed RD column



The assumptions taken in this modelling and simulation can be written as follows:

1. In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.
2. The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.
3. The RD column operates at the steady-state condition.
4. There are three phases that occur in the system, namely vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).
5. The reaction takes place in the organic phase (liquid-2).
6. Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.
7. The RD column is modelled based on the NEQ approach. Hence, the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three-phase RD are summarised as follows. The mass balances of each compound in the vapour, liquid-1 and liquid-2 phases are formulated in equations (3)–(5), respectively:

$$\frac{dy_{i,G}}{dz} = \frac{(-\dot{R}_{i,G}) - y_i \frac{dV'}{dz}}{V'} \tag{3}$$

$$\frac{dx_{i,L_1}}{dz} = \frac{(-\dot{R}_{i,L_1}) - x_i \frac{dL_1'}{dz}}{L_1'} \tag{4}$$

$$\frac{\mathrm{d}x_{i,L_2}}{\mathrm{d}z}=\frac{-(-\dot{R}_{i,L_2})-x_i\frac{\mathrm{d}L_2'}{\mathrm{d}z}}{L_2'}. \tag{5}$$

Meanwhile, the total mass balance of the vapour, liquid-1 and liquid-2 phase is presented in equations (6)–(8), respectively:

$$\frac{\mathrm{d}V'}{\mathrm{d}z}=-\sum\dot{R}_{i,G} \tag{6}$$

$$\frac{\mathrm{d}L_1'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_1}\right) \tag{7}$$

$$\frac{\mathrm{d}L_2'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_2}\right) \tag{8}$$

To solve equations (3)–(8), the rate process equations are necessary. The rate process equations for the gas, liquid-1 and liquid-2 phases are equations (9)–(11), respectively.

$$\dot{R}_{i,G}=-(\dot{N}_i^{GL_1}+\dot{N}_i^{GL_2}) \tag{9}$$

$$\dot{R}_{i,L_1}=\dot{N}_i^{GL_1}-\dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2}=-\dot{N}_i^{GL_2}+\dot{N}_i^{L_1L_2}+v_i\dot{r}. \tag{11}$$

The result outputted from the RD simulation is utilised for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorous method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e., EXL owing to the temperature change, phase change, mixing in liquid and vapour phase and chemical reaction. The loss in reboiler and condenser is also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3 Graphical Ex-N-A methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, i.e., EXL owing to changes of the concentration (mixing), phase of the component and temperature, have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL owing to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (A) is explained as (Srinophakun et al., 2001):

$$A=\frac{E\dot{X}L}{\Delta H}. \tag{12}$$

EXL is then defined by the following equation.

$$\dot{EXL} = \Delta H - T_0 \Delta S. \tag{13}$$

Hence,

$$A = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{14}$$

It illustrates the maximum fraction of energy, which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{\text{Chem}} = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{15}$$

On the equilibrium condition in which the reaction does not occur, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T}. \tag{16}$$

In this condition, energy level *A* generally can be written as:

$$A = \left(1 - \frac{T_0}{T}\right). \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{\text{Liq}} = \left(1 - \frac{T_0}{T}\right). \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{\text{Gas}} = \left(1 - \frac{T_0}{T}\right). \tag{19}$$

T in the energy-level formula depends on the phase. *T* is the gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL owing to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL owing to the chemical reaction can be written as:

$$\dot{EXL}_{\text{Chem}} = (A_{\text{Liq}} - A_{\text{Chem}})\Delta H. \tag{20}$$

4 Display of packed reactive distillation column on graphical Ex-N-A diagram

4.1 Base case analysis

Ex-N-A diagram is an exergy-feature-based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous

graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008) and Budiman et al. (2011) composed the graph for EXL owing to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 \ln x_j$ as ordinate for the liquid phase and $\Re T_0 \ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A diagram is made by placing the two types of diagram in a single feature. The height of the column (*N*) is put as ordinate whereas the total EXL, the non-chemical reaction EXL and *A* (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of *N* as ordinate whereas total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which *N* was put as ordinate and *A* is set as abscissa. The other two diagrams exhibiting the correlation between the column height and total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared with the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL owing to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub-processes EXL is much larger than the others. It can also combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy-level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy-level difference between A_{gas} and A_{liq} ($A_{\text{gas}} - A_{\text{liq}}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy-level difference and exergy consumption as the shaded area in the diagrams. Hence, it does not clearly show the exergy profile at different levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (*N*) is plotted as abscissa against the total EXL, non-chemical reaction EXL and energy level. On the basis of this diagram, the graphical correlation between total EXL, non-chemical reaction EXL and energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) is incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph, which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of subgraphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL owing to the chemical reaction and non-chemical EXL (i.e., losses owing to the temperature change, mixing and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, i.e., EXL owing to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, and temperature change in liquid phase and temperature change in gas phases, is displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses owing to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. On the basis of this N-A graph, the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (*N*) was 3 m, the column diameter was 0.5 m and the molar ratio of methanol to oleic acid was 2 : 1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited in Figures 3–5, respectively. These data are required for the EXL calculation.

Figure 3 Concentration profiles of the compounds in liquid-1, liquid-2 and vapour phases at different column height (see online version for colours)

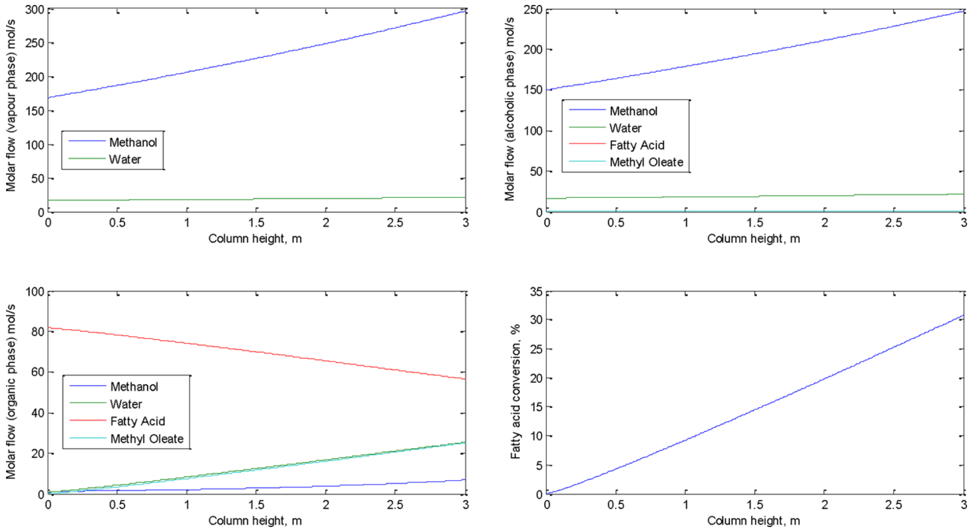


Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. In Figure 6(a), EXL of the reboiler and condenser is shown by the scale of 1/5 because of their large values. The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

Figure 4 Total molar flow of each phase at different column height (see online version for colours)

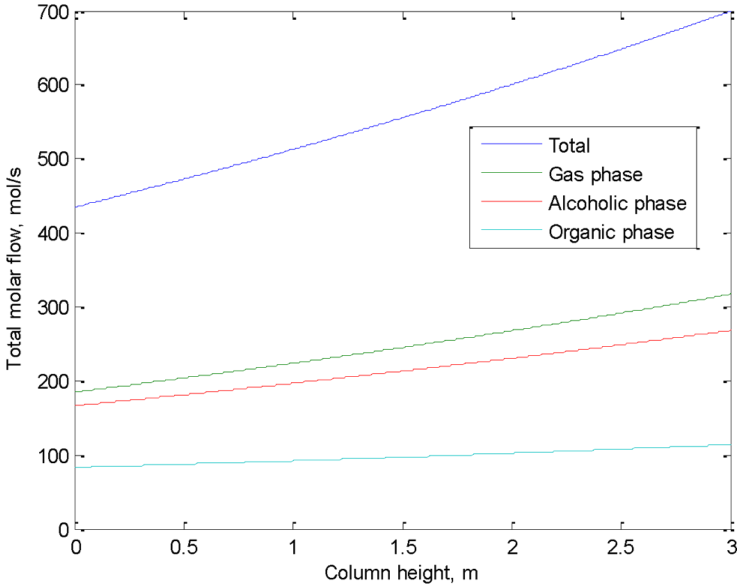
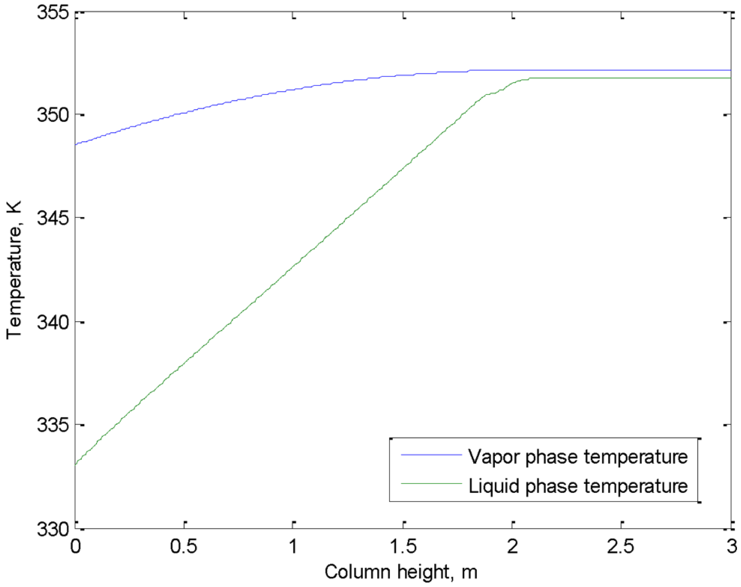


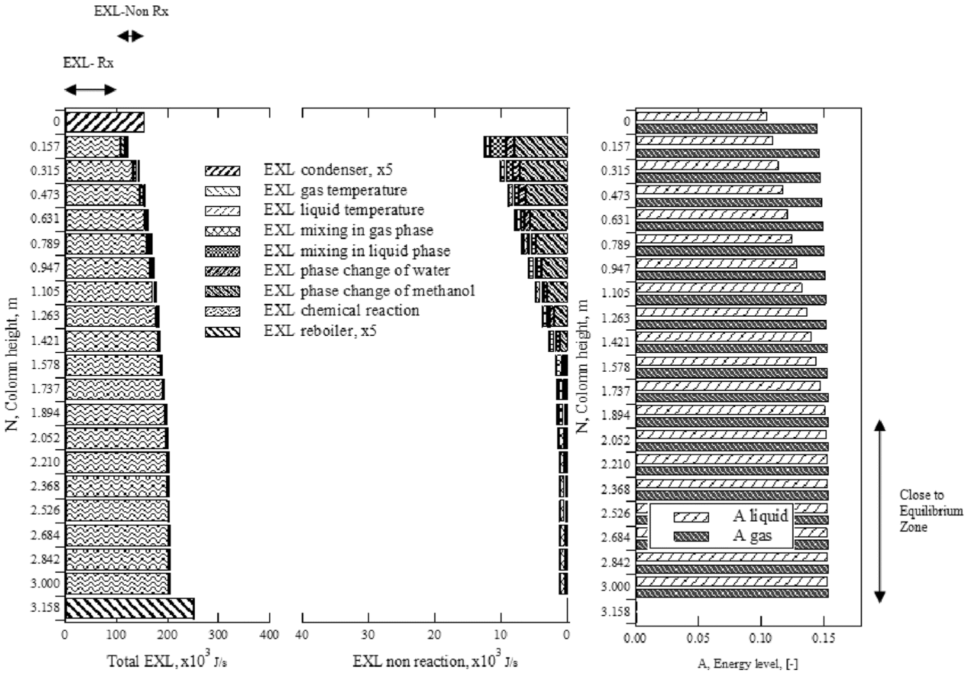
Figure 5 Temperature profile of liquid and vapour phase at different column height (see online version for colours)



The incremental assessment on the RD column using Ex-N-A diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6(a) shows that the non-chemical EXL, i.e., the summation of EXL owing to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, starting from $N = 2$ m from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the

A-N diagram in Figure 6(b), which displays the profile of the energy-level difference between gas and liquid ($A_{gas} - A_{liq}$) inside the column or the so-called driving force. Energy-level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy-level difference.

