KRONOLOGIS (KORESPONDENSI) PUBLIKASI ARTIKEL
PADA JURNALINTERNASIONAL BEREPUTASI DAN BERDAMPAK FAKTOR

NO	TANGGAL	AKTIVITAS
1.	22 Februari 2018	Submit manuskrip pertama kali di Chinese Journal of Chemical Engineering
2.	5 April 2018	Reviews complete and decision pending for your manuscript CJCHE_2018_233
3.	10 April 2018	Invitation to revise manuscript CJCHE_2018_233
4.	15 Mei 2018	Submit revisi pertama oleh penulis
5.	18 Mei 2018	Manuskrip siap untuk di review kembali
6.	4 Juni 2018	Reviews complete and decision pending for your manuscript CJCHE_2018_233_R1
7.	8 Juni 2018	Permintaan revisi kedua
8.	8 Juli 2018	Under Revision - CJCHE_2018_233_R2
9.	23 Juli 2018	Submit revisi kedua oleh penulis
10.	1 Agustus 2018	Manuskrip diterima (Accepted)
11.	30 Agustus 2018	Permintaan sedikit revisi format artikel
12.	4 September 2018	Track your article [CJCHE_1237] accepted in Chinese Journal of Chemical Engineering
13.	4 September 2018	Production has begun on your article [CJCHE_1237] in Chinese Journal of Chemical Engineering
14.	4 September 2018	Rights and Access form completed for your article [CJCHE_1237]

15.	4 September 2018	Publishing Agreement completed for your article [CJCHE_1237]
16.	5 September 2018	Publication of your article [CJCHE_1237] in Chinese Journal of Chemical Engineering is on hold due to file problems
17.	7 September 2018	Your accepted manuscript [CJCHE_1237] is now available online
18.	9 September 2018	Permintaan proof reading dari Elsevier
19.	12 September 2018	Manuskrip diterima Elsevier
20.	17 November 2018	Your article [CJCHE_1237] - is now available online (Elsevier)

1. Submit manuskrip pertama kali di Chinese Journal of Chemical Engineering

Successfully received: submission Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models for Chinese Journal of Chemical Engineering Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com> Thu, Feb 22, 2018, 1:26 PM
to me

This message was sent automatically. Please do not reply.

Ref: CJCHE_2018_233
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

Thank you for submitting your manuscript for consideration for publication in Chinese Journal of Chemical Engineering. Your submission was received in good order.

To track the status of your manuscript, please log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE and locate your submission under the header 'My Submissions with Journal' on your 'My Author Tasks' view.

Thank you for submitting your work to this journal.

Kind regards,

Chinese Journal of Chemical Engineering

Manuscript Details

Manuscript number	CJCHE_2018_233_R1
Title	Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Short title	Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Article type	Research Paper

Abstract

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technology for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which contained in bio-oil. The correlation between experimental data and calculations shows that the UNIQUAC Functional-group Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non Random Two Liquid (NRTL) equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

Keywords	biomass, pyrolysis, bio-oil, UNIFAC, NRTL
Manuscript category	Chemical engineering thermodynamics
Corresponding Author	dewi selvia fardhyanti
Order of Authors	dewi selvia fardhyanti, bayu triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani
Suggested reviewers	Catherine Peters, dhori hartanto, Ming-Jer Lee

Submission Files Included in this PDF

File Name [File Type]

cover-letter-Dewi SF_Indonesia.docx [Cover Letter]

CJCHE Comments.docx [Response to Reviewers]

DS Fardhyanti - Indonesia.docx [Title Page (with Author Details)]

CJCHE_2018_233_R1.docx [Manuscript File]

copyright transfer form_CJCHE_2018_233.docx [Copyright Transfer Form]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
The data that has been used is confidential

February 22, 2018

Weiyang FEI
Editor-in-Chief of Chinese Journal of Chemical

Dear Weiyang FEI:

I was excited and interrested to publish my article research in Chinese Journal of Chemical, and I hope you can accept paper.

I am a lecturer at Chemical Engineering Department of Universitas Negeri Semarang since 1999.

Thank you for your attention and I have been waiting for your response of my paper.

Sincerely,

Dr. Dewi Selvia Fardhyanti, S.T., M.T.
Chemical Engineering Department
Universitas Negeri Semarang
Semarang
Indonesia
e-mail: dewiselvia@mail.unnes.ac.id

Liquid Phase Equilibrium of Phenol Extraction

from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models

Dewi Selvia Fardhyanti*, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati & Windy Oktaviani

Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang 50236, Indonesia.

*Corresponding author Phone: +6282227611946; E-mail: dewiselvia@mail.unnes.ac.id

ABSTRACT

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technology for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. Bio-oil from coffee shells contains 34% phenol, while 40.01% as for phenol content of coconut shell. The content of phenol compounds in corrosive bio-oils still quite high, causes the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which contained in bio-oil.

The correlation between experimental data and calculations shows that the UNIFAC equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the NRTL equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

Keywords: biomass, pyrolysis, bio-oil, UNIFAC, NRTL.

1. INTRODUCTION

The role of fossil fuels still be crucial, but their effects will gradually be over taken by new and renewable energy sources. Along with the depletion of world oil reserves and environmental issues, various researches on renewable energy are being actively conducted by various parties. Therefore, technology needs be able to overcome the problem. One technology that can be used is pyrolysis technology where the material used comes from organic waste (biomass). Pyrolysis technology can overcome organic waste problems and make the environment healthy also convert it into value-added end product.

Biomass is an organic material derived from plants, algae, animal waste, industrial waste, forestry, and agricultural waste [1]. Biomass can be used as pyrolysis raw material to produce liquid (bio-oil), gas and solid products. Various kinds of biomass waste can be used as raw materials for the manufacture of bio-oils, such as corncobs [2], sawdust and wheat bran [3], castor [4], oak [5], durian shell [6] and coconut shell [7].

Indonesia is the third largest coffee producer in the world after Brazil and Vietnam by contributing about 6% of the world's total coffee production, also world's fourth largest coffee exporter with a market share of around 11% across the world. Coffee is one of the plantations with high economic value besides chocolate and tea. Based on data from Indonesian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 691,160 tons with a plantation area of 47,800 Ha [8]. Waste from coffee processing that abundant and not utilized optimally is the coffee shell. Large waste of coffee shells derived from plantations was approximately 11.08% which potentially cause environment hazard. Coffee shells are a waste that has high lignocellulose content which have potential to be used as bio-oil. Bio-oil is a blackish liquid fuel derived from biomass such as wood, coffee shells and other biomass. Bio-oil contains lignin components (23.4%), cellulose (34.2%) and hemicellulose (24.5%) [9].

In Indonesia, in addition to the shell, one of the available biomass resources is coconut shell. Availability of coconut shell can be seen from the production of coconut fruit in Indonesia. Coconut is one of Indonesia's main commodities with an average production of 3,000,000 tons / year [10]. The utilization of coconut is very diverse, but for the utilization and way of handling waste is still limited. Coconut fruit can be used as food in daily life for the purpose of consumed directly. Coconut shells nowadays, lots of it become garbage that can not be utilized. One of the waste handling is to utilize coconut shell waste as a base material in the manufacture of bio-oil. Characterization studies on coconut shells have been done through proximate, ultimate, and thermo gravimetric (TG) analyzes. The results of this analysis indicate that coconut shell has a high potential to produce fuel fluid by pyrolysis conversion process [11]. Chemical content of coconut shell is cellulose (34%), hemicellulose (21%), lignin (27%) and ash (18%) [12].

Before converted into bio-oil, coconut shell waste and coffee shell need to be treated first. It takes a process before converting the waste of coffee shell into bio-oil which is pyrolysis. Pyrolysis is the process of decomposition of a substance or material that is done at a relatively high temperature. Pyrolysis results in the form of gas, liquid and solid. The solid result of this process is char (char). Gas and liquid products can be used as a source of bio-oil. Bio-oil can be used as an alternative fuel that is easier to store and distribute than biomass in solid form. Bio-oil made from coconut shell material using slow pyrolysis with pyrolysis temperature 250-300 ℃ produces liquid which very acidic and corrosive. The largest organic component in bio-oil is the lignin derivative of phenol, alcohol, organic acids and carbonyl compounds such as ketones, aldehydes and esters [13]. The nature of the acid is caused by the content of the dominant phenol compounds.

Phenol compounds in addition to causing the smell of smoke in bio-oil, also showed antioxidant activity and corrosive [14]. Therefore, the use of this bio-oil will directly cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive and unstable [6].

Phenol needs to be extracted from bio-oil to reduce its corrosive properties. In addition, phenol is a compound that has a high economic value because of its expensive and widely used. Phenols have many important uses such as disinfectants, resins, pesticides, explosives, and drugs. The method that can be used to extract phenol compounds from bio-oil is by liquid-liquid extraction method using methanol solvent. This has been done by Jazbinsek [15] on the isolation of phenol compounds from bio-oils from pyrolysis of forest waste and Mantilla [16] on the extraction of phenol compounds from bio-oils from pyrolysis of agricultural waste. Dahlia [17] conducted research on liquid-liquid extraction of phenol compound from bio-oil of pyrolysis resulted of palm oil empty bunch using methanol solvent. The yield of phenol resulting from this extraction is 40%. In this study, it is expected that the liquid-liquid extraction method can be used to separate the phenol compounds from coconut shell pyrolysis bio-oils. The purpose of phenol extraction is to improve the quality of bio-oil and reduce the corrosivity, so when used as fuel, it will cause no damage to the engine.

