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by Ratna Dewi Kusumaningtyas

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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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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:

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

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

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

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$_2$)$_7$CH=CH(CH$_2$)$_7$COOH	632.85
Methanol (B)	CH$_3$OH	337.7
Methyl-oleate (C)	CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOCH$_3$	616.85
Water (D)	H$_2$O	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
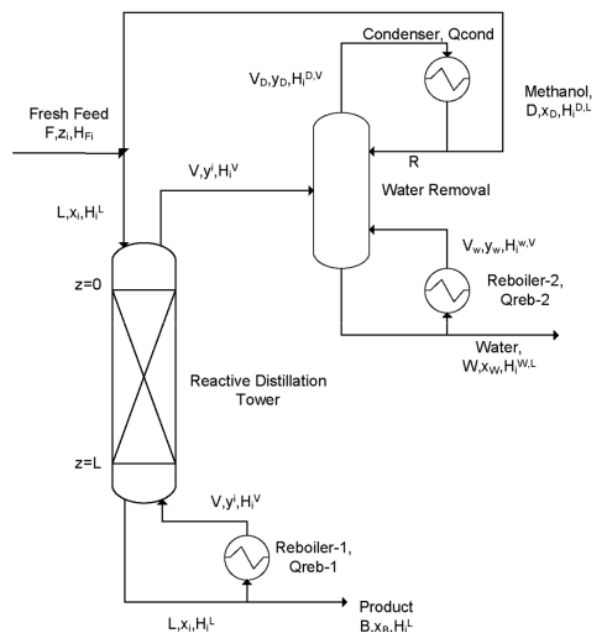
The simulation of the packed RD column was performed based on the novel NEQ model combined with the three-phase approach. The unit cell for the NEQ model for three-phase RD is shown in Figure 2. It is an innovative approach since the previous work using this sophisticated model has merely been proposed 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
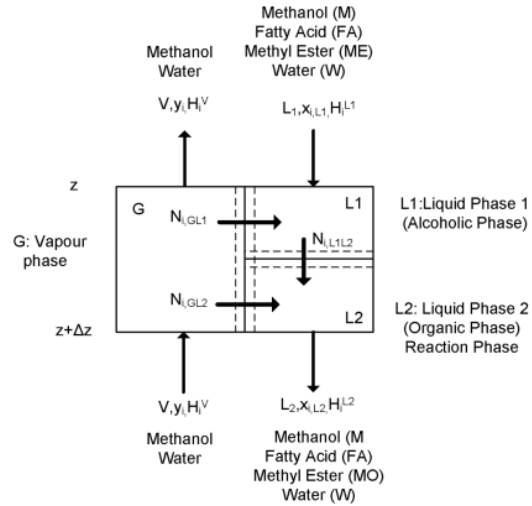
The assumptions taken in this modelling and simulation can be written as follows:

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:

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

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

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

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

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

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

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

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

$$\dot{R}_{i,L_1} = \dot{N}_i^{GL_1} - \dot{N}_i^{L_1 L_2}$$
(10)

$$\dot{R}_{i,L_2} = -\dot{N}_i^{GL_2} + \dot{N}_i^{L_1 L_2} + v_i \dot{r}.$$
(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 feature 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):

$$A = \frac{E\dot{X}L}{\Delta H}.$$
(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} ($A_{gas} - A_{liq}$) 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 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 ($A_{gas} - A_{liq}$) 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)
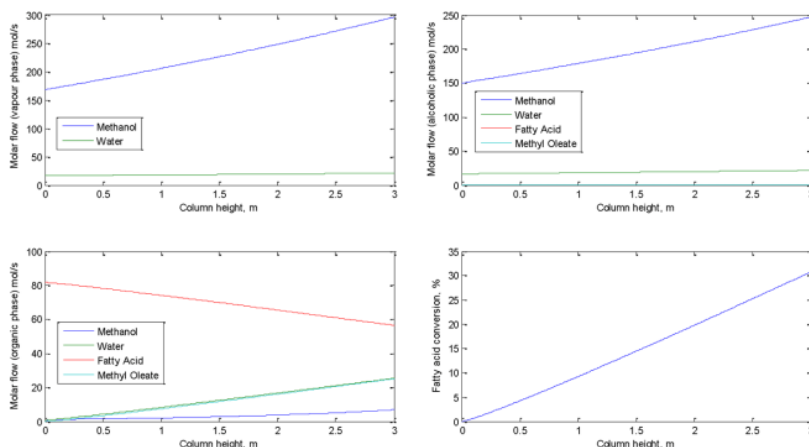