Figure 6 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses that are influenced by temperature are zero. Hence, simply the EXL owing to the mixing exists at $N = 2$ m moved downwards. EXL owing to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL owing to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near-equilibrium condition has been reached. In this condition, a macro-heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium (NEQ) zone, and the second one is the close-to-equilibrium zone.

Two regions, NEQ and close-to-equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close-to-equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small temperature difference between gas and liquid, which also results in a very small (near to zero) energy-level difference. The condition where the energy-level difference or the driving force is very small (let us say 'zero') is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column, all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual and the near-to-equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy-level difference (driving force) between gas and liquid at the column top (A-N diagram in Figure 6(b)). In addition, the energy-level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the close-to-equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6(a). Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis owing to the chemical reaction. However, assessment on the EXL owing to chemical reaction incrementally has never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N diagrams in Figure 6(a) expose a different tendency between the profile of the total EXL and EXL owing to the chemical reaction, on the one side, and EXL owing to the non-chemical reaction, on the other side. The profile of total EXL and EXL owing to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL owing to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL owing to chemical reaction profile.

On the basis of the Ex-N diagram, it is revealed that the amount of EXL owing to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher the amount of reactants reacts, the higher the EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL owing to chemical reaction as well as total EXL increase from the top to the bottom.

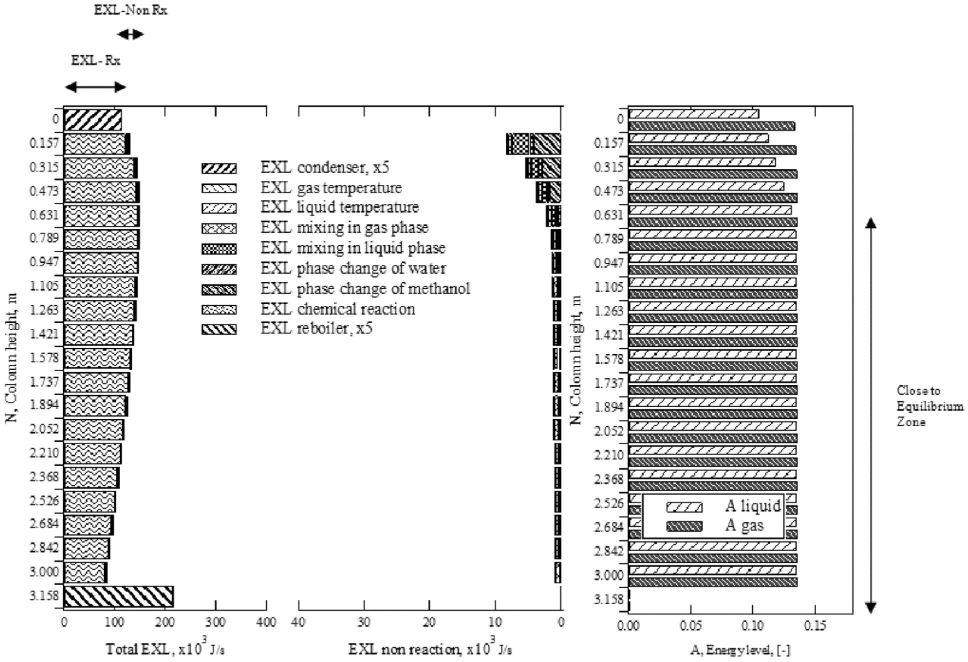
Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (*N*). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimisation graphically.

4.2 Effect of the molar ratio of the reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, first, the molar ratio of total methanol and oleic acid entering the column is increased from 2 : 1 to 6 : 1 at the same column height of 3 m ($N = 3$) and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, it is shown that the reaction conversion enhances about two times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7(a) shows that the profile of non-chemical EXL does not change so much compared with the result given by the molar ratio of 2 : 1. At molar ratio of 6 : 1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, whereas the upper part is NEQ zone. However, enhancing molar ratio from 2 : 1 to 6 : 1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7(b) shows that, when molar ratio of 6 : 1 is applied, the close-to-equilibrium zone starts at $N = 0.75$ m downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the NEQ zone inside the column. The larger area of the close-to-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of CEP gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1 : 1 with $N = 3$. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in Figure 8(b), all the areas in RD column are NEQ zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses owing to mixing, phase and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

Figure 7 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 6 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram



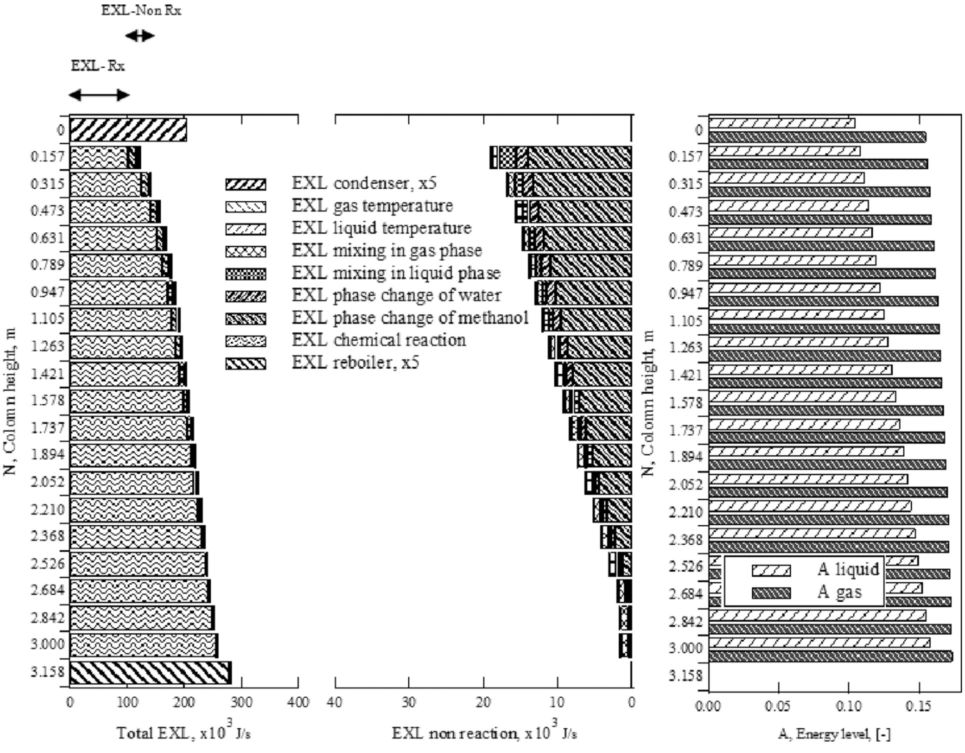
(a) (b)

To evaluate the impact of varying the molar ratio on the value of the EXL owing to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1 : 1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2 : 1.

However, if molar ratio of the reactants is drastically enhanced to 6 : 1, the new Ex-N profile seems interesting. It is shown that EXL owing to the chemical reaction gets higher from the top downward as seen on the Ex-N diagram in Figure 7(a). In spite of this, at a certain point in the column, EXL owing to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL owing to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to react easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease in the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL owing to chemical reaction in the column. It can be observed that EXL owing to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point, it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

Figure 8 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 1 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram

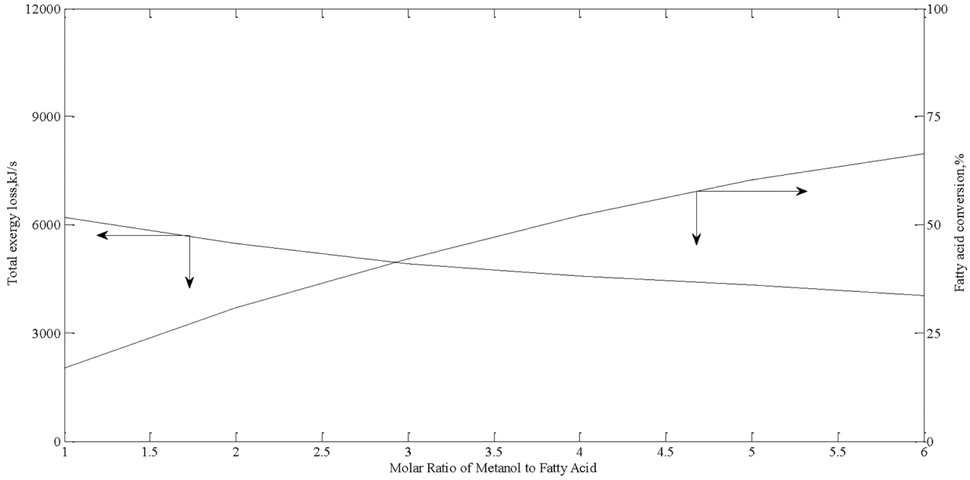


(a) (b)

4.3 *Effect of the height of the packed column (N)*

The subsequent important aspect to be analysed is the height of the column (*N*). To study this parameter, *N* is increased from 3 m to 6 m with the similar reactants molar ratio of 2 : 1, whereas the column diameter is kept the same (0.5 m). Hence, it reveals that the reaction conversion is enhanced from 30.76% to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N diagram in Figure 10(a) shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared with the profile of the column with the height of 3 m ($N = 3$). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the $N = 2$ m from the top, EXL of the sub-processes, which depends on temperature (loss owing to temperature and phase changes), approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N diagram in Figure 10(b). Nevertheless, it is shown that the energy-level difference between gas and liquid decreases from the top downward. Then, starting at $N = 2$ m downward, the energy-level difference is near to zero. Thus, the area in the column can be separated into two regions, i.e., the NEQ zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to $N = 2$, whereas the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the NEQ area. However, it just prolongs the close-to-equilibrium zone. The existing of NEQ region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