Biomass pyrolysis converted to bio-oil studies have been conducted. Bio-oil produced from the pyrolysis process can be used as fuel for engines, turbines and boilers. The bio-oil which processed further by liquid-liquid extraction process will reduce the corrosive nature of bio-oil and obtained chemicals which one of them is phenol. Research on extraction of phenol compounds from bio-oil is still very limited. In addition, thermodynamic modelling study on liquid-liquid equilibrium of phenol extraction process from bio-oil still needs to be investigated further.

To design extraction columns required various information such as liquid-liquid equilibrium data (Liquid-liquid Equilibrium). Thermodynamic models such as Equation of State or Activity Coefficient are used to correlate the experimental data to obtain optimal interaction parameters. Optimal parameters can be used to predict liquid-liquid equilibrium data to produce an equilibrium graph that is used to design extraction columns [18]. The study on liquid-liquid equilibrium include NRTL, e-NRTL, UNIQUAC, and UNIFAC.

Given the importance of thermodynamic modeling in this liquid-liquid extraction process and the price and benefits of phenol in the industrial world, this research becomes an important thing to do. From the equilibrium data, the optimum condition will be obtained where the highest yield of extract obtained in the extraction process of phenol compound from bio-oil from coconut pyrolysis. Liquid-liquid equilibrium data of the components of the system can be used in the design of the equipment in separation process.

2. EXPERIMENTAL SECTION

2.1 Chemicals

All reagents used here are A.R. grade and used as received without further purification. Methanol, acetic acid, and chloroform were purchased from e-Merck (Germany). The distilled water is available at the laboratory. Coffee shell and coconut shell were obtained from public market in Semarang.

2.2 Equilibrium Procedure

Instruments used in this study:
a) Shaker bath, product by Memmert WB14, SV1422, Scwabach, Germany.
b) Gas Chromatography (GC), product by GC 6820 Agilent Technologies, column: Rastek RXi-5MS002E.
c) Gas Chromatography-Mass Spectroscopy (GC-MS), product by GCMS-QP2010S Shimadzu, column: Rastek RXi-5MS.

The material systems and experimental conditions for the equilibrium extraction are summarized in Table 1.

Table 1. Material Systems and Conditions for Equilibrium Extraction

The bio-oil feed solution that containing phenol was extracted using two-stage extraction. The first stage uses aquadest as a polar solvent and chloroform as a non-polar solvent. Extraction was conduct with ice-bath method at 4-5ºC, 200 rpm and stirring time for 2 hours. The extracts obtained at this first stage are used as feeds on the second stage extraction. At the second stage extraction, each extract was extracted using a methanol solvent under operating conditions shown in Table 1. The extraction equipment set can be seen in Figure 1.

Figure 1. Extraction Equipment

2.3 Analysis and Characterization

After equilibrium attained (60 minutes), the mixtures were poured into a separating funnel, settled for an hour and separated into two phases. Then the two phases were weighed. The extract phase and the raffinate phase of each extraction processes are analyzed by GC to obtain the concentration of each component. The principal conditions of this analysis are shown in Table 2.

Table 2. Conditions of Analysis Using GC

3. RESULTS AND DISCUSSION

3.1 Bio-Oil Content

Gas Chromatography-Mass Spectrometry (GC-MS) analysis used to determine total content of phenol in coconut shell bio-oil. It shows that coconut shell bio-oil contained total phenol for 40.01%. The results of GC-MS bio-oil analysis of coconut shell pyrolysis results can be seen in Figures 2 and 3.

Figure 2. Analysis of GC-MS from Coconut shell Bio-oil

Table 3. Component of Bio-oil from Coconut shell

Figure 3. Analysis of GC-MS from Coffee Shell Bio-oil

Table 4. Component of Bio-oil from Coffee Shell

Figure 2 and 3, Table 3 and 4 represent that bio-oil contains more than 5 main components. The percentage (%) of the compositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the height of the peak in the chromatograms. Using a method of GC-MS, this work presents a composition of the bio-oil generated in the experiment. The total phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). It was caused by the pyrolysis processing at 300-350ºC (low temperature carbonization) that produce more substances contain ester and phenolic compounds. The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil.

3.2 Equilibrium data on phenol extraction of bio-oil from coconut pyrolysis results

In this research the variables studied were temperatur, speed of stirring and type of solvents (aqueous methanol and aqueous acetic acid). Generaly, all extracts are rich of phenol but the mole fraction significantly depends on extraction conditions: temperatur, speed of stirring and type of solvents. Methanol and acetic acid need to be mixed with water because their polarities are not strong enough to form immiscible mixture with bio-oil [19].

The mole fractions of any components in the raffinate phase and the extract phase, xi and yi, are constant after 60 minutes, so the system is assumed to be in equilibrium. The amount of water transfered from the solvent into the raffinate phase was negligible [19].

In this work, we are reported experimental data for the phenol extraction from bio-oil produced from tempurung kelapa and the phenol extraction from bio-oil produced from cangkang kopi.

Table 5 and 6 show the equilibrium of single-components extraction data for aqueous acetone and aqueous methanol solvent in the extract phase and raffinate phase.

Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Methanol from Bio-oil Produced from Coconut Shell.

Table 6. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Acetic Acid from Bio-oil Produced from Coffee Shell.

3.3 Liquid-liquid Equilibrium for The Phenol Extraction Process using UNIFAC dan NRTL Models.

The UNIFAC and NRTL models were used to correlate the experimental data obtained for the systems under study. UNIFAC equation and NRTL equation (Smith, 1996) were used to correlate experimental phase equilibrium data. The activity coefficient models applied in this study are as follows:

a) UNIFAC: [20]

UNIFAC is a UNIQUAC Functional-group Activity Coefficients model based on the UNIQUAC equation by using functional groups of a molecule contained in the mixture to calculate the activity coefficients. This model was developed by Fredenslund, Jones, and Prausnitz (1975). The UNIFAC modeling is a continuation of the UNIQUAC modeling development. This model has the advantage of performing phase equilibrium estimation even in the absence of experimental data. This thermodynamic model is used to predict the estimation of non-electrolyte activity in non-ideal mixtures. The UNIFAC model calculates the activity coefficients by using functional groups present in the molecules that form the liquid mixture. If the value of the component activity coefficient has a value close to one, this indicates that the component is in the ideal state in the system [21]. The correlation in the UNIFAC model is used in order to reduce the number of binary interactions measured to predict the state of the system. The correlation for the UNIFAC model is shown as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{1}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \tag{2}$$

$$\ln \gamma_i^R = q_i\left[1 - \sum_k\left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki}\ln\frac{\beta_{ik}}{s_k}\right)\right] \tag{3}$$

$$J_i = \frac{r_i}{\sum_j r_j x_j} \tag{4}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \tag{5}$$

$$r_i = \sum_k v_k^{(i)} R_k \tag{6}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{7}$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \tag{8}$$

$$\beta_{ik} = \sum_m e_{mi}\tau_{mk} \tag{9}$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \tag{10}$$

$$s_k = \sum_m \theta_m \tau_{mk} \tag{11}$$

$$\tau_{mk} = \exp\frac{-a_{mk}}{T} \tag{12}$$

Where:

$\ln \gamma_i^C$ = Combinatorial component

$\ln \gamma_i^R$ = residual component

J_i = component surface area component (i)

L_i = component volume fraction (i)

r_i = pure component surface area parameter (i)

x_i = pure component mol fraction (i)

q_i = pure component volume parameter (i)

$v_k^{(i)}$ = number of sub-group (k) on component (i)

R_k = parameter area for sub-group (k) ($R_k = A_{wk}/(2.5 \times 10^9)$, where A_{wk} is number of sub-group van der Walls surface arera)

Q_k = number of parameter volume subgroup (k) ($Q_k = V_{wk}/15.17$, where V_{wk} is number of Van der Waals volume subgroup)

a_{mk} = group of interaction parameter from group m and k.[18]

x_i = liquid mol fraction of component (i)

UNIFAC equation can be obtained to :

$$\ln \gamma_i = \ln\left[1 - J_i + \ln J_i + 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right)\right] + \ln\left\{q_i\left[1 - \sum_k\left(\frac{\sum_i x_i q_i e_{ki} \sum_m e_{mi}\tau_{mk}}{\sum_j x_j q_j / \sum_m \theta_m \tau_{mk}} - \frac{v_k^{(i)} Q_k}{q_i}\ln\frac{\sum_m e_{mi}\tau_{mk}}{\sum_m \theta_m \tau_{mk}}\right)\right]\right\} \tag{13}$$

b) NRTL: [20]

Non Random Two Liquid (NRTL) is derived from the Scott two liquid model and it is assumed that randomness is the same as the model used on the Wilson model. The NRTL model has a non-random parameter (α_{12}) making it possible to use in a wide variety of mixtures. The NRTL model uses only binary parameters to calculate the phase equilibrium properties.

The NRTL (Non Random Two-Liquid) equation was first developed by Renon and Prausnitz (1968). The NRTL model is derived from the Scott two liquid model and it is assumed that the non-random parameter is the same as the model used in the Wilson Model. The NRTL equation is developed based on a two-fluid theory

with the addition of a non-random parameter (α), which makes the equation applicable to different types of liquid-liquid mixture and equilibrium by choosing the appropriate α price. The parameter estimation for this equation is done by setting the α value at a certain value and subsequently optimizing the objective function to obtain two optimal parameter interactions. The recommended α value is 0.2 - 0.47. The value of α is often adjusted to certain conditions, but usually the value of α = 0.3. Unlike the Wilson equation which contains two adjustable parameters, the NRTL equation contains three parameters, so the NRTL equation can be an alternative model if other models are inadequate. This equation can also estimate the equilibrium of multicomponent systems without additional parameters.