Figure 6 demonstrates the Ex-N-A diagram over the whole column for the base case condition. The EXL profile shows large EXL at the condenser and reboiler compared with the other parts of the column. Hence, this serves as an account of the large driving forces for heat and mass transfer at these regions. 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
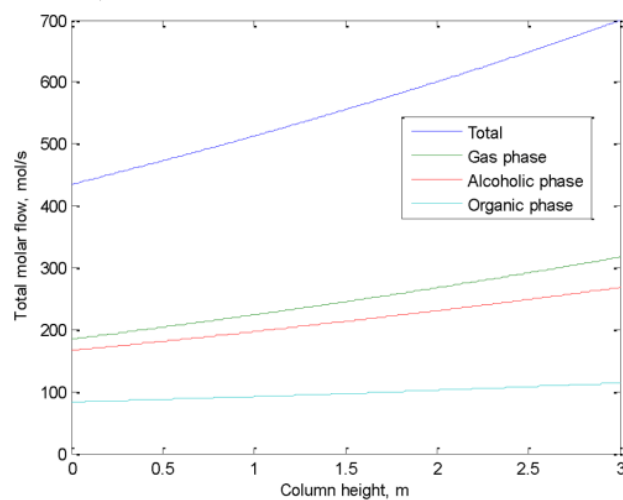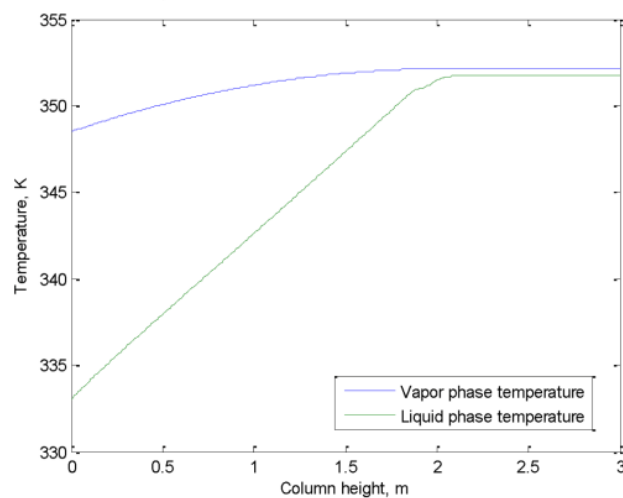for colours)