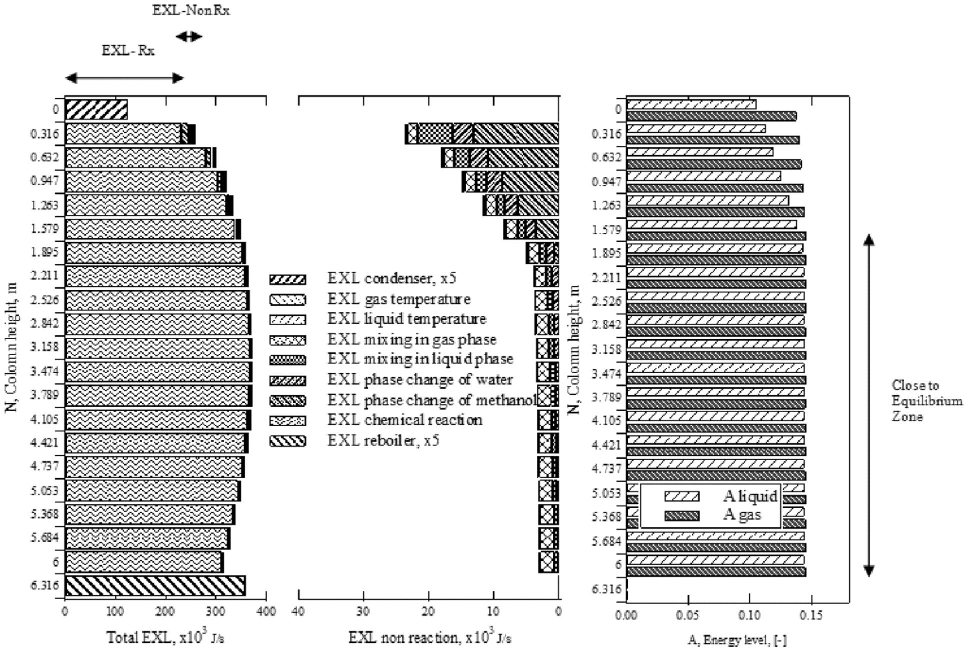
Figure 9 Profile of total exergy loss and fatty acid conversion at different reactant molar ratio



Effect of the column height (N) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment of $N = 2$, EXL owing to the chemical reaction values remains almost constant, and finally decreases at $N = 4$ to bottom. EXL owing to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared with the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

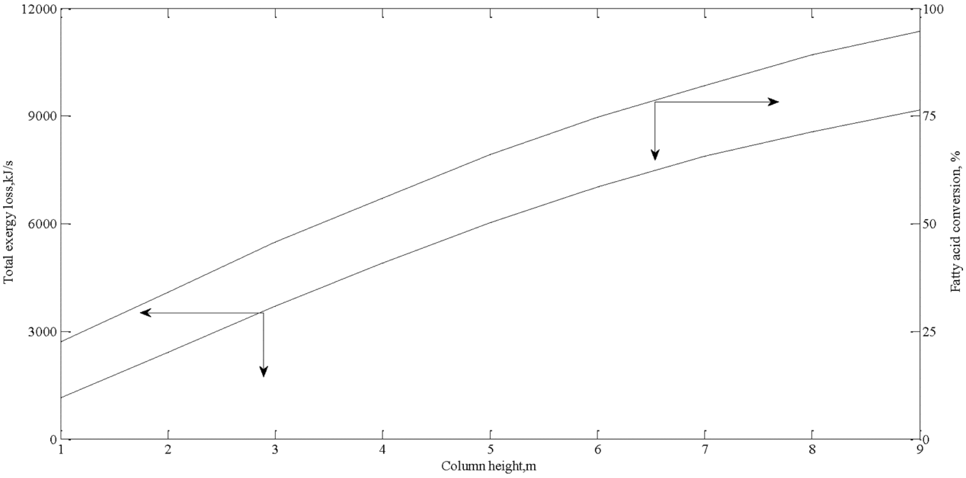
To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Figure 10 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 6$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height



Conclusively, there are some findings obtained by analysing the effects of the reactant molar ratio and column height. On the basis of the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height, which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5 Conclusions

- A graphical method called Ex-N-A diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy-level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-processes has a much larger EXL than the others.
- The base case of the RD simulation was studied at $N = 3$ m, the column diameter of 0.5 m and the molar ratio of methanol to oleic acid of 2 : 1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom, which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2 : 1 to 6 : 1 at the similar N of 3 m and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1 : 1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, N is increased from 3 m to 6 m, whereas the reactants molar ratio and column diameter are kept at 2 : 1 and 0.5 m, respectively. This reveals that the conversion is enhanced from 30.76% to 58.52%. Thus, the increase in the column height does not change the NEQ area; nevertheless, it just prolongs the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase

C_{cat}	Concentration of the solid catalyst ($\text{kg}_{\text{cat}}/\text{m}^3$)
E_a	Activation energies (J/mol)
$\dot{EXL}$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant ($\text{mol}\cdot\text{m}^3/\text{kg}_{\text{cat}}{}^2/\text{s}$)
k_2	Reverse reaction rate constant ($\text{mol}\cdot\text{m}^3/\text{kg}_{\text{cat}}{}^2/\text{s}$)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component *i* from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component *i* from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{GL_1L_2}$	Mass transfer rate of component *i* from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
$\mathrm{d}z$	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase
L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase
Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation

Gmail **dewinino <dewinino@gmail.com>**

Re: REPLY - IJEx 16104 Kusumaningtyas et al. (4) - Revises

abudiman@chemeng.ugm.ac.id <abudiman@chemeng.ugm.ac.id> Sun, Feb 2, 2014 at 7:08 AM
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Cc: abudiman@chemeng.ugm.ac.id, "dewinino ." <dewinino@gmail.com>, spurwono@chemeng.ugm.ac.id, rochmadi@chemeng.ugm.ac.id

Title: Graphical exergy analysis of reactive distillation column for biodiesel production

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Gmail **dewinino <dewinino@gmail.com>**

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To: abudiman@chemeng.ugm.ac.id
Cc: abudiman@chemeng.ugm.ac.id, "dewinino ." <dewinino@gmail.com>, spurwono@chemeng.ugm.ac.id, rochmadi@chemeng.ugm.ac.id

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----- Original Message ----- From: <abudiman@chemeng.ugm.ac.id>
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Int. J. Exergy, Vol. 15, No. 4, 2014 447

Graphical exergy analysis of reactive distillation column for biodiesel production

Ratna Dewi Kusumaningtyas, Suryo Purwono, Rochmadi Rochmadi and Arief Budiman*

Faculty of Engineering,
Chemical Engineering Department,
Gadjah Mada University,
Yogyakarta 55281, Indonesia
E-mail: dewinino@gmail.com
E-mail: spurwono@chemeng.ugm.ac.id
E-mail: rochmadi@chemeng.ugm.ac.id
E-mail: abudiman@chemeng.ugm.ac.id
*Corresponding author

Abstract: This paper brings the novelty of the exergy analysis technique using Ex-N-A diagram to a packed reactive distillation (RD) column for biodiesel production. In this study, biodiesel is produced through the esterification of fatty acid with methanol. The simulation of the column was performed based on the non-equilibrium (NEQ) model of a three-phase packed RD system. The graphical Ex-N-A method was utilised to evaluate exergy features of the internal RD column. This technique rigorously demonstrated the value of exergy losses at each increment of the column, i.e., losses owing to the temperature change, phase change, mixing in liquid and vapour phases and chemical reaction. The effects of the molar ratio of the reactant and the height of the packed column on the conversion and exergy losses were examined and displayed in a simple figure.

Keywords: exergy analysis; reactive distillation; esterification; Ex-N-A; biodiesel.

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Biographical notes: Ratna Dewi Kusumaningtyas is a PhD student at the Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. She received her Bachelor's and Master's degrees from the same department in 2000 and 2004, respectively. She is also among the Erasmus Mundus Euro Asia awardees for PhD exchange programme in Politecnico di Torino, Italy (2010–2012). She is the author and co-author of 12 journal and international conference papers during her PhD study. She works as a Lecturer of Chemical Engineering Department, Faculty of Engineering, Semarang State University, Indonesia. Her research interests are renewable energy, reactive distillation system and exergy analysis.

Suryo Purwono is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University and the Vice Director of the Graduate School, Gadjah Mada University. He received his PhD from Chemical Engineering Department, University of Waterloo, Waterloo, Ontario,

Canada, in 1993. His research focuses on distillation, petroleum and renewable energy development. He is the author or co-author of 80 papers and university textbooks. He is also a Visiting Researcher for distillation at Chalmers University of Technology, Sweden (2003), De La Salle University, Philippines (2005), Tokyo Institue of Technology, Japan (2007), and Kyushu University, Japan (2008).

Rochmadi Rochmadi is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He obtained his PhD from the Imperial College, London, UK, in 1991. His research topic is polymer and bio-fuel development. He is the author or co-author of 55 scientific papers. He is also the Coordinator of many industrial–university projects on bio-fuel and biomass development, both in national and international scope.

Arief Budiman is a Professor of Chemical Engineering Department in the Faculty of Engineering, Gadjah Mada University. He received his DEng from Tokyo Institute of Technology, Japan, in 1997. His research focuses on thermodynamics and exergy analysis for system engineering. He is the author or co-author of 40 papers and university textbooks. He is also a Visiting Researcher of exergy methodology for distillation at Tokyo Institute of Technology, Japan (1999, 2001, 2003, 2005, 2009 and 2011) and Visiting Professor at Kyushu University (2012).

1 Introduction

Reactive distillation (RD) is a promising alternative process for equilibrium-limited reaction, such as biodiesel production via fatty acid esterification scheme. It is caused by the fact that the continuous removal of one product will shift the equilibrium to the product formation. Besides, RD integrates the reaction and separation in one shell (Dragomir and Jobson, 2005; Dimian et al., 2009; Gómez-Castro et al., 2010). However, the process involving distillation process is usually associated with the high energy consumption. Therefore, thermodynamic analysis, or specifically recognised as exergy analysis, on an RD column is important to evaluate the energy efficiency of the process.

Exergy is a type of useful or available energy (Ao et al., 2012). Exergy analysis is a robust analysis tool that is based on the first and the second law of thermodynamics. It is efficient for examining the energy quantity and quality of a process accurately (Suphanit et al., 2007). This analysis can be used to find the locations, source and magnitudes of exergy losses in the energy systems and process, hence it plays an important role for designing, developing and optimising an energy-efficient RD process (Budiman and Ishida, 2004; Colpan, 2012).

Various methods of exergy analysis have been proposed for distillation process. Le Goff et al. (1996) introduced the *Carnot-factor-specific enthalpy diagram*. This method is easy to utilise for calculating the exergy target, but it cannot describe the stage-by-stage exergy characteristic. Dhole and Linnhoff (1993) proposed a procedure for composing a T-H curve called the *column grand composite curve* (CGCC). Demirel (2006) suggested that the CGCC is useful for exploring the energy-saving potential, determining the targets for column modifications and recommending retrofits. This method, however, is simple but does not offer information with respect to exergy loss caused by chemical reaction.