The NRTL equation can represent liquid-liquid equilibrium for both binary and multicomponent systems only with binary parameters. The equation is simpler than the UNIQUAC equation, but it has disadvantage because it contains three parameters for each pair of components. The third parameter (α) is estimated based on the state of the component and sometimes for certain substances the extreme number is obtained. The NRTL equation is expressed:

$$\frac{G^E}{nRT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} \tag{14}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{15}$$

$$g_{ii} = g_{jj} = g_{kk} = 0 \tag{16}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \tag{17}$$

$$\alpha_{ij} = \alpha_{ji} \tag{18}$$

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ij} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \tau_{ij} - \sum_{k=1}^{n} \frac{x_j \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k} \tag{19}$$

$$X_i = exp \frac{\sum_{i=1}^{n} \tau_{ji} G_{ji} x_i^E}{\sum_{k=1}^{n} G_{ki} x_k^E} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k^E}(\tau_{ij} - \sum_{k=1}^{n} \frac{x_j \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k^E}) \tag{20}$$

$$Y_i = exp \frac{\sum_{i=1}^{n} \tau_{ji} G_{ji} x_i^R}{\sum_{k=1}^{n} G_{ki} x_k^R} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k^R}(\tau_{ij} - \sum_{k=1}^{n} \frac{x_j \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k^R}) \tag{21}$$

Where:

G^E = molar Gibbs energy
R = gas constant
T = temperature
x = liquid phase mol fraction
i,j,k = component of 1, 2, 3, …, n
α = non-random parameter for NRTL

9

g, G = component parameter
γ = activity coefficient
τ = empirical constant for NRTL

Table 7. The Activity Coefficients were Calculated by UNIFAC Model.

Table 8. The Activity Coefficients were Calculated by NRTL Model.

Table 7 and 8 shows the value of activity coefficient on phenol extraction using methanol solvent obtained from calculation with UNIFAC and NRTL modeling, from coefficient value of activity on each component shows that methanol and acetic acid component in extract phase is in ideal condition because the value of activity coefficient obtained close to one. The activity coefficient value of phenol and water activity in the extract phase is not close to one, it means that the phenol and water components are in less than ideal conditions in the system. The ideal conditions of the components in the system show that the component is dominant, so the properties of the mixture are closer to the dominant component properties either in the extract or rafinate phase. In raffinate it is known that the solvent has a coefficient of activity close to the one, indicating that the solvent is in ideal conditions in the system, while the phenol and bio-oil components are in less than ideal conditions. So non-ideality studies are very important for those systems [21].

Figure 4. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 298 K.

Where:

Xa: mole fraction of component in extract phase
Xb: mole fraction of solvent in extract phase
Xc: mole fraction of water in extract phase
Ya: mole fraction of component in raffinate phase
Yb: mole fraction of solvent in raffinate phase
Yd: mole fraction of bio-oil in raffinate phase

Figure 5. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 313 K.

Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 323 K.

Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 298 K.

Figure 8. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 313 K.

10

Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 323 K.

Figure 10. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 298 K.

Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 313 K.

Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 323 K.

Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 298 K.

Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 313 K.

Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Acetic Acid by NRTL Model at 323 K.

The result of correlation of liquid-liquid equilibrium data by using UNIFAC and NRTL modeling gives good agreement between experimental data and calculation. This is shown by the value of SSE (Sum of the Square of the Error) approaching the value of 0. SSE values in UNIFAC and NRTL modeling can be seen in Table 8.

Table 8. Sum of the Square of the Error (SSE)

Based on Table 8, it can be seen that extraction with methanol solvent with temperature of 323 K has the smallest SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC model) and 0.015 (for NRTL model). The smaller the SSE values obtained show that the correlation between the experimental data and the calculation data indicates a better correlation.

Good correlation results show that equilibrium modeling of UNIFAC and NRTL can be used to predict liquid-liquid equilibrium in phenol extraction process from coconut shell pyrolysis bio-oil and coffee shell using methanol solvent and acetic acid at 323 K.

4. CONCLUSION

The UNIFAC modeling provides a good correlation to liquid-liquid equilibrium data for ternary systems on phenol extraction of coconut shell pyrolysis bio-oils using methanol solvent under conditions of temperature of 323 K given by SSE of 0.053.

11

NRTL modeling gives a good correlation to liquid-liquid equilibrium data for ternary system on phenol extraction of bio-oil from pyrolysis of coffee shell using methanol solvent at temperature condition of 323 K given by SSE of 0,015.

The activity coefficients of methanol, acetic acid, and phenol in the extract phase and raffinate phase are far from unity. It means that they are far from ideal condition. The activity coefficients of water and kerosene in their phases are close to one. It means that they are nearly ideal in their phases.

REFERENCES

[1] N. Sriram, *Renewable biomass energy*. Chicago: Illions Institute of Technology (2005).

[2] I. Demiral, A. Eryazici, S. Sensoz, S., Bio-oil production from pyrolysis of corncob (zea mays l.), *Biomass Bioenergy* 36 (2012) 43-49.

[3] M. Bertero, G. de la Puente, U. Sedran, Fuels from bio-oils: bio-oil production from different residual sources, characterization and thermal conditioning, *Fuel* 95 (2012) 263-271.

[4] V.C. Pandey, K. Singh, J.S. Singh, A. Kumar, B. Singh, R.P.Singh, Jatropha curcas: A potential bio-fuel plant for sustainable environmental development, *Renew. Sustain. Energy Rev.* 16 (2012) 2870-2883.

[5] C.J. Ellens, R.C. Brown, Optimization of a free-fall reactor for production of fast pyrolysis bio-oil, *Biores. Technol.* 103 (2012) 374-380.

[6] S. Ismadji, S., Kulit durian sebagai bahan baku pembuatan *bio-oil*: sumber energi terbarukan, *Prosiding Seminar Nasional Teknik Kimia Soebardjo Brotohardjono 1*, Prodi Teknik Kimia UPN Veteran Jawa Timur (2012) 1-4.

[7] W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal Analytical Applied Pyrolysis*. 76 (2006) 230–237.

[8] Badan Pusat Statistik, 2015.

[9] C.E. Wyman, *Potential Synergies and Challenges in Refining Cellulosic Biomass to Fuels*. Biotechnol Progress (2002).

[10] Direktorat Jendeal Perkebunan. *Produksi Buah Kelapa di Indonesia* (2016).

[11] Joardder. *Pyrolysis of coconut shell for bio-oil*. Bangladesh: Department Of Mechanical Engineering Rajshahi University Of Engineering & Technology (2011).

12

8

[12] D. Tarnado, E. Budi, R. Wirawan, H. Dwi, A. Tyaswuri, E. Sulistiani, E. Asma. Sifat termal karbon aktif berbahan arang tempurung kelapa. Seminar Nasional Fisika Universitas Negeri Jakarta (2013).

[13] S. Wang, *High Efficiency Separation of Bio-Oil*. InTech (2013).

[14] Kasim, Fitriani, A.N. Fitrah, E. Hambali. Aplikasi asap cair pada lateks. *Jurnal PASTI* 9(1) (2012) 28–34.

[15] A. Jazbinšek, G. Viktor, L.F. Žilnik. *Isolation of phenol and phenolic compounds from fast pyrolysis bio-oil of forestry residue*. Slovenia: National Institute of Chemistry (2008).

[16] S.V. Mantilla., A.M. Manrique, A. Gauthier-Maradei, Methodology for extraction of phenolic compounds of bio-oil from agricultural biomass wastes, *Waste Biomass Valor* 6 (2015) 371–383.

[17] Dahlia. *Pra rancangan pabrik pembuatan fenol dari tandan kosong kelapa sawit dengan proses pirolisis dengan kapasitas produksi 10.000 ton/tahun*. Medan: Departemen Teknik Kimia Universitas Sumatera Utara (2012).

[18] D. Hartanto, B. Triwibowo, Review model dan parameter interaksi pada korelasi kesetimbangan uap-cair dan cair-cair sistem etanol (1) + air (2) + ionic liquids (3) dalam pemurnian bioetanol. *Jurnal Rekayasa Proses* 8(1) (2014).

[19] D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Complex extraction of phenol, o-cresol, and p-cresol from model coal tar using methanol and acetone solutions, *British J Appl. Sci.& Technol* 8(5) (2015) 427-436.

[20] J.M. Smith, H.C. Van Ness, M.M. Abbott, *Introduction to chemical engineering thermodynamics*, 5th edition, Mc Graw Hill International Book Company, New York (1996).

[21] D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Predicting the liquid phase equilibrium of multi-components extraction by thermodynamic models, *Int. J. Thermodyn*. 19(2) (2015) 110-119.

Table 1. Material Systems and Conditions for Equilibrium Extraction.

	Quantity
feed	bio-oil
feed volume	2.5 mL
solvent	aqueous methanol
	aqueous acetic acid
mole fraction of water in solvent	0.2
solvent-feed mass ratio	1
shaking time	60 minutes
amplitudo of shaking	150, 200, 250 rpm
temperature	298, 313, 323K.