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 ($A_{gas} - A_{liq}$) 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
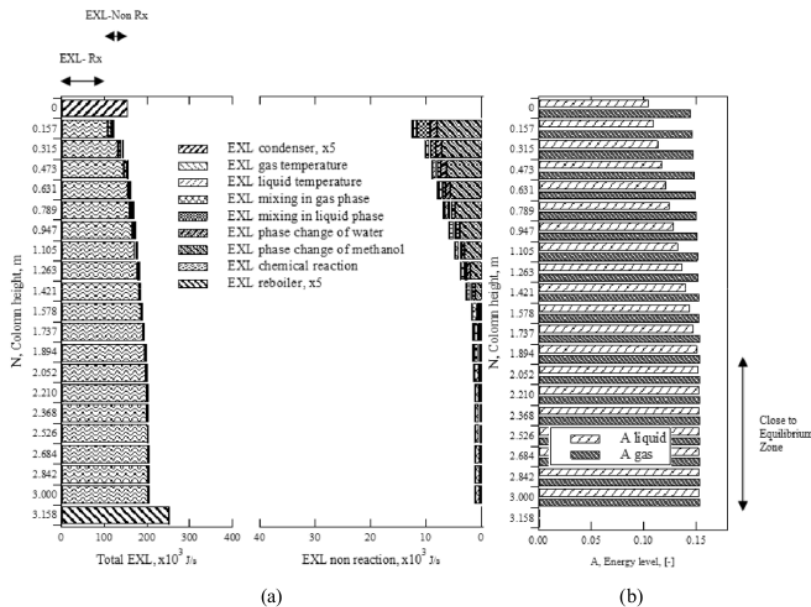
On the basis of the A-N diagram in Figure 6(b), it is disclosed that there is a large gas-liquid temperature difference at the top, which then gets smaller towards the bottom. Subsequently, at the height of 2 m from the top ($N = 2$), the liquid temperature almost reaches the similar temperature to that 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
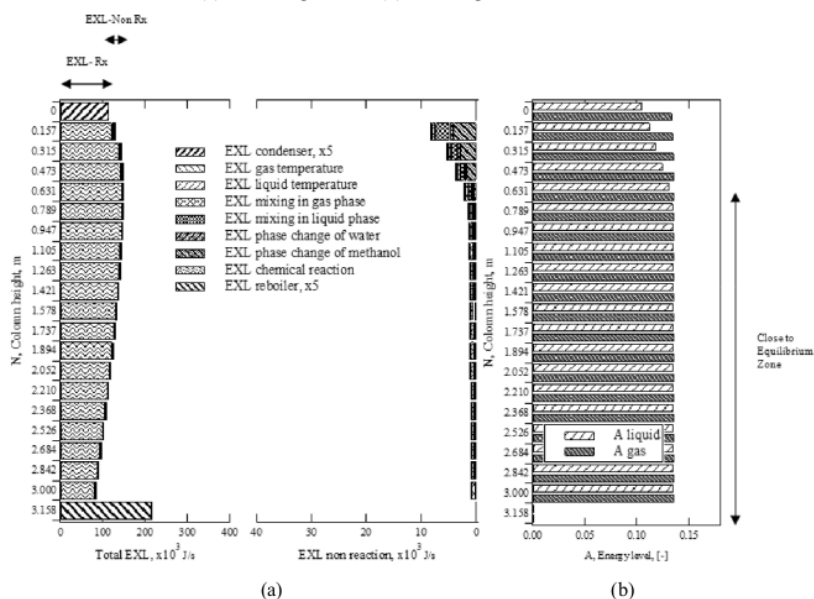
To evaluate the impact of varying the molar ratio on the value of the EXL owing to
chemical reaction, both the diagrams in Figures 7 and 8 are examined. It is exhibited on
the Ex-N diagram in Figures 7 and 8 that the EXL owing to the chemical reaction is
clearly affected by the changing of molar ratio 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
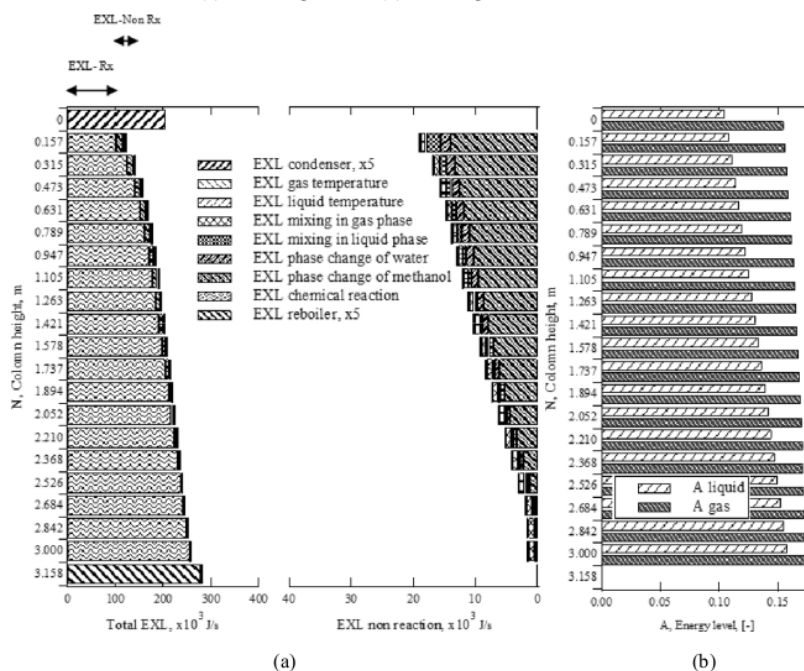