A more advanced method was developed by Taprap and Ishida (1996), named *energy utilisation diagram* (EUD). This method is functional for analysing stage-by-stage exergy loss inside the distillation column. The overall exergy loss in the column can be broken down into six types of exergy losses (EXLs), namely EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation and evaporation. Each can be individually displayed in a graph. EUD method gives more detailed information for exergy characteristic. However, it is not convenient when the number of plates in a column is increased. The EUD method was then modified by Budiman and Ishida (1998) into a more compact graphical method called integrated energy utilisation diagram (IEUD). This method thus exhibits all the different types of EXL in a simple diagram. IEUD can show the exergy characteristic in the whole column stage-by-stage, but it cannot reveal the separation performance. To overcome this drawback, Budiman and Ishida (2004) introduced the material-utilisation diagram (MUD) graphical method. This method is able to present the separation performance and the EXL stage-by-stage in the column profile simultaneously. However, MUD diagram becomes very complicated when one of the sub-processes EXL is much larger than the others. Therefore, it is necessary to compose such a simpler and easier diagram to understand a complex RD process.

On this note, the development of the novel Ex-N-A graphical method for exergy analysis in a complex RD system was studied in this work. Compared with the literature works, this graphical method is superior. The Ex-N-A method is constructed simply by plotting the height of the column (N) as ordinate whereas the total EXL, the non-chemical reaction EXL and A (energy level) as abscissa. This plotting results in a simple diagram, which is easy to understand, but it can display the detailed exergy characteristic of a packed RD column entirely. The graphical Ex-N-A diagram is efficient to disclosure the EXL owing to the cooling, heating, mixing in the vapour and liquid phases, condensation, and evaporation and chemical reaction incrementally. And, it is yet easy to understand even in a case when one of the sub-processes EXL is much larger than the others. This diagram can also obviously exhibit the correlation of the exergy losses owing to chemical and non-chemical sub-processes with the energy-level difference at various heights of column.

A thermodynamic analysis using the graphical Ex-N-A diagram to a packed RD column for biodiesel production was carried out in this work. Biodiesel is produced via an esterification reaction of free fatty acid (FFA) with methanol. This route is preferred rather than transesterification of triglyceride scheme, since today employing waste and non-edible feedstock is an obligation to meet with the ecological and ethical requirement for bio-fuels (Dimian et al., 2009). Waste oil and low-grade feedstock contains a considerable value of FFA. Therefore, esterification of FFA is the best scheme for biodiesel production using waste and non-edible oil as feedstock.

In this work, NEQ model with three-phase approach is applied for the RD system. This model brings a novelty since the combination of the three-phase and NEQ model has been merely studied for a distillation process, which does not involve any reaction in the system (Higler et al., 2004). This paper aims at displaying the graphical Ex-N-A exergy analysis for presenting the energy feature of the RD column for biodiesel production. The effect of some parameters on the reaction conversion and exergy loss is also revealed. This finding will facilitate the designer to identify the thermodynamic problem and help to enhance the conversion as well as improve the energy efficiency of the RD system.

2 Model and simulation for reactive distillation (RD) column

A packed RD column was utilised for the biodiesel production via fatty acid esterification. In this case, oleic acid was taken as a compound representing the FFAs. As a case study, esterification of oleic acid and methanol in the presence of solid acid catalyst namely ion-exchange polymeric resin of relite CFS (Tesser et al., 2005) in RD column was examined. The generic esterification reaction of an FFA and methanol is shown here:

$$\text{RCOOH}(\text{A}) + \text{CH}_3\text{OH}\ (\text{B}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{RCOOCH}_3\,(\text{C}) + \text{H}_2\text{O}\ (\text{D}) \tag{1}$$

For the RD simulation, the pseudo-homogeneous second-order equilibrium is selected to express the reaction rate (Tesser et al., 2005):

$$\dot{r} = (k_1 x_A x_B - k_2 x_A x_B) C_{\text{cat}}. \tag{2}$$

The values of the pre-exponential factors and activation energies (E_a) for the direct (1) and reverse reaction (2) are reported in Table 1. The reaction is slightly endothermic with $\Delta H_r = 11213.12$ J/mol. The compounds involved in the reaction are oleic acid and methanol as reactants. On the other hand, water and methyl oleate (biodiesel) are products. Table 2 reports the molecular structure of the chemical compounds involved in the reaction as well as their normal boiling points.

Table 1 Kinetic parameters of the pseudo-homogeneous model

Reaction rate constant (mol $\text{m}^3/\text{kg}_{\text{cat}}^2/\text{s}$)	*Ln*(*pre-exponential factor*)	E_a (J/mol)
k_1	0.2155	58576.0000
k_2	0.1460	47362.8800

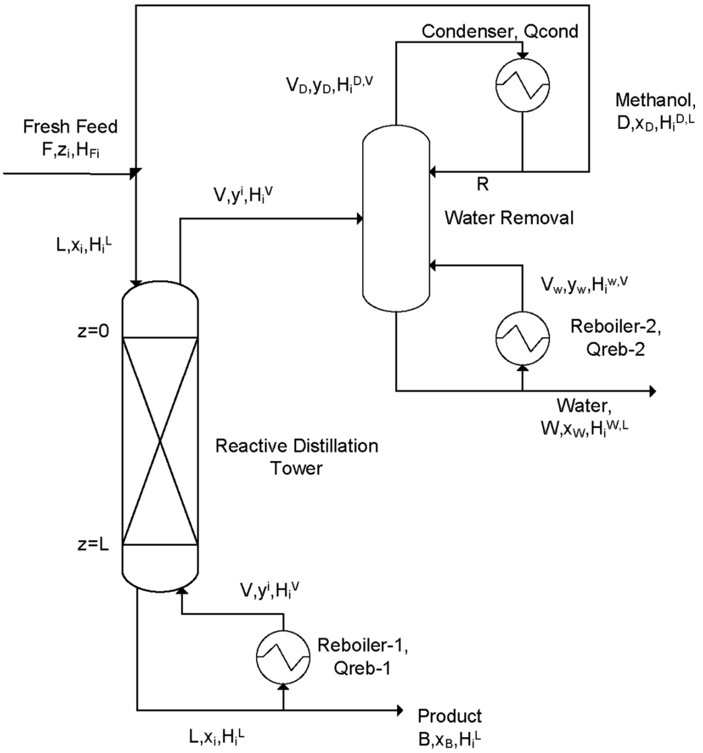
Table 2 Molecular structure and normal boiling points of all the chemical compounds

Compounds	*Molecular structure*	*Boiling point* (K)
Oleic acid (A)	$\text{CH}_3(\text{CH}_2)_7\text{CH=CH}(\text{CH}_2)_7\text{COOH}$	632.85
Methanol (B)	CH_3OH	337.7
Methyl-oleate (C)	$\text{CH}_3(\text{CH}_2)_7\text{CH=CH}(\text{CH}_2)_7\text{COOCH}_3$	616.85
Water (D)	H_2O	373

The esterification reaction was carried out in a packed RD column. Configuration of the RD in this work is modified from the conventional RD scheme. In this case, RD applies a continuous water removal system, in which the top product containing a mixture of methanol and water is separated in an additional column. The mixture of methanol and water vapour at the top is condensed. Subsequently, they are introduced to an additional distillation column for separation. Water is continuously withdrawn, while methanol is recycled to the main column as a reflux. Reflux of the methanol and both the fresh feed of methanol and fatty acid are introduced at the top of the column. On the other hand, methyl ester (biodiesel) is drawn off at the bottom. The detailed configuration of the packed RD column is shown in Figure 1. RD is operated in co-current mode between the reactants, and counter-current mode between the liquid and gas. The increment of the

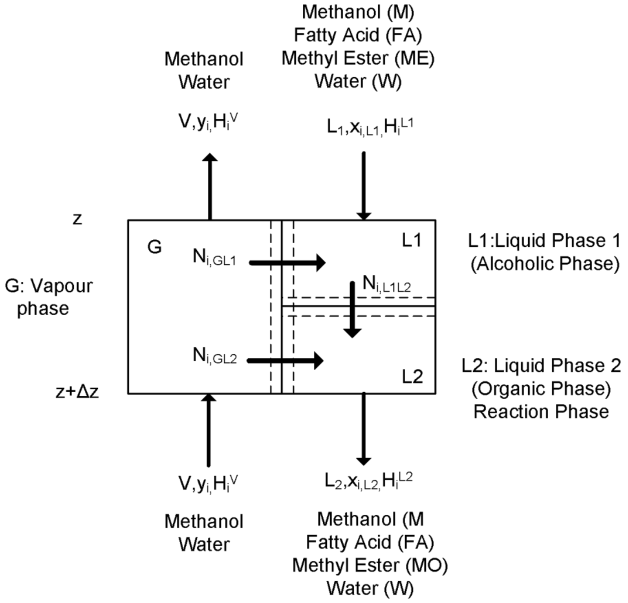
column starts from the top, hence $N = 0$ m is the top of the column, while $N = n$ m is the lowest part of the column. The base case condition employs the packed column with the height of 3 m with the column diameter of 0.5 m. The ratio of oleic acid to total methanol entering the column is set constant at 2 : 1 inside the column. Flow rate of oleic acid feed is 83.33 mol/s and total methanol inputted to the column is 166.67 mol/s. Flow rates of total vapour leaving the column and products discharging from the reboiler are 185 and 69.52 mol/s, respectively.

Figure 1 The configuration of packed RD column for biodiesel production



The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed for the conventional tray distillation column (Higler et al., 2004; Lao and Taylor, 1994). The NEQ model assumes that the vapour from the lower position of the packing is brought into contact with liquid moving down from the upper position, allowing an exchange of mass and energy across the interface between these phases. This system involves four components, namely methanol, oleic acid, methyl ester and water. The organic compounds (oleic acid and methyl ester) and the polar compounds (water and methanol) are immiscible, thus will separate into two liquid phases. Therefore, the three phases are defined as vapour phase, which contains only methanol and water, alcoholic liquid phase, which contains mainly water and methanol, and organic liquid phase, which primarily contains fatty acid and methyl oleate. The reaction is assumed to occur in the organic phase.

Figure 2 Schematic representation of one cell of three-phase packed RD column



The assumptions taken in this modelling and simulation can be written as follows:

1 In the FFA esterification reaction, oleic acid is taken as a compound representing the FFA in the vegetable oil.

2 The FFA esterification is expressed by the pseudo-homogeneous second-order equilibrium kinetic model.

3 The RD column operates at the steady-state condition.

4 There are three phases that occur in the system, namely vapour phase, alcoholic phase (liquid-1) and organic phase (liquid-2).