Table 2. Conditions of Analysis Using GC

Column: Rastek RXi-5MS		
Column:		
Inner diameter	[m]	3.2×10^{-4}
Length	[m]	30
Carrier gas		He
Split ratio	[-]	153
Flow rate	[cm/sec]	26.6
Sample volume	m³	1.10^{-6}
Injection temperature	[K]	553
Column temperature	[K]	313 – 573
Pressure column	kPa	10.0
Column flow	mL/min	0.54
Detector (FID) temperature	[K]	573

Table 3. The Main Components of Bio-oil Produced by Pyrolysis of Coconut Shells

Peak	Component	Procentage
1	Ethyl ester	37.60
2	Formic acid	4.02
3	1-Hydroxy-2-butanone	3.89
4	Furfural	5.45
5	Phenol	40.01
7	2-Methoxy-phenol	7.02

Table 4. The Main Components of Bio-oil Produced by Pyrolysis of Coffee Shells

Peak	Component	Procentage
1	Urea	5%
2	Acetic acid	26%
5	Furfural	6%
6	Phenol	34%
7	Phenol, 2-methoxy-	7%
8	Phenol, 2,6-dimethoxy	4%

Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Methanol from Bio-oil Produced from Coconut Shell

Temperature	Speed	X_A	X_B	X_C	Y_A	Y_B	Y_B
	150	0.007	0.973	0.020	0.161	0.316	0.524
298 K	200	0.007	0.973	0.019	0.116	0.313	0.572
	250	0.009	0.967	0.024	0.094	0.488	0.418
	150	0.009	0.963	0.027	0.085	0.549	0.365
313 K	200	0.008	0.970	0.022	0.086	0.414	0.501
	250	0.010	0.963	0.027	0.062	0.555	0.383
	150	0.010	0.962	0.028	0.069	0.567	0.363
323 K	200	0.009	0.965	0.026	0.065	0.525	0.410
	250	0.012	0.959	0.029	0.029	0.615	0.356

Table 6. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Acetic Acid from

Bio-oil Produced from Coffee Shell.

Temperature	Speed	X_A	X_B	X_C	Y_A	Y_B	Y_B
	150	0,054	0,247	0,365	0,281	0,047	0,672
298 K	200	0,042	0,370	0,204	0,107	0,537	0,357
	250	0,024	0,551	0,093	0,019	0,878	0,104
	150	0,012	0,707	0,068	0,025	0,907	0,069
313 K	200	0,011	0,744	0,047	0,008	0,958	0,034
	250	0,010	0,764	0,036	0,003	0,979	0,019
	150	0,006	0,841	0,026	0,004	0,980	0,016
323 K	200	0,004	0,883	0,016	0,002	0,986	0,012
	250	0,004	0,903	0,012	0,281	0,047	0,672

9

Table 7. The Activity Coefficients were Calculated by UNIFAC Model.

Solution	Temperature	Speed	γ_A^I	γ_B^I	γ_C^I	γ_A^{III}	γ_B^{III}	γ_D^{III}
Methanol	298	150	0.176	0.769	0.037	2.360	2.063	1.025
		200	0.032	0.794	0.004	2.398	2.098	1.020
		250	0.019	0.799	0.003	2.435	2.143	1.015
	313	150	0.149	0.789	0.006	2.143	2.655	1.016
		200	0.119	0.791	0.003	2.215	2.700	1.012
		250	0.112	0.792	0.003	2.191	2.685	1.013
	323	150	0.049	0.788	0.007	2.181	2.504	1.007
		200	0.028	0.788	0.001	2.222	2.515	1.006
		250	0.034	0.788	0.001	2.191	2.519	1.006
Acetic Acid	298	150	0.199	1.191	0.020	3.108	1.980	1.011
		200	0.132	1.002	0.001	3.150	1.996	1.009
		250	0.073	1.015	0.001	3.198	2.0161	1.006
	313	150	0.196	1.000	0.003	2.798	1.805	1.005
		200	0.152	0.999	0.013	2.857	1.824	1.002
		250	0.141	0.999	0.014	2.836	1.815	1.003
	323	150	0.055	0.999	0.037	2.705	1.701	1.006
		200	0.035	0.999	0.004	2.728	1.701	1.004
		250	0.042	0.999	0.006	2.719	1.711	0.999

Table 8. The Activity Coefficients were Calculated by NRTL Model

Solution	Temperature	Speed	γ_A^I	γ_B^I	γ_C^I	γ_A^{III}	γ_B^{III}	γ_D^{III}
Methanol	298	150	0.077	0.926	0.381	0.265	2.037	0.655
		200	0.064	0.482	0.337	0.001	0.039	0.065
		250	0.063	0.283	0.387	1.3×10^{-6}	0.001	7.6×10^{-6}
	313	150	4.47×10^{-8}	0.942	0.010	8.4×10^{-7}	1.050	0.044
		200	2.71×10^{-6}	0.986	0.056	1.5×10^{-11}	1.014	1.1×10^{-6}
		250	1.80×10^{-5}	0.944	0.039	4.9×10^{-19}	0.880	2.4×10^{-12}
	323	150	7.92×10^{-8}	0.980	0.010	3.6×10^{-3}	1.028	0.025
		200	3.48×10^{-6}	0.977	0.022	4.1×10^{-14}	1.006	4.1×10^{-12}
		250	9.44×10^{-6}	0.972	0.024	3.5×10^{-22}	0.937	1.1×10^{-26}
Acetic Acid	298	150	0.045	0.644	0.218	0.432	1.087	0.678
		200	0.039	0.331	0.210	0.015	0.361	0.552
		250	0.036	0.193	0.232	9.5×10^{-5}	0.017	0.027
	313	150	0.000	0.734	0.037	0.036	0.995	0.551
		200	0.003	0.732	0.050	0.030	0.999	0.444
		250	0.013	0.749	0.069	0.028	1.000	0.374
	323	150	0.000	0.734	0.037	0.035	1.139	0.011
		200	0.003	0.732	0.050	0.001	1.010	0.039
		250	0.013	0.749	0.069	8.9×10^{-6}	0.694	9.6×10^{-7}

Table 8. Sum of the Square of the Error (SSE)

Model	Temperature	SSE	
		Methanol	Acetic Acid
UNIFAC	298	0.087	0.132
	313	0.065	0.083
	323	0.053	0.084
NRTL	298	0.024	0.065
	313	0.026	0.544
	323	0.015	0.017

Figure 1. Extraction Equipment.

Figure 2. Analysis Result by GC-MS for the Bio-oil Produced by Coconut Shells Pyrolysis

Figure 3. Analysis Result by GC-MS for the Bio-oil Produced by Coffee Shells Pyrolys

Figure 4. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 298 K.
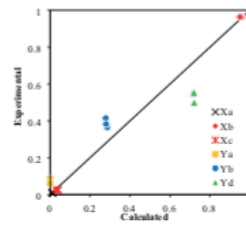

Figure 5. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 313 K.
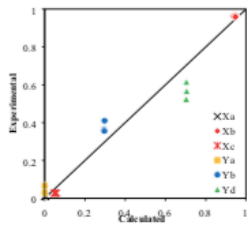
Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 323 K.
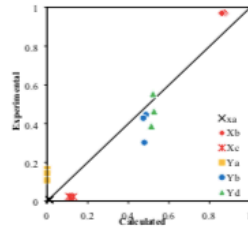

Figure 8. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 313 K.
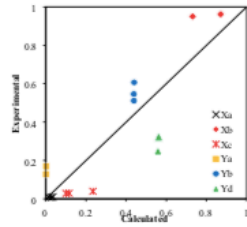

Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 298 K.
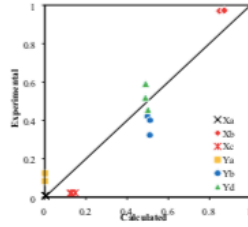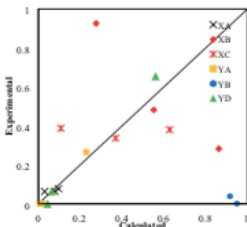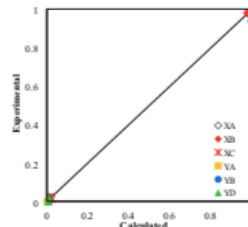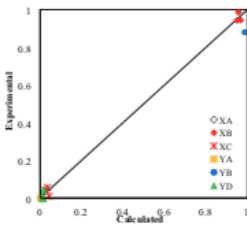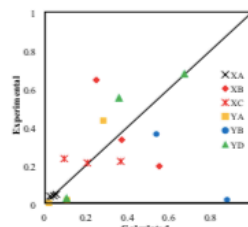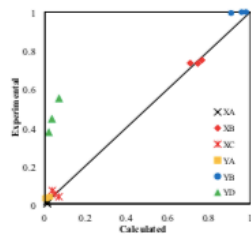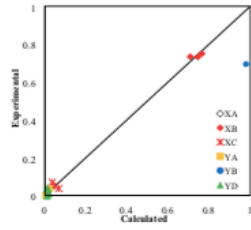

Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 323 K.

21

22

Figure 10. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 298 K

Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 323 K

Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 313 K

Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 298 K

23

24

11

Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 313 K

Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Acetic Acid by NRTL Model at 323 K

25

2. Reviews complete and decision pending for your manuscript CJCHE_2018_233

Reviews complete and decision pending for your manuscript CJCHE_2018_233 Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com>   Thu, Apr 5, 2018, 8:46 PM
to me

Reference: CJCHE_2018_233
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

I am pleased to inform you that I have received all the required reviews, which I will now evaluate before making a decision on your manuscript referenced above.

In the event that I need to seek the opinion of an additional reviewer, you may see the status of your manuscript revert briefly from 'Ready for Decision' to 'Under Review'.

To track the status of your manuscript, please log into EVISE® http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE and go to 'My Submissions'.

I will inform you once I have made a decision.

Thank you again for submitting your manuscript to Chinese Journal of Chemical Engineering and for giving me the opportunity to consider your work.