4.3   Effect of the height of the packed column (N)

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
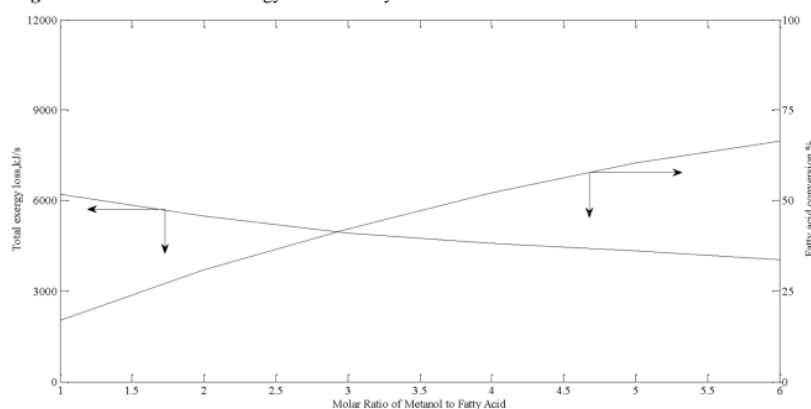
Effect of the column height (N) on the EXL owing to the chemical reaction is evaluated, as well. Ex-N diagram in Figure 10 presents the profile of EXL owing to the chemical reaction. It is observed that EXL owing to the chemical reaction increases from the top downward. When it reaches the increment 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
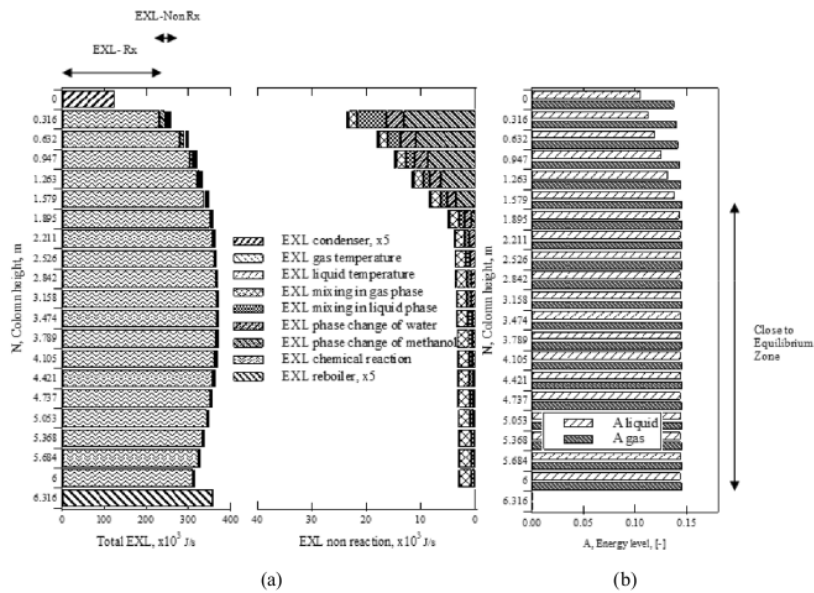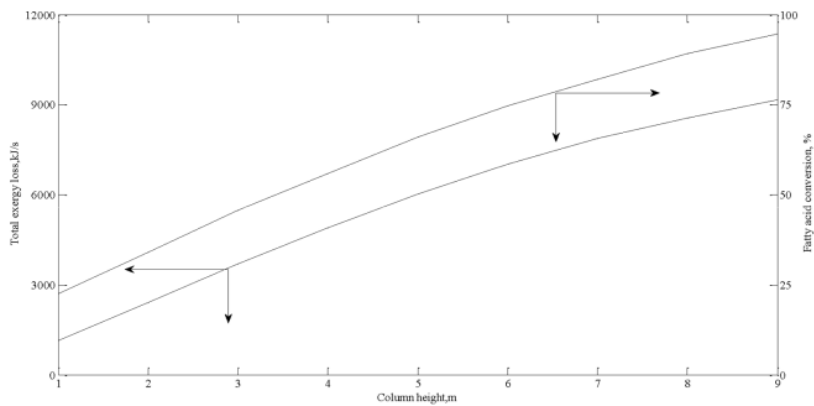

Figure 11 Profile of total exergy loss and fatty acid conversion at different column height

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 (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 ($mol \cdot m^3/kg_{cat}^2/s$)
k_2	Reverse reaction rate constant ($mol \cdot m^3/kg_{cat}^2/s$)
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

Graphical exergy analysis of reactive distillation column for biodiesel production