5 The reaction takes place in the organic phase (liquid-2).

6 Temperatures of the alcoholic phase (liquid-1) and organic phase (liquid-2) are similar, which is called temperature of liquid.

7 The RD column is modelled based on the NEQ approach. Hence, the interfacial mass transfer rates play a significant role in the calculation.

The equations applied for the NEQ model of three-phase RD are summarised as follows. The mass balances of each compound in the vapour, liquid-1 and liquid-2 phases are formulated in equations (3)–(5), respectively:

$$\frac{\mathrm{d}y_{i,G}}{\mathrm{d}z} = \frac{(-\dot{R}_{i,G}) - y_i \frac{\mathrm{d}V'}{\mathrm{d}z}}{V'} \tag{3}$$

$$\frac{\mathrm{d}x_{i,L_1}}{\mathrm{d}z} = \frac{(-\dot{R}_{i,L_1}) - x_i \frac{\mathrm{d}L_1'}{\mathrm{d}z}}{L_1'} \tag{4}$$

$$\frac{\mathrm{d}x_{i,L_2}}{\mathrm{d}z}=\frac{-(-\dot{R}_{i,L_2})-x_i\frac{\mathrm{d}L_2'}{\mathrm{d}z}}{L_2'}. \tag{5}$$

Meanwhile, the total mass balance of the vapour, liquid-1 and liquid-2 phase is presented in equations (6)–(8), respectively:

$$\frac{\mathrm{d}V'}{\mathrm{d}z}=-\sum\dot{R}_{i,G} \tag{6}$$

$$\frac{\mathrm{d}L_1'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_1}\right) \tag{7}$$

$$\frac{\mathrm{d}L_2'}{\mathrm{d}z}=-\left(-\sum\dot{R}_{i,L_2}\right) \tag{8}$$

To solve equations (3)–(8), the rate process equations are necessary. The rate process equations for the gas, liquid-1 and liquid-2 phases are equations (9)–(11), respectively.

$$\dot{R}_{i,G}=-(\dot{N}_i^{GL_1}+\dot{N}_i^{GL_2}) \tag{9}$$

$$\dot{R}_{i,L_1}=\dot{N}_i^{GL_1}-\dot{N}_i^{L_1L_2} \tag{10}$$

$$\dot{R}_{i,L_2}=-\dot{N}_i^{GL_2}+\dot{N}_i^{L_1L_2}+v_i\dot{r}. \tag{11}$$

The result outputted from the RD simulation is utilised for the exergy analysis by means of the graphical Ex-N-A methods. The Ex-N-A thermodynamic analysis is a rigorous method to evaluate the exergy features of the internal RD column. It is simple but powerful to reveal the value of EXL at each increment of the RD column, i.e., EXL owing to the temperature change, phase change, mixing in liquid and vapour phase and chemical reaction. The loss in reboiler and condenser is also examined. Effects of the main parameters, specifically molar ratio and the column height, on the conversion and EXL inside the column are also analysed.

3 Graphical Ex-N-A methods

Thermodynamic analysis using graphical Ex-N-A methods departs from the basic exergy concept and the second law of thermodynamics (Suphanit et al., 2007). The formula of non-chemical EXL calculation refers to the work of Budiman and Ishida (2004). Determination of the non-chemical reaction loss, i.e., EXL owing to changes of the concentration (mixing), phase of the component and temperature, have been described in their work and are adopted for calculation in this study. On the other hand, the formula for finding out the EXL owing to the chemical reaction starts from the concept of the energy level. Availability factor or energy level (A) is explained as (Srinophakun et al., 2001):

$$A=\frac{E\dot{X}L}{\Delta H}. \tag{12}$$

EXL is then defined by the following equation.

$$E\dot{X}L = \Delta H - T_0 \Delta S. \tag{13}$$

Hence,

$$A = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{14}$$

It illustrates the maximum fraction of energy, which can be converted to useful work. Thus, energy level of the chemical reaction is expressed by:

$$A_{\text{Chem}} = \left(1 - T_0 \frac{\Delta s}{\Delta H}\right). \tag{15}$$

On the equilibrium condition in which the reaction does not occur, entropy can be defined as:

$$\Delta S = \frac{\Delta H}{T}. \tag{16}$$

In this condition, energy level *A* generally can be written as:

$$A = \left(1 - \frac{T_0}{T}\right). \tag{17}$$

Hence, for the liquid flowing along the column, the energy level is expressed as:

$$A_{\text{Liq}} = \left(1 - \frac{T_0}{T}\right). \tag{18}$$

For the gas flowing along the column, the energy level is expressed as:

$$A_{\text{Gas}} = \left(1 - \frac{T_0}{T}\right). \tag{19}$$

T in the energy-level formula depends on the phase. *T* is the gas temperature for the energy level of the gas, and it is liquid temperature for the energy level of the liquid. The reaction takes place in the liquid phase. Thus, EXL owing to the chemical reaction is closely related to the difference between the energy level of the liquid and that of the chemical reaction. Hence, EXL owing to the chemical reaction can be written as:

$$E\dot{X}L_{\text{Chem}} = (A_{\text{Liq}} - A_{\text{Chem}})\Delta H. \tag{20}$$

4 Display of packed reactive distillation column on graphical Ex-N-A diagram

4.1 Base case analysis

Ex-N-A diagram is an exergy-feature-based diagram that is designed to present exergy characteristic of separation and chemical processes in a simple diagram. In this work, the Ex-N-A presentation was developed based on the fundamental concept of the previous

graphical methods (Budiman and Ishida, 2004; Taprap and Ishida, 1996). In the previous work on MUD, Budiman and Ishida (2004), Budiman (2008) and Budiman et al. (2011) composed the graph for EXL owing to concentration, phase and temperature changes by putting the mole number (n_j) as abscissa and $\Re T_0 \ln x_j$ as ordinate for the liquid phase and $\Re T_0 \ln y_j$ for the gas phase. Meanwhile, in this work, the Ex-N-A diagram is made by placing the two types of diagram in a single feature. The height of the column (*N*) is put as ordinate whereas the total EXL, the non-chemical reaction EXL and *A* (energy level) are placed as abscissa. The first type of the diagram is entitled the Ex-N diagram, which consists of *N* as ordinate whereas total EXL and non-chemical reaction EXL (Ex) as abscissa. The second type of the diagram is called the A-N diagram, in which *N* was put as ordinate and *A* is set as abscissa. The other two diagrams exhibiting the correlation between the column height and total EXL and reaction conversion are also composed.

The graphical Ex-N-A method has numerous advantages compared with the previous literature work. It is a simple diagram, however, can display the detailed exergy characteristic in the whole RD column. The Ex-N-A diagram describes all the EXL sub-processes, namely the chemical EXL and non-chemical EXL (EXL owing to the cooling, heating, mixing in the vapour and liquid phases, as well as phase change) incrementally. This graphical method does not reveal a complicated diagram even in a case when one of the sub-processes EXL is much larger than the others. It can also combine two types of graphs (Ex-N and A-N graphs) in a single diagram.

This Ex-N-A diagram implements the principle of energy-level difference. In this concept, every process must donate or accept energy. The process donating energy is referred to as the energy donor and the one accepting energy is referred to as the energy acceptor (Srinophakun et al., 2001). The energy-level difference between A_{gas} and A_{liq} ($A_{\text{gas}} - A_{\text{liq}}$) indicates the driving force for the energy transformation (Budiman and Ishida, 2004). In the literature work, this concept is commonly applied for a graphical methodology to exemplify the driving force as the energy-level difference and exergy consumption as the shaded area in the diagrams. Hence, it does not clearly show the exergy profile at different levels of the column.

On the other hand, in composing the Ex-N-A diagram, column height (*N*) is plotted as abscissa against the total EXL, non-chemical reaction EXL and energy level. On the basis of this diagram, the graphical correlation between total EXL, non-chemical reaction EXL and energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) is incrementally revealed along the column. The Ex-N-A diagram is illustrated in the form of a bar graph, which consists of the two graphs, namely the Ex-N and the N-A graphs. Ex-N graph also splits into two types of subgraphs. The first Ex-N graph shows the EXL in the reboiler and condenser, EXL owing to the chemical reaction and non-chemical EXL (i.e., losses owing to the temperature change, mixing and phase change) incrementally from top to the bottom. EXL in the condenser and reboiler are shown on the uppermost part and the bottom of the graph, respectively. Meanwhile, at each increment, EXL of all the sub-processes, i.e., EXL owing to chemical reaction, phase change of methanol, phase change of water, mixing process in the liquid phase, mixing in the vapour phase, and temperature change in liquid phase and temperature change in gas phases, is displayed in a bar graph from the left to the right, correspondingly.

The second Ex-N diagram shows the non-chemical reaction EXL. It consists of losses owing to phase change of methanol compounds, phase change of water compounds, mixing process in the liquid phase, mixing process in the vapour phase, temperature change in liquid phase and temperature change in liquid phase, which are drawn from the right to the left, respectively. On the other hand, the N-A diagram exhibits the bar indicating the energy level (A) of the liquid and gas incrementally. For each increment, the energy level (A) of the liquid is placed at the upper position, whereas the energy level (A) of the gas is placed at the lower position. On the basis of this N-A graph, the energy-level difference between gas and liquid ($A_{gas} - A_{liq}$) incrementally can be exposed.

In this work, the base case of the simulation was set up with the following condition: the height of the column (*N*) was 3 m, the column diameter was 0.5 m and the molar ratio of methanol to oleic acid was 2 : 1. It resulted in total oleic acid conversion of 30.76%. The concentration of the compounds, total molar flow rate of each phase and temperature profiles at the different heights of the columns are exhibited in Figures 3–5, respectively. These data are required for the EXL calculation.

Figure 3 Concentration profiles of the compounds in liquid-1, liquid-2 and vapour phases at different column height (see online version for colours)

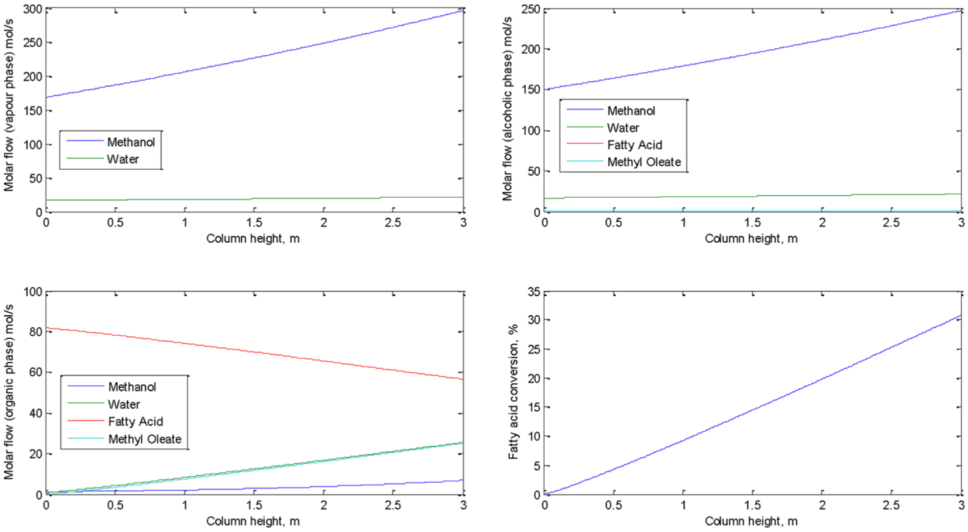


Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. In Figure 6(a), EXL of the reboiler and condenser is shown by the scale of 1/5 because of their large values. The larger EXL at the reboiler than at condenser is not surprising. This could be as a consequence of the large concentration of compounds as well as the high heat load at reboiler than those at condenser. This phenomenon agrees with the result previously obtained by Budiman and Ishida (2004) and Khoa et al. (2010).