Kind regards,

Chinese Journal of Chemical Engineering

3. Invitation to revise manuscript CJCHE_2018_233

Invitation to revise manuscript CJCHE_2018_233 Inbox x

Jianzhong Wu (Chinese Journal of Chemical Engineering) <EviseSupport@... Apr 10, 2018, 1:50 AM
to me

Ref: CJCHE_2018_233
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

Thank you for submitting your manuscript to Chinese Journal of Chemical Engineering. We have completed the review of your manuscript. A summary is appended below. While revising the paper please consider the reviewers' comments carefully. We look forward to receiving your detailed response and your revised manuscript.

To submit your revised manuscript:

- Log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE
- Locate your manuscript under the header 'My Submissions that need Revisions' on your 'My Author Tasks' view
- Click on 'Agree to Revise'
- Make the required edits
- Click on 'Complete Submission' to approve

What happens next?
After approving your submission you will receive a notification that the submission is complete. To track the status of your paper throughout the editorial process, log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE

I look forward to receiving your revised manuscript as soon as possible.

Kind regards,

Jianzhong Wu
Associate editor
Chinese Journal of Chemical Engineering

Comments from the editors and reviewers:
-Reviewer 1

-

In this study, the author used the liquid-liquid extraction method to separate the phenol compounds from coconut shell pyrolysis bio-oils. The results show that the correlation between experimental data and calculations shows that the UNIFAC equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the NRTL equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells. Generally, this study presents some important data on the development of liquid-liquid equilibrium in the extraction process towards pyrolysis bio-oil. This paper fits into the scope of liquid-liquid equilibrium in the extraction process. However, before that, the following minor points should be carefully responded and revised.

Specific comments:

1. Abstract

"34% phenol"

"The content of phenol compounds in corrosive bio-oils still quite high, **the use of this bio-oil** directly will cause various difficulties in the combustion system due to high viscosity"

Please give the full name for "UNIFAC equilibrium" and "NRTL equilibrium"

2.   Introduction

Paragraph 1 Please add the related contents and references in this paragraph

3.   2.2 Equilibrium Procedure

"For the first stage, the aqua was used as a polar solvent, and chloroform as a non-polar solvent." may be better

What is "aquadest"? Error

"was conduct"should be "was conducted"

4.   Please revise the x-coordinate and y-coordinate （Figure 7-11）, and obtain the correct format

5.   You mentioned"Gas Chromatography-Mass Spectrometry (GC-MS) analysis used to determine total content of phenol in coconut shell bio-oil."Please add the detection details.

-Reviewer 2

-

1. According to the meaning of context, "In Indonesia, in addition to the shell, one of the available biomass resources is coconut shell." should be replaced by "In Indonesia, in addition to the coffee shell, one of the available biomass resources is coconut shell." in the introduction.
2. In the section 2.2, why was the extraction conducted with ice-bath method at 4-5 °C? Is this operating temperature suitable for industrial applications?
3. In the section 3.1, "The results of GC-MS bio-oil analysis of coconut shell pyrolysis results can be seen in Figures 2 and 3." should be rewritten to understand better.
4. There were some mistakes in writing. Such as :
In Table 3 and Table 4, "Procentage" should be replaced by "Percentage".
In the section 3.2, "temperatur" should be rewritten as "temperature".
In the section 3.2, "temperatur" should be rewritten as "temperature".
5. In the section 3.1, there were two sentences, "It shows that coconut shell bio-oil contained total phenol for 40.01%." and "The total phenolic compounds contained in bio-oil is 47.03% (coconut shell)." . The percentages of total phenolic compounds pointed out in these sentences should be consistent.
6. In general, the speed of stirring has no effect on liquid-liquid equilibrium. The speed of stirring has a significant effect on the composition of liquid-liquid equilibrium from the Table 5 and Table 6. Why?
7. The data were too few to describe the liquid-liquid equilibrium well. Enough datas are required.
8. In the section 3.3, "This is shown by the value of SSE (Sum of the Square of the Error) approaching the value of 0." This expression is inappropriate because the errors between calculated values and experimental data are not small from Fig.3 to Fig.15.
9. In the conclusion, the author pointed out that the UNIFAC modeling provides a good correlation to liquid-liquid equilibrium data under conditions of temperature of 323 K. Then, can the UNIFAC model be used to describe the liquid-liquid equilibrium under other temperatures? There is the same problem for the NRTL equation.

🏠 Home   Reports

CJCHE_2018_233 | Research Paper

Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models

dewi selvia fardhyanti | E1 2nd floor building of faculty of engineering, kampus Sekaran, Indonesia.

Status: **Under Revision (1 days)** | Submitted: **22/Feb/2018** - Revision due date: **08/Jun/2018**

⬇ Zip File

Overview   Decision

📁 Files   ✉ Messages

View decision letter

Reviewer 1

In this study, the author used the liquid-liquid extraction method to separate the phenol compounds from coconut shell pyrolysis bio-oils. The results show that the correlation between experimental data and calculations shows that the UNIFAC equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the NRTL equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells. Generally, this study presents some important data on the development of liquid-liquid equilibrium in the extraction process towards pyrolysis bio-oil. This paper fits into the scope of liquid-liquid equilibrium in the extraction process. However, before that, the following minor points should be carefully responded and revised.

Specific comments:

1.   Abstract

"34% phenol"

"The content of phenol compounds in corrosive bio-oils still quite high, **the use of this bio-oil** directly will cause various difficulties in the combustion system due to high viscosity"

Please give the full name for "UNIFAC equilibrium" and "NRTL equilibrium"

2.   Introduction

Paragraph 1 Please add the related contents and references in this paragraph

3.   2.2 Equilibrium Procedure

"For the first stage, the aqua was used as a polar solvent, and chloroform as a non-polar solvent." may be better

What is "aquadest"? Error

"was conduct"should be "was conducted"

4.   Please revise the x-coordinate and y-coordinate （Figure 7-11）, and obtain the correct format

5.   You mentioned"Gas Chromatography-Mass Spectrometry (GC-MS) analysis used to determine total content of phenol in coconut shell bio-oil."Please add the detection details.

Reviewer 2

1. According to the meaning of context, "In Indonesia, in addition to the shell, one of the available biomass resources is coconut shell." should be replaced by "In Indonesia, in addition to the coffee shell, one of the available biomass resources is coconut shell." in the introduction.

2. In the section 2.2, why was the extraction conducted with ice-bath method at 4-5 ℃? Is this operating temperature suitable for industrial applications?

3. In the section 3.1, "The results of GC-MS bio-oil analysis of coconut shell pyrolysis results can be seen in Figures 2 and 3." should be rewritten to understand better.

4. There were some mistakes in writing. Such as :

In Table 3 and Table 4, "Procentage" should be replaced by "Percentage".

In the section 3.2, "temperatur" should be rewritten as "temperature".

5. In the section 3.1, there were two sentences, "It shows that coconut shell bio-oil contained total phenol for 40.01%." and "The total phenolic compounds contained in bio-oil is 47.03% (coconut shell)." . The percentages of total phenolic compounds pointed out in these sentences should be consistent.

6. In general, the speed of stirring has no effect on liquid-liquid equilibrium. The speed of stirring has a significant effect on the composition of liquid-liquid equilibrium from the Table 5 and Table 6. Why?

7. The data were too few to describe the liquid-liquid equilibrium well. Enough datas are required.

8. In the section 3.3, "This is shown by the value of SSE (Sum of the Square of the Error) approaching the value of 0." This expression is inappropriate because the errors between calculated values and experimental data are not small from Fig.3 to Fig.15.

9. In the conclusion, the author pointed out that the UNIFAC modeling provides a good correlation to liquid-liquid equilibrium data under conditions of temperature of 323 K. Then, can the UNIFAC model be used to describe the liquid-liquid equilibrium under other temperatures? There is the same problem for the NRTL equation.

4. Submit revisi oleh penulis

Received revision CJCHE_2018_233_R1 Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com>   Tue, May 15, 2018, 1:32 PM
to me

This message was sent automatically. Please do not reply.

Ref: CJCHE_2018_233_R1
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

Thank you for submitting your revised manuscript for consideration for publication in Chinese Journal of Chemical Engineering. Your revision was received in good order.

To track the status of your manuscript, please log into EVISE® http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE and locate the submission under the header 'My Submissions with Journal' on your 'My Author Tasks' view.

We appreciate your submitting your revision to this journal.

Kind regards,

Chinese Journal of Chemical Engineering

Have questions or need assistance?
For further assistance, please visit our Customer Support site. Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about EVISE® via interactive tutorials. You can also talk 24/5 to our customer support team by phone and 24/7 by live chat and email.

5. Naskah Revisi

Manuscript Details

Manuscript number	CJCHE_2018_233_R1
Title	Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Short title	Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Article type	Research Paper

Abstract

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technology for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which contained in bio-oil. The correlation between experimental data and calculations shows that the UNIQUAC Functional-group Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non Random Two Liquid (NRTL) equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

Keywords	biomass, pyrolysis, bio-oil, UNIFAC, NRTL
Manuscript category	Chemical engineering thermodynamics
Corresponding Author	dewi selvia fardhyanti
Order of Authors	dewi selvia fardhyanti, bayu triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani
Suggested reviewers	Catherine Peters, dhoni hartanto, Ming-Jer Lee

Submission Files Included in this PDF

File Name [File Type]

cover-letter-Dewi SF_Indonesia.docx [Cover Letter]

CJCHE Comments.docx [Response to Reviewers]

DS Fardhyanti - Indonesia.docx [Title Page (with Author Details)]

CJCHE_2018_233_R1.docx [Manuscript File]

copyright transfer form_CJCHE_2018_233.docx [Copyright Transfer Form]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
The data that has been used is confidential

PART 1:

Journal Name:	**Chinese Journal of Chemical Engineering**
Manuscript Number:	**CJCHE_2018_233**
Title of the Manuscript:	**Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models**

PART 2:

Reviewer A (Yellow Highlight)	Authors' response to reviewer's comments
1. Abstract "34% phenol" "The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity" Please give the full name for "UNIFAC equilibrium" and "NRTL equilibrium"	1. The manuscript has been revised. Line 19. Line 19–21. Line 24-25 and 26-27.
2. Introduction Paragraph 1 please add the related contents and references in this paragraph	2. The manuscript has been revised.
3. 2.2. Equilibrium Procedure	3. The manuscript has been revised.

"For the first stage, the aqua was used as a polar solvent, and chloroform as a non-polar solvent." may be better What is "aqualent"? Error "was conduct" should be "was conducted"	Line 128-129. Line 129.
4. Please revise the x-coordinate and y-coordinate （ Figure 7-11）, and obtain the correct format.	4. The manuscript has been revised. Line 440-522.
5. You mentioned "Gas Chromatography-Mass Spectrometry (GC-MS) analysis used to determine total content of phenol in coconut shell bio-oil". Please add the detection details.	5. The manuscript has been revised. Line 145-155.

PART 3:

Reviewer B (Green Highlight)	Authors' response to reviewer's comments
1. According to the meaning of content, "In Indonesia, in addition to the shell, one of the available biomass resources is coconut shell." should be replaced by "In Indonesia, in addition to the coffee shell, one of the available biomass resources is coconut shell." in the introduction.	1. The manuscript has been revised. Line 56.
2. In the section 2.2, why was the extraction conducted with ice-bath method at 4-5℃? Is this operating temperature suitable for industrial applications?	2. This operating temperature has not been yet used for industrial application. It is still used for laboratory system.
3. In the section 3.1, "The results of GC-MS bio-oil analysis of coconut shell pyrolysis results can be seen in Figures 2 and 3." should be rewritten to understand better.	3. The manuscript has been revised. Line 145-155.
4. There were some mistakes in writing. Such as: In Table 3 and Table 4, "Procentage" should be replaced by "Percentage". In the section 3.2, "temperatur" should be rewritten as "temperature".	4. The manuscript has been revised. Line 152. Line 161 and 163.
5. In the section 3.1, there were two sentences, "It shows that coconut shell bio-oil contained total phenol for 40.01%." and "The total phenolic compounds contained in bio-oil is 47.07% (coconut shell)". The percentages of total phenolic compounds pointed out in these sentences should be consistent.	5. The manuscript has been revised. Line 155-156.

6. In general, the speed of stirring has no effect on liquid-liquid equilibrium. The speed of stirring has a significant effect on the composition of liquid-liquid equilibrium from the Table 5 and Table 6. Why?	6. In general, the speed of stirring has no effect for LLE. It was showed from the Table 5 and Table 6 that almost all the compositions of the extract phase and raffinate phase for each temperature has approaching the same value. For example: T=298 K, X_A for speed 150 is 0.007, for speed 200 is 0.007, and for speed 250 is 0.009, etc. Only a few data showed a big difference.
7. The data were too few to describe the liquid-liquid equilibrium well. Enough datas are required.	7. One of the important thing to describe the LLE is the Activity Coefficient. It was showed the ideal conditions for each component in the system. UNIFAC and NRTL is used to calculate the activity coefficient for each component and calculated the calculated data, and then the calculated data and experimental data are compared to describe and showed the better conditions for each temperature. The activity coefficients for each model are shown in Table 7 and Table 8. Line 267-277 showed the explanation of the activity coefficient of each model and conditions.

8. In the section 3.3, "This is shown by the value of SSE (Sum of the Square of the Error) approaching the value of 0." This expression is inappropriate because the errors between calculated values and experimental data are not small from Fig.3 to Fig.15.	8. The manuscript has been revised. Line 310-311. Table 8 showed that the value of SSE is 0,015 – 0,554.
9. In the conclusion, the author pointed out that the UNIFAC modeling provides a good correlation to liquid-liquid equilibrium data under conditions of temperature of 323 K. Then, can the UNIFAC model be used to describe the liquid-liquid equilibrium under other temperatures? There is the same problem for the NRTL equation.	9. The manuscript has been revised. Line 326-331. It was explained in line 314-323. So, the UNIFAC and NRTL model could not be used to describe the liquid-liquid equilibrium under or up 323 K.

1 **Liquid Phase Equilibrium of Phenol Extraction**

2 **from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models**

3 Dewi Selvia Fardhyanti*, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati & Windy
4 Oktaviani

5

6 Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang

7 50236, Indonesia.

8

9

0 *Corresponding author Phone: +6282227611946; E-mail: dewiselvia@mail.unnes.ac.id

ABSTRACT

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technology for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which contained in bio-oil.

The correlation between experimental data and calculations shows that the UNIQUAC Functional-group Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non Random Two Liquid (NRTL) equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

Keywords: biomass, pyrolysis, bio-oil, UNIFAC, NRTL..

1. INTRODUCTION

The role of fossil fuels still be crucial, but their effects will gradually be over taken by new and renewable energy sources. Along with the depletion of world oil reserves and environmental issues, various researches on renewable energy are being actively conducted by various parties. Therefore, technology needs be able to overcome the problem. One technology that can be used is pyrolysis technology where the material used comes from organic waste (biomass). Pyrolysis technology can overcome organic waste problems and make the environment healthy also convert it into value-added end product.

Biomass is an organic material derived from plants, algae, animal waste, industrial waste, forestry, and agricultural waste [1]. Biomass can be used as pyrolysis raw material to produce liquid (bio-oil), gas and solid products. Various kinds of biomass waste can be used as raw materials for the manufacture of bio-oils, such as corncobs [2], sawdust and wheat bran [3], castor [4], oak [5], durian shell [6] and coconut shell [7].

Indonesia is the third largest coffee producer in the world after Brazil and Vietnam by contributing about 6% of the world's total coffee production, also world's fourth largest coffee exporter with a market share of around 11% across the world. Coffee is one of the plantations with high economic value besides chocolate and tea. Based on data from Indonesian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 691,160 tons with a plantation area of 47,800 Ha [8]. Waste from coffee processing that abundant and not utilized optimally is the coffee shell. Large waste of coffee shells derived from plantations was approximately 11.08% which potentially cause environment hazard. Coffee shells are a waste that has high lignocellulose content which have potential to be used as bio-oil. Bio-oil is a blackish liquid fuel derived from biomass such as wood, coffee shells and other biomass. Bio-oil contains lignin components (23.4%), cellulose (34.2%) and hemicellulose (24.5%) [9].

In Indonesia, in addition to the coffee shell, one of the available biomass resources is coconut shell. Availability of coconut shell can be seen from the production of coconut fruit in Indonesia. Coconut is one of Indonesia's main commodities with an average production of 3,000,000 tons / year [10]. The utilization of coconut is very diverse, but for the utilization and way of handling waste is still limited. Coconut fruit can be used as food in daily life for the purpose of consumed directly. Coconut shells nowadays, lots of it become garbage that can not be utilized. One of the waste handling is to utilize coconut shell waste as a base material in the manufacture of bio-oil. Characterization studies on coconut shells have been done through proximate, ultimate, and thermo gravimetric (TG) analyzes. The results of this analysis indicate that coconut shell has a high potential to produce fuel fluid by pyrolysis

conversion process [11]. Chemical content of coconut shell is cellulose (34%), hemicellulose (21%), lignin (27%) and ash (18%) [12].

Before converted into bio-oil, coconut shell waste and coffee shell need to be treated first. It takes a process before converting the waste of coffee shell into bio-oil which is pyrolysis. Pyrolysis is the process of decomposition of a substance or material that is done at a relatively high temperature. Pyrolysis results in the form of gas, liquid and solid. The solid result of this process is char (char). Gas and liquid products can be used as a source of bio-oil. Bio-oil can be used as an alternative fuel that is easier to store and distribute than biomass in solid form. Bio-oil made from coconut shell material using slow pyrolysis with pyrolysis temperature 250-300 °C produces liquid which very acidic and corrosive. The largest organic component in bio-oil is the lignin derivative of phenol, alcohol, organic acids and carbonyl compounds such as ketones, aldehydes and esters [13]. The nature of the acid is caused by the content of the dominant phenol compounds.

Phenol compounds in addition to causing the smell of smoke in bio-oil, also showed antioxidant activity and corrosive [14]. Therefore, the use of this bio-oil will directly cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive and unstable [6].

Phenol needs to be extracted from bio-oil to reduce its corrosive properties. In addition, phenol is a compound that has a high economic value because of its expensive and widely used. Phenols have many important uses such as disinfectants, resins, pesticides, explosives, and drugs. The method that can be used to extract phenol compounds from bio-oil is by liquid-liquid extraction method using methanol solvent. This has been done by Jazbinsek [15] on the isolation of phenol compounds from bio-oils from pyrolysis of forest waste and Mantilla [16] on the extraction of phenol compounds from bio-oils from pyrolysis of agricultural waste. Dahlia [17] conducted research on liquid-liquid extraction of phenol compound from bio-oil of pyrolysis resulted of palm oil empty bunch using methanol solvent. The yield of phenol resulting from this extraction is 40%. In this study, it is expected that the liquid-liquid extraction method can be used to separate the phenol compounds from coconut shell pyrolysis bio-oils. The purpose of phenol extraction is to improve the quality of bio-oil and reduce the corrosivity, so when used as fuel, it will cause no damage to the engine.