Figure 4 Total molar flow of each phase at different column height (see online version for colours)

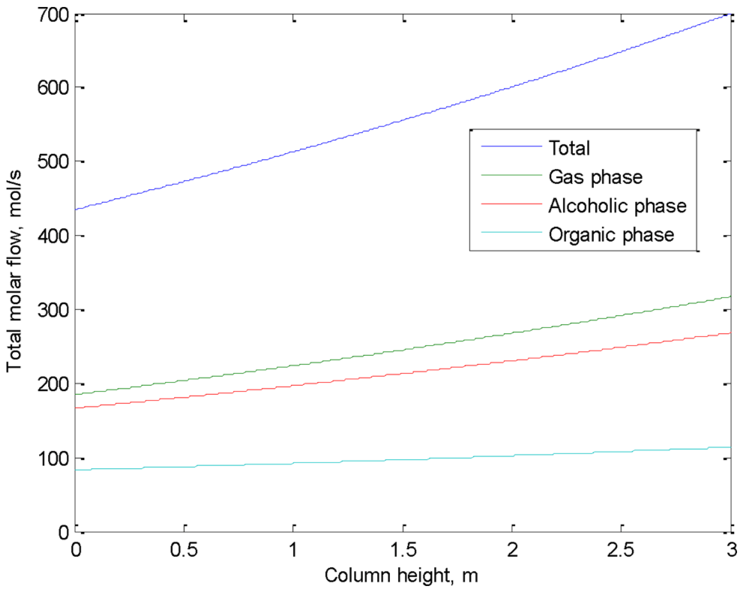
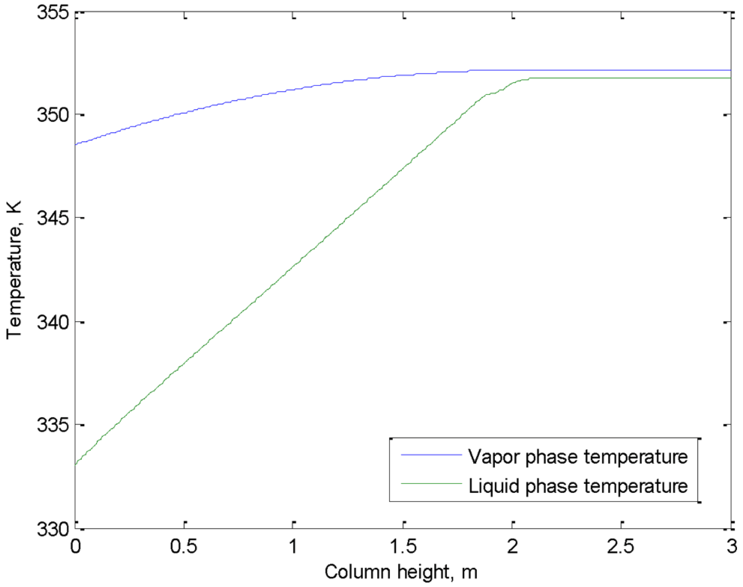


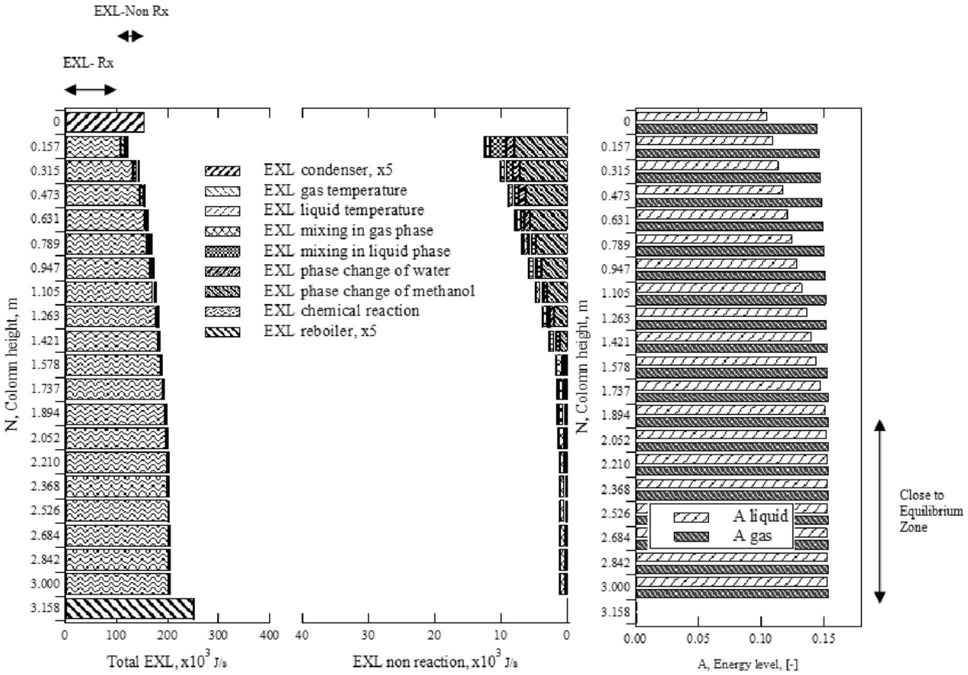
Figure 5 Temperature profile of liquid and vapour phase at different column height (see online version for colours)



The incremental assessment on the RD column using Ex-N-A diagram was also depicted in Figure 6. The Ex-N diagram in Figure 6(a) shows that the non-chemical EXL, i.e., the summation of EXL owing to the concentration change (mixing), temperature and phase changes, decreases from the top to bottom. Then, starting from $N = 2$ m from the top, the non-chemical EXL turns into a very small quantity. This tendency agrees with the

A-N diagram in Figure 6(b), which displays the profile of the energy-level difference between gas and liquid ($A_{\text{gas}} - A_{\text{liq}}$) inside the column or the so-called driving force. Energy-level difference between gas and liquid strongly corresponds to the temperature profile along the RD column. The temperature difference between gas and liquid will result in the energy-level difference.

Figure 6 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 3$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that of the gas, which is represented by the equal value of the gas and liquid energy level. This condition has an important effect on the non-chemical reaction EXL value. The diagram exhibits that, for the non-chemical reaction EXL, the values of all the losses that are influenced by temperature are zero. Hence, simply the EXL owing to the mixing exists at $N = 2$ m moved downwards. EXL owing to mixing is affected only by the concentration change, so the alteration of the temperature does not provide so much influence. On the other hand, EXL owing to the temperature and phase change absolutely depend on the temperature difference between gas and liquid. When the temperature of the liquid is just about equal to the gas temperature, it can be said that the near-equilibrium condition has been reached. In this condition, a macro-heat transfer between the two phases does not occur. Therefore, the section inside the column can be divided into two regions. The first region is the non-equilibrium (NEQ) zone, and the second one is the close-to-equilibrium zone.

Two regions, NEQ and close-to-equilibrium zones, exist in the packed RD column in this operation. Non-equilibrium zone takes place at the upper part of the column. Meanwhile, the close-to-equilibrium zone comes about at the lower part of the column. At the lower part of the column, there is an abundant heat supply from reboiler, leading to an excellent heat transfer between the gas and liquid phase. It causes a very small temperature difference between gas and liquid, which also results in a very small (near to zero) energy-level difference. The condition where the energy-level difference or the driving force is very small (let us say 'zero') is described as the ideal column with minimum thermodynamic condition (Pinto et al., 2011). This condition has brought about the close-to-equilibrium zone on the lower part of the column. An intensive discussion on close-to-equilibrium zone, or sometimes called close-to-equilibrium point (CEP), has also been presented by Budiman et al. (2011), in which CEP is shown on MUD for the minimum reflux ratio. Pinto et al. (2011) and Budiman et al. (2011) suggest that the procedure to improve the energy efficiency of a distillation column should involve the use of the so-called minimum thermodynamic condition of columns.

Non-equilibrium zone emerges at the upper part of the column. At the top of the column, all feeds are introduced; explicitly both the fresh feed of methanol and oleic acid, as well as methanol reflux. The abundant liquid stream entering the column has drastically changed the gas-liquid composition and brings about a distance between the actual and the near-to-equilibrium condition. It causes an inefficient heat transfer between the gas flowing from the lower increment and the liquid stream. Thus, there is a large temperature difference between the gas as the heat donor and the liquid as the heat acceptor. This large temperature difference is shown by the large energy-level difference (driving force) between gas and liquid at the column top (A-N diagram in Figure 6(b)). In addition, the energy-level difference decreases from the top to the bottom. Ultimately, at a certain height of the column, it comes up to the close-to-equilibrium zone. The A-N diagram profile agrees with the non-chemical reaction EXL profile as shown on Ex-N diagram in Figure 6(a). Thus, it depicts that the largest non-chemical reaction EXL is located at the top of the column. This finding is valuable for guiding the improvement on RD design.

A comprehensive thermodynamic analysis on a packed RD column should involve the EXL analysis owing to the chemical reaction. However, assessment on the EXL owing to chemical reaction incrementally has never been discussed intensively in the previous literature. In this work, this type of EXL becomes one main focus to evaluate. Ex-N diagrams in Figure 6(a) expose a different tendency between the profile of the total EXL and EXL owing to the chemical reaction, on the one side, and EXL owing to the non-chemical reaction, on the other side. The profile of total EXL and EXL owing to chemical reaction increases from the top to the bottom. This fact is absolutely the opposite of the profile of the non-chemical reaction EXL. It indicates that EXL owing to chemical reaction gives a dominant contribution to the total EXL at each increment. Hence, the profile of total EXL is reminiscent of the EXL owing to chemical reaction profile.

On the basis of the Ex-N diagram, it is revealed that the amount of EXL owing to chemical reaction increases from the top to the bottom. The higher EXL is probably correlated to the amount of the mole reacting at each increment. The higher the amount of reactants reacts, the higher the EXL is resulted. In this RD system, at the top of the column, the fresh feed and reflux of methanol meets the fresh feed of oleic acid. Methanol has a small solubility with long fatty acid. Therefore, at the beginning of the column, only a little mole of methanol diffuses into the organic liquid phase, which contains mainly oleic acid. While flowing downward the column, more amount of methanol is dissolved into the organic phase and reacts with fatty acids. It results in a higher conversion at each increment as well as higher EXL. Therefore, it is found that the EXL owing to chemical reaction as well as total EXL increase from the top to the bottom.