Biomass pyrolysis converted to bio-oil studies have been conducted. Bio-oil produced from pyrolysis process can be used as fuel for engines, turbines and boilers. The bio-oil which processed further by liquid-liquid extraction process will reduce the corrosive nature of bio-oil and obtained chemicals which one of them is phenol. Research on extraction of phenol compounds from bio-oil is still very limited. In addition, thermodynamic modelling study on liquid-liquid equilibrium of phenol extraction process from bio-oil still needs to be investigated further.

To design extraction columns required various information such as liquid-liquid equilibrium data (Liquid-liquid Equilibrium). Thermodynamic models such as Equation of State or Activity Coefficient are used to correlate the experimental data to obtain optimal interaction parameters. Optimal parameters can be used to predict liquid-liquid equilibrium data to produce an equilibrium graph that is used to design extraction columns [18]. The study on liquid-liquid equilibrium include NRTL, e-NRTL, UNIQUAC, and UNIFAC.

Given the importance of thermodynamic modeling in this liquid-liquid extraction process and the price and benefits of phenol in the industrial world, this research becomes an important thing to do. From the equilibrium data, the optimum condition will be obtained where the highest yield of extract obtained in the extraction process of phenol compound from bio-oil from coconut pyrolysis. Liquid-liquid equilibrium data of the components of the system can be used in the design of the equipment in separation process.

2. EXPERIMENTAL SECTION

2.1 Chemicals

All reagents used here are A.R. grade and used as received without further purification. Methanol, acetic acid, and chloroform were purchased from e-Merck (Germany). The distilled water is available at the laboratory. Coffee shell and coconut shell were obtained from public market in Semarang.

2.2 Equilibrium Procedure

Instruments used in this study:

a) Shaker bath, product by Memmert WB14, SV1422, Scwabach, Germany.

b) Gas Chromatography (GC), product by GC 6820 Agilent Technologies, column: Rastek RXi-5MS002E.

c) Gas Chromatography-Mass Spectroscopy (GC-MS), product by GCMS-QP2010S Shimadzu, column: Rastek RXi-5MS.

The material systems and experimental conditions for the equilibrium extraction are summarized in Table 1.

Table 1. Material Systems and Conditions for Equilibrium Extraction

The bio-oil feed solution that containing phenol was extracted using two-stage extraction. The first stage uses distilled water as a polar solvent and chloroform as a non-polar solvent. Extraction was conducted with ice-bath method at 4-5°C, 200 rpm and stirring time for 2 hours. The extracts obtained at this first stage are used as feeds on the second stage extraction. At the second stage extraction, each extract was extracted using a methanol solvent under operating conditions shown in Table 1.

2.3 Analysis and Characterization

After equilibrium attained (60 minutes), the mixtures were poured into a separating funnel, settled for an hour and separated into two phases. Then the two phases were weighed. The extract phase and the raffinate phase of each extraction processes are analyzed by GC to obtain the concentration of each component. The principal conditions of this analysis are shown in Table 2.

Table 2. Conditions of Analysis Using GC

3. RESULTS AND DISCUSSION

3.1 Bio-Oil Content

The chromatograms of the GC-MS analysis are shown in Fig. 2 and 3. The results of the GC-MS analysis of the bio-oil showed that they contained more than six chemical compounds such as ethyl ester, phenol, furfural, acetic acid, and others.

Figure 2. The Chromatogram of Bio-Oil Produced from Coconut Shell Pyrolysis

Table 3. The Components of Bio-oil Produced from Coconut Shell Pyrolysis

Figure 3. The Chromatogram of Bio-Oil Produced from Coffee Shell Pyrolysis

Table 4. Component of Bio-oil Produced from Coffee Shell Pyrolysis

Table 3 and 4 represent that bio-oil contains more than 6 main components. The percentage (%) of the compositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the height of the peak in the chromatograms. Using a method of GC-MS, this work presents a composition of the bio-oil generated in the experiment. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). It was caused by the pyrolysis processing at 300-350°C (low temperature carbonization) that produce more substances contain ester and phenolic compounds. The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil.

3.2 Equilibrium data on phenol extraction of bio-oil from coconut pyrolysis results

In this research the variables studied were temperature, speed of stirring and type of solvents (aqueous methanol and aqueous acetic acid). Generaly, all extracts are rich of phenol but the mole fraction significantly depends on extraction conditions: temperature, speed of stirring and type of solvents. Methanol and acetic acid need to be mixed with water because their polarities are not strong enough to form immiscible mixture with bio-oil [19].

The mole fractions of any components in the raffinate phase and the extract phase are constant after 60 minutes, so the system is assumed to be in equilibrium. The amount of water transfered from the solvent into the raffinate phase was negligible [19].

In this work, we are reported experimental data for the phenol extraction from bio-oil produced from coconut shell and the phenol extraction from bio-oil produced from coffee shell.

Table 5 and 6 show the equilibrium of multi-components extraction data for aqueous acetone and aqueous methanol solvent in the extract phase and raffinate phase.

Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Methanol from Bio-oil Produced from Coconut Shell.

Table 6. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Acetic Acid from Bio-oil Produced from Coffee Shell.

3.3 Liquid-liquid Equilibrium for The Phenol Extraction Process using UNIFAC dan NRTL Models.

The UNIFAC and NRTL models were used to correlate the experimental data obtained for the systems under study. UNIFAC equation and NRTL equation (Smith, 1996) were used to correlate experimental phase equilibrium data. The activity coefficient models applied in this study are as follows:

a) UNIFAC: [20]

UNIFAC is a UNIQUAC Functional-group Activity Coefficients model based on the UNIQUAC equation by using functional groups of a molecule contained in the mixture to calculate the activity coefficients. This model was developed by Fredenslund, Jones, and Prausnitz (1975). The UNIFAC modeling is a continuation of the UNIQUAC modeling development. This model has the advantage of performing phase equilibrium estimation even in the absence of experimental data. This thermodynamic model is used to predict the estimation of non-electrolyte activity in non-ideal mixtures. The UNIFAC model calculates the activity coefficients by using functional groups present in the molecules that form the liquid mixture. If the value of the component activity coefficient has a value close to one, this indicates that the component is in the ideal state in the system [21]. The correlation in the UNIFAC model is used in order to reduce the number of binary interactions measured to predict the state of the system. The correlation for the UNIFAC model is shown as follows:

$$ln\,\gamma_i = ln\,\gamma_i^C + ln\,\gamma_i^R \tag{1}$$

$$ln\,\gamma_i^C = 1 - J_i + ln\,J_i - 5q_i\left(1 - \frac{J_i}{L_i} + ln\frac{J_i}{L_i}\right) \tag{2}$$

$$ln\,\gamma_i^R = q_i\left[1 - \sum_k\left(\theta_k\frac{\beta_{ik}}{s_k} - e_{ki}ln\frac{\beta_{ik}}{s_k}\right)\right] \tag{3}$$

$$J_i = \frac{r_i\beta_i}{\sum_j r_j\beta_j} \tag{4}$$

$$L_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{5}$$

$$r_i = \sum_k v_k^{(i)}R_k \tag{6}$$

$$q_i = \sum_k v_k^{(i)}Q_k \tag{7}$$

$$e_{ki} = \frac{v_k^{(i)}Q_k}{q_i} \tag{8}$$

$$\beta_{ik} = \sum_m e_{mi}\tau_{mk} \tag{9}$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \tag{10}$$

$$s_k = \sum_m \theta_m\tau_{mk} \tag{11}$$

$$\tau_{mk} = exp\frac{-a_{mk}}{T} \tag{12}$$

Where:

$ln\,\gamma_i^C$ = Combinatorial component

$ln\,\gamma_i^R$ = residual component

J_i = component surface area component (i)

L_i = component volume fraction (i)

r_i = pure component surface area parameter (i)

x_i = pure component mol fraction (i)

q_i = pure component volume parameter (i)

$v_k^{(i)}$ = number of sub-group (k) on component (i)

R_k = parameter area for sub-group (k) ($R_k = A_{wk}/(2.5 \times 10^9)$, where A_{wk} is number of sub-group van der Walls surface arera

Q_k = number of parameter volume subgroup (k) ($Q_k = V_{wk}/15.17$, where V_{wk} is number of Van der Waals volume subgroup)

a_{mk} = group of interaction parameter from group m and k [18]

x_i = liquid mol fraction of component (i)

UNIFAC equation can be obtained to :

$$ln\,\gamma_i = ln\left[1 - J_i + ln\,J_i + 5q_i\left(1 - \frac{J_i}{L_i} + ln\frac{J_i}{L_i}\right)\right] + ln\left\{q_i\left[1 - \sum_k\left(\frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j}\cdot\frac{\sum_m e_{mi}\tau_{mk}}{\sum_m \theta_m\tau_{mk}} - \frac{v_k^{(i)}Q_k}{q_i}ln\frac{\sum_m e_{mi}\tau_{mk}}{\sum_m \theta_m\tau_{mk}}\right)\right]\right\} \tag{13}$$

b) NRTL: [20]

Non Random Two Liquid (NRTL) is derived from the Scott two liquid model and it is assumed that randomness is the same as the model used on the Wilson model. The NRTL model has a non-random parameter (a_{12}) making it possible to use in a wide variety of mixtures. The NRTL model uses only binary parameters to calculate the phase equilibrium properties.