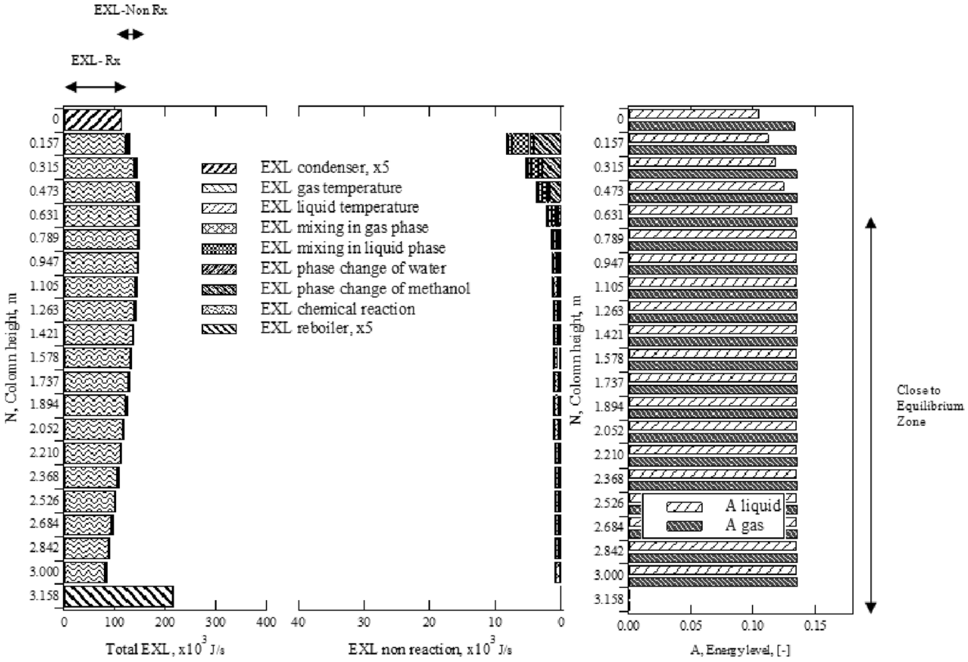
Fitzmorris and Mah (1980) underline that analysing EXL in a distillation column can provide a useful understanding and insights, leading to a better design of a distillation system. Thus, to acquire an in-depth understanding of the thermodynamic aspects of an RD column, examination on the influence of the main process parameters should be conducted. Parameters observed in this study are molar ratio of the reactants and column height (*N*). The knowledge of their effects on RD performance and thermodynamic behaviour is useful for the designer to judge the process feasibility and perform the optimisation graphically.

4.2 Effect of the molar ratio of the reactants

To understand the influence of molar ratio on the thermodynamic behaviour and RD performance, first, the molar ratio of total methanol and oleic acid entering the column is increased from 2 : 1 to 6 : 1 at the same column height of 3 m ($N = 3$) and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, it is shown that the reaction conversion enhances about two times from 30.76% to 66.41%. However, the Ex-N diagram in Figure 7(a) shows that the profile of non-chemical EXL does not change so much compared with the result given by the molar ratio of 2 : 1. At molar ratio of 6 : 1, the area in the packed RD column splits into two regions. The lower part of the column is the close-to-equilibrium zone with near to zero driving force, whereas the upper part is NEQ zone. However, enhancing molar ratio from 2 : 1 to 6 : 1 has considerably extended the area of the close-to-equilibrium zone. The A-N diagram in Figure 7(b) shows that, when molar ratio of 6 : 1 is applied, the close-to-equilibrium zone starts at $N = 0.75$ m downward. Hence, the area of the close-to-equilibrium zone is notably larger than that of the NEQ zone inside the column. The larger area of the close-to-equilibrium zone occurs since there is a far excess of methanol in the mixture. The large excess of methanol to oleic acid eases a good contact to the two phases and leads to the excellent distribution of methanol in the organic phase. When the ideal condition is approached and the driving force is near to zero, the equilibrium condition will be easier to reach. Consequently, the region of CEP gets larger when the higher molar ratio of reaction is applied.

It can be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column. This statement is convinced by the result obtained when applying the molar ratio of methanol to oleic acid of 1 : 1 with $N = 3$. At this operation condition, the oleic acid conversion drops to 9.57%. Meanwhile, the thermodynamic evaluation depicts that the CEP cannot be reached with this low molar ratio. As shown on the A-N diagram in Figure 8(b), all the areas in RD column are NEQ zone, disclosed by the existence of the driving force and all the non-chemical reaction EXL (losses owing to mixing, phase and temperature changes) along the column. The amount of non-chemical reaction EXL decreases from the top to the bottom.

Figure 7 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 6 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram



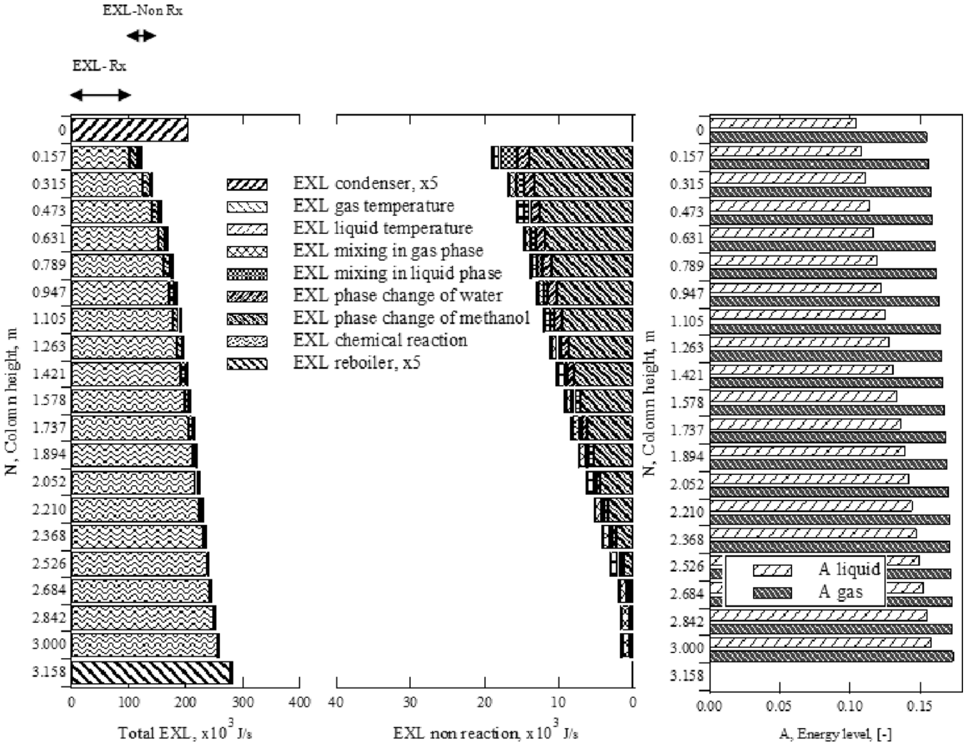
(a) (b)

To evaluate the impact of varying the molar ratio on the value of the EXL owing to chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is clearly affected by the changing of molar ratio of the reactants. As displayed in Figure 8, when the molar ratio of 1 : 1 is employed, the Ex-N profile is almost similar to the result gotten by applying molar ratio of 2 : 1.

However, if molar ratio of the reactants is drastically enhanced to 6 : 1, the new Ex-N profile seems interesting. It is shown that EXL owing to the chemical reaction gets higher from the top downward as seen on the Ex-N diagram in Figure 7(a). In spite of this, at a certain point in the column, EXL owing to chemical reaction tends to decrease and achieve the minimum value at the lowest increment of the column. The value of EXL owing to chemical reaction strongly corresponds to the number of moles that reacts at each increment. Hence, this phenomenon can be explained as follows. When the high molar ratio of methanol to oleic acid is applied, the mass transfer of methanol to organic phase becomes easier. An excellent dispersion of methanol in the organic phase leads the reactants to react easily. Consequently, from the top downward, there is a severe increase in the number of moles of reactants involved in the reaction at each increment, which causes high reaction rate enhancement at the upper part of the column. However, at a certain point, the remaining unreacted oleic acid is too small to achieve high reaction rate. At this increment, only a small number of oleic acid involves in the reaction, which results in the decrease in the reaction rate from this point to the bottom. The profile of the reaction rate is identical to the profile of the EXL owing to chemical reaction in the column. It can be observed that EXL owing to the chemical reaction increases significantly at each increment on the upper part of the column. However, at a certain point, it decreases and reaches a minimum point at the lowest increment.

To obtain the appropriate molar ratio of the reactants that provides high RD performance but low total EXL, an integrated graphical examination should be composed. Figure 9 presents the profile of oleic acid conversion and total EXL against the reactant molar ratio. It is revealed that the higher molar ratio results in the higher reaction conversion but lower EXL. Thus, the higher molar ratio of methanol to oleic acid will give great benefit, both from the RD performance and the thermodynamic aspect's point of view.

Figure 8 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 1 : 1 at *N* = 3 m: (a) Ex-N diagram and (b) A-N diagram

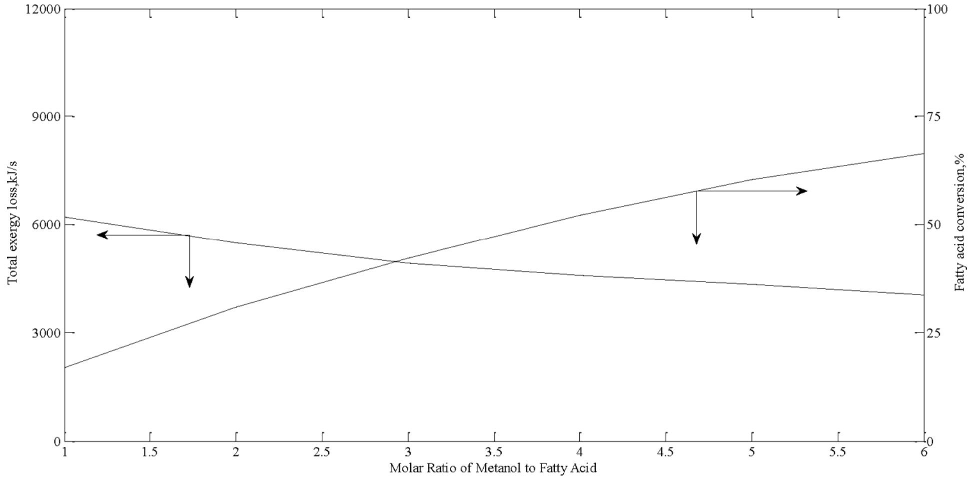


(a) (b)

4.3 *Effect of the height of the packed column (N)*

The subsequent important aspect to be analysed is the height of the column (*N*). To study this parameter, *N* is increased from 3 m to 6 m with the similar reactants molar ratio of 2 : 1, whereas the column diameter is kept the same (0.5 m). Hence, it reveals that the reaction conversion is enhanced from 30.76% to 58.52%. On the other hand, the result of the thermodynamic evaluation is displayed in Figure 10. The Ex-N diagram in Figure 10(a) shows that increasing the height of the column does not so much change the profile of the non-chemical reaction EXL compared with the profile of the column with the height of 3 m (*N* = 3). The highest value of non-chemical EXL occurs at the top of the column, thereafter it decreases downward. Subsequently, starting from the *N* = 2 m from the top, EXL of the sub-processes, which depends on temperature (loss owing to temperature and phase changes), approaches zero. This tendency agrees with the trend of the driving force profile exhibited on the A-N diagram in Figure 10(b). Nevertheless, it is shown that the energy-level difference between gas and liquid decreases from the top downward. Then, starting at *N* = 2 m downward, the energy-level difference is near to zero. Thus, the area in the column can be separated into two regions, i.e., the NEQ zone and the close-to-equilibrium zone. Non-equilibrium region covers the section from the top to *N* = 2, whereas the rest are the close-to-equilibrium zone. Thus, the increasing of the column height does not change the NEQ area. However, it just prolongs the close-to-equilibrium zone. The existing of NEQ region is mostly caused by the extremely abundant input of the reactants and reflux at the top. Conclusively, the changing on the molar flow rate will provide more influence on it than the variation on the column height.

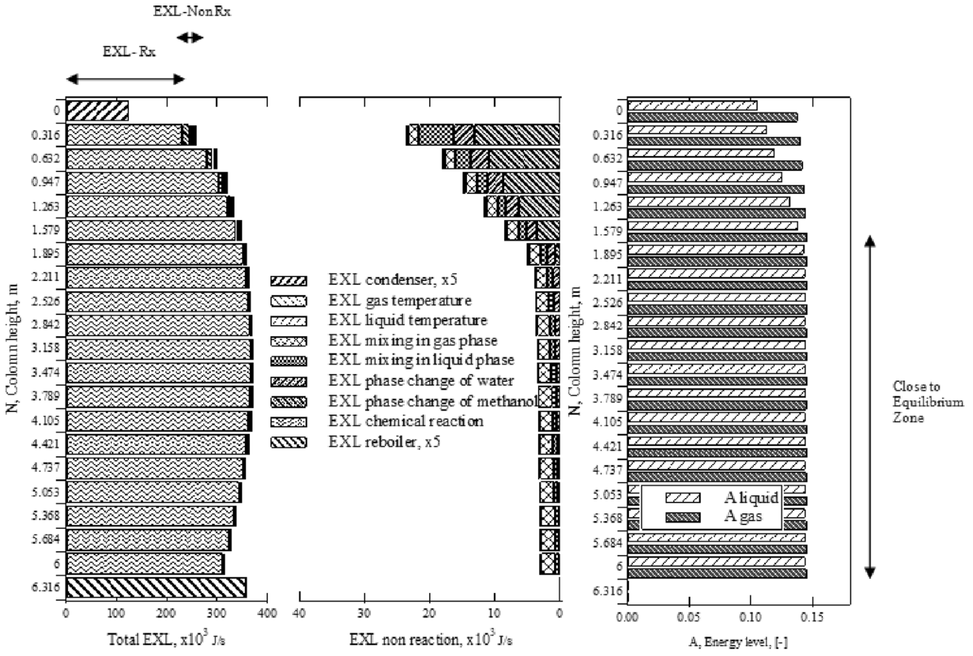
Figure 9 Profile of total exergy loss and fatty acid conversion at different reactant molar ratio



Effect of the column height (*N*) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment of *N* = 2, EXL owing to the chemical reaction values remains almost constant, and finally decreases at *N* = 4 to bottom. EXL owing to the chemical reaction is strongly affected by the reaction behaviour. In this operation condition, reaction rate at each increment in the upper part of the column increases from the top downward. However, at a certain height, the remaining moles of the unreacted oleic acid are not sufficient to continuously enhance the reaction rate. Hence, the reaction rate at a certain increment turns into constant if compared with the rate at the upper increment. Finally, the rate decreases at a certain increment downward.

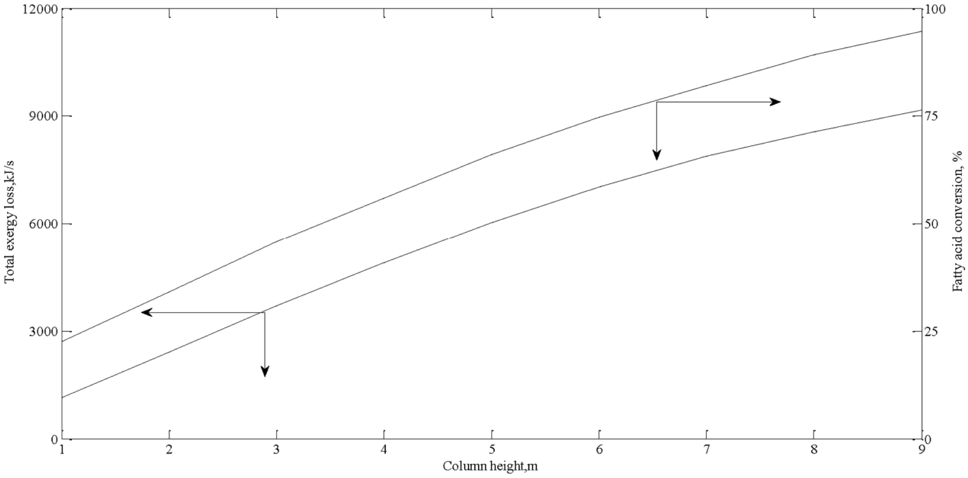
To obtain a more profound comprehension on the influence of the column height to the RD performance and thermodynamic behaviour, a diagram presenting the profile of total EXL and reaction conversion against the column height is composed. Figure 11 discloses that the increase in the column height leads to the higher conversion and the larger total EXL. Thus, the best point on the column yielding an excellent performance on the reaction conversion and the thermodynamic efficiency should be determined.

Figure 10 Exergy loss profile (Ex-N-A diagram) for molar ratio of methanol to FFA of 2 : 1 at $N = 6$ m: (a) Ex-N diagram and (b) A-N diagram



(a) (b)

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height



Conclusively, there are some findings obtained by analysing the effects of the reactant molar ratio and column height. On the basis of the thermodynamic point of view, EXL can be reduced by distributing the inlet of the reactants at different places. For example, shifting the feed point location of one reactant from the top will reduce the load at the top and lessen EXL. It probably facilitates the reduction of the driving force and enlarges the close-to-equilibrium region inside the column. This suggestion agrees with the work on exergy analysis using MUD (Budiman et al., 2011). Besides, the optimum efficiency of the RD can be achieved by determining the best column height, which results in low EXL but high reaction conversion. The other way to improve the reaction performance and reduce EXL is through employing higher molar ratio of the reactants, which can be done by increasing the reflux ratio as suggested by Pinto et al. (2011), or by introducing higher fresh feed stream.

5 Conclusions

- A graphical method called Ex-N-A diagram has been applied to assess the performance and efficiency of a packed RD column. This technique displays the reaction performance, EXL and energy-level characteristic incrementally over the whole packed RD column in a simple way. Nevertheless, it is easy to understand, even when one of the sub-processes has a much larger EXL than the others.
- The base case of the RD simulation was studied at *N* = 3 m, the column diameter of 0.5 m and the molar ratio of methanol to oleic acid of 2 : 1. This results in total oleic acid conversion of 30.76%. The total EXL at reboiler is 1256638.9211 J/s whereas in condenser it is 769351.3847 J/s. The incremental assessment on the RD column shows that the non-chemical EXL decreases from the top to bottom, which agrees with the A-N profile.
- The influence of molar ratio is examined by changing the molar ratio of total methanol to oleic acid entering the column of 2 : 1 to 6 : 1 at the similar *N* of 3 m and column diameter of 0.5 m. By employing the molar ratio of 6 : 1, the reaction conversion enhances from 30.76% to 66.41%. On the contrary, it drops to 9.57% by applying the molar ratio of 1 : 1. It can also be confirmed that the higher molar ratio of the reactants leads to the wider equilibrium region in the column.
- To study the effect of column height, *N* is increased from 3 m to 6 m, whereas the reactants molar ratio and column diameter are kept at 2 : 1 and 0.5 m, respectively. This reveals that the conversion is enhanced from 30.76% to 58.52%. Thus, the increase in the column height does not change the NEQ area; nevertheless, it just prolongs the close-to-equilibrium zone.
- The changing on molar flow rate provides more effect on reaction conversion and EXL profile than the variation on column height.

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Nomenclature

Symbols	
A	Energy level
A_{Chem}	Energy level of the chemical reaction
A_{Gas}	Energy level of the gas phase
A_{Liq}	Energy level of the liquid phase

C_{cat}	Concentration of the solid catalyst ($\text{kg}_{\text{cat}}/\text{m}^3$)
E_a	Activation energies (J/mol)
$\dot{EXL}$	Exergy loss rate (J/s)
ΔH	Enthalpy change (J/mol)
ΔH_r	Heat of reaction (J/mol)
k_1	Direct reaction rate constant ($\text{mol}\cdot\text{m}^3/\text{kg}_{\text{cat}}^2/\text{s}$)
k_2	Reverse reaction rate constant ($\text{mol}\cdot\text{m}^3/\text{kg}_{\text{cat}}^2/\text{s}$)
L_1	Molar liquid flow rate of liquid phase 1 (mol/s)
L_2	Molar liquid flow rate of liquid phase 2 (mol/s)
N	Height of the column (m)
$\dot{N}_i^{GL_1}$	Mass transfer rate of component *i* from the gas phase to liquid 1 phase (mol/s)
$\dot{N}_i^{GL_2}$	Mass transfer rate of component *i* from the gas phase to liquid 2 phase (mol/s)
$\dot{N}_i^{GL_1L_2}$	Mass transfer rate of component *i* from the liquid 1 phase to liquid 2 phase (mol/s)
$\dot{r}$	Reaction rate (mol/s)
$\dot{R}$	Rate of the compounds generated (mol/s)
ΔS	Entropy change (J/mol/K)
T	Temperature (K)
T_0	Reference temperature (K)
T_b	Boiling point (K)
V	Molar liquid flow rate of vapour phase (mol/s)
x	Mole fraction of the compounds in the liquid phase
y	Mole fraction of the compounds in the vapour phase
$\mathrm{d}z$	Increment of the column height (m)
v_i	Reaction coefficient
Subscripts	
A, B, C, D	Fatty acid (oleic acid), methanol, biodiesel (methyl oleate), water, respectively
i	Component index
G	Referring to gas phase
L_1	Referring to liquid 1 phase
L_2	Referring to liquid 2 phase
Abbreviation	
EXL	Exergy loss
FFA	Free fatty acid
NEQ	Non equilibrium
RD	Reactive distillation