The NRTL (Non Random Two-Liquid) equation was first developed by Renon and Prausnitz (1968). The NRTL model is derived from the Scott two liquid model and it is assumed that the non-random parameter is the same as the model used in the Wilson Model. The NRTL equation is developed based on a two-fluid theory with the addition of a non-random parameter (α), which makes the equation applicable to different types of liquid-liquid mixture and equilibrium by choosing the appropriate α price. The parameter estimation for this equation is done by setting the α value at a certain value and subsequently optimizing the objective function to obtain two optimal parameter interactions. The recommended α value is 0.2 - 0.47. The value of α is often adjusted to certain conditions, but usually the value of α = 0.3. Unlike the Wilson equation which contains two adjustable parameters, the NRTL equation contains three parameters, so the NRTL equation can be an alternative model if other models are inadequate. This equation can also estimate the equilibrium of multicomponent systems without additional parameters.

The NRTL equation can represent liquid-liquid equilibrium for both binary and multicomponent systems only with binary parameters. The equation is simpler than the UNIQUAC equation, but it has disadvantage because it contains three parameters for each pair of components. The third parameter (α) is estimated based on the state of the component and sometimes for certain substances the extreme number is obtained. The NRTL equation is expressed:

$$\frac{G^E}{nRT} = \sum_{i=1}^n x_i\frac{\sum_{k=1}^n \tau_{ji}G_{ji}x_j}{\sum_{k=1}^n G_{ki}x_k} \tag{14}$$

$$\tau_{ij} = \frac{g_{ij}-g_{jj}}{RT} \tag{15}$$

$$g_{ij} = g_{ji} = g_{kk} = 0 \tag{16}$$

$$G_{ij} = exp\left(-\alpha_{ij}\tau_{ij}\right) \tag{17}$$

$$\alpha_{ij} = \alpha_{ji} \tag{18}$$

$$ln\,\gamma_i = \frac{\sum_{j=1}^n \tau_{ji}G_{ji}x_j}{\sum_{k=1}^n G_{ki}x_k} + \sum_{j=1}^n\frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj}x_k}\tau_{ij} - \sum_{k=1}^n\frac{x_j\tau_{kj}G_{kj}}{\sum_{k=1}^n G_{kj}x_k} \tag{19}$$

$$X_i = exp\frac{\frac{\sum_{j=1}^n \tau_{ji}G_{ji}x_j}{\sum_{k=1}^n G_{ki}x_k} + \sum_{j=1}^n\frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj}x_k}}{\left(\tau_{ij} - \sum_{k=1}^n\frac{x_j\tau_{kj}G_{kj}}{\sum_{k=1}^n G_{kj}x_k}\right)} \tag{20}$$

254
$$Y_i = exp\left(\frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_{k=1}^n x_k \tau_{kj} G_{kj}}{\sum_{k=1}^n G_{kj} x_k}\right)\right)$$ (21)

255 Where:

256 G^x = molar Gibbs energy
257 R = gas constant
258 T = temperature
259 x = liquid phase mol fraction
260 i,j,k = component of 1, 2, 3, …, n
261 α = non-random parameter for NRTL
262 g, G = component parameter
263 γ = activity coefficient
264 τ = empirical constant for NRTL

265 **Table 7. The Activity Coefficients were Calculated by UNIFAC Model.**

266 **Table 8. The Activity Coefficients were Calculated by NRTL Model.**

267 Table 7 and 8 shows the value of activity coefficient on phenol extraction using methanol solvent
268 obtained from calculation with UNIFAC and NRTL modeling, from coefficient value of activity on each
269 component shows that methanol and acetic acid component in extract phase is in ideal condition because
270 the value of activity coefficient obtained close to one. The activity coefficient value of phenol and water
271 activity in the extract phase is not close to one, it means that the phenol and water components are in less
272 than ideal conditions in the system. The ideal conditions of the components in the system show that the
273 component is dominant, so the properties of the mixture are closer to the dominant component properties
274 either in the extract or rafinate phase. In raffinate it is known that the solvent has a coefficient of activity
275 close to the one, indicating that the solvent is in ideal conditions in the system, while the phenol and bio-
276 oil components are in less than ideal conditions. So non-ideality studies are very important for those
277 systems [21].

278 **Figure 4. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
279 **using Aqueous Methanol by UNIFAC Model at 298 K.**

280 Where:
281 Xa : mole fraction of component in extract phase
282 Xb : mole fraction of solvent in extract phase
283 Xc : mole fraction of water in extract phase
284 Ya : mole fraction of component in raffinate phase

285 Yb : mole fraction of solvent in raffinate phase
286 Yd : mole fraction of bio-oil in raffinate phase

287 **Figure 5. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
288 **using Aqueous Methanol by UNIFAC Model at 313 K.**

289 **Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
290 **using Aqueous Methanol by UNIFAC Model at 323 K.**

291 **Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
292 **using Aqueous Acetic Acid by UNIFAC Model at 298 K.**

293 **Figure 8. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
294 **using Aqueous Acetic Acid by UNIFAC Model at 313 K.**

295 **Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
296 **using Aqueous Acetic Acid by UNIFAC Model at 323 K.**

297 **Figure 10. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
298 **using Aqueous Methanol by NRTL Model at 298 K.**

299 **Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
300 **using Aqueous Methanol by NRTL Model at 313 K.**

301 **Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
302 **using Aqueous Methanol by NRTL Model at 323 K.**

303 **Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
304 **using Aqueous Acetic Acid by NRTL Model at 298 K.**

305 **Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
306 **using Aqueous Acetic Acid by NRTL Model at 313 K.**

307 **Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction**
308 **using Acetic Acid by NRTL Model at 323 K.**

309 The result of correlation of liquid-liquid equilibrium data by using UNIFAC and NRTL modeling gives
310 good agreement between experimental data and calculation. This is shown by the value of SSE (Sum of
311 the Square of the Error) is very small. The SSE values in UNIFAC and NRTL modeling can be seen in
312 Table 8. The value of SSE is 0,015 – 0,554.

313 **Table 8. Sum of the Square of the Error (SSE)**

314 Based on Table 8, it can be seen that extraction with methanol solvent with temperature of 323 K has

10

11

---

315 the smallest SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC model) and
316 0.015 (for NRTL model). The smaller the SSE values obtained show that the correlation between the
317 experimental data and the calculation data indicates a better correlation. Good correlation results show
318 that equilibrium modeling of UNIFAC and NRTL can be used to predict liquid-liquid equilibrium in
319 phenol extraction process from coconut shell pyrolysis bio-oil and coffee shell using methanol solvent
320 and acetic acid at 323 K.

321 Figure 4-12 shows that the visual comparison of calculated and experimental mole fractions in the
322 extract phase and the raffinate phase for the methanol solvent system by UNIFAC and NRTL at 323 K
323 are better than the other conditions.

324

325 **4. CONCLUSION**

326 The UNIFAC modeling provides a good correlation to liquid-liquid equilibrium data for ternary systems
327 on phenol extraction of coconut shell pyrolysis bio-oils using methanol solvent under conditions of
328 temperature of 323 K given by SSE of 0.053.

329 NRTL modeling gives a good correlation to liquid-liquid equilibrium data for ternary system on phenol
330 extraction of bio-oil from pyrolysis of coffee shell using methanol solvent at temperature condition of
331 323 K given by SSE of 0.015.

332 The activity coefficients of methanol, acetic acid, and phenol in the extract phase and raffinate phase
333 are far from unity. It means that they are far from ideal condition. The activity coefficients of water and
334 kerosene in their phases are close to one. It means that they are nearly ideal in their phases.

335
336

342
343 **REFERENCES**
344
345 [1] N. Sriram, *Renewable biomass energy*. Chicago: Illions Institute of Technology (2005).
346 [2] I. Demiral, A. Eryazici, S. Sensoz, S., Bio-oil production from pyrolysis of corncob (zea mays 1.),
347 *Biomass Bioenergy* 36 (2012) 43-49.

348 [3] M. Bertero, G. de la Puente, U. Sedran, Fuels from bio-oils: bio-oil production from different residual
349 sources, characterization and thermal conditioning, *Fuel* 95 (2012) 263-271.
350 [4] V.C. Pandey, K. Singh, J.S. Singh, A. Kumar, B. Singh, R.P. Singh, Jatropha curcas: A potential bio-
351 fuel plant for sustainable environmental development, *Renew. Sustain. Energy Rev.* 16 (2012) 2870-
352 2883.
353 [5] C.J. Ellens, R.C. Brown, Optimization of a free-fall reactor for production of fast pyrolysis bio-oil,
354 *Bisores. Technol.* 103 (2012) 374-380.
355 [6] S. Ismadji, S., Kulit durian sebagai bahan baku pembuatan *bio-oil*: sumber energi terbarukan,
356 *Prosiding Seminar Nasional Teknik Kimia Soebardjo Brotohardjono 1*, Prodi Teknik Kimia UPN
357 Veteran Jawa Timur (2012) 1-4.
358 [7] W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell
359 in an induction-heating reactor. *Journal Analytical Applied Pyrolysis*. 76 (2006) 230-237.
360 [8] Badan Pusat Statistik, 2015.
361 [9] C.E. Wyman, *Potential Synergies and Challenges in Refining Cellulosic Biomass to Fuels*.
362 Biotechnol Progress (2002).
363 [10] Direktorat Jenderal Perkebunan. *Produksi Buah Kelapa di Indonesia* (2016).
364 [11] Joardder. *Pyrolysis of coconut shell for bio-oil*. Bangladesh: Department Of Mechanical Engineering
365 Rajshahi University Of Engineering & Technology (2011).
366 [12] D. Tamado, E. Budi, R. Wirawan, H. Dwi, A. Tyaswuri, E. Sulistiani, E. Asma. Sifat termal karbon
367 aktif berbahan arang tempurung kelapa. Seminar Nasional Fisika Universitas Negeri Jakarta (2013).
368 [13] S. Wang, *High Efficiency Separation of Bio-Oil*. InTech (2013).
369 [14] Kasim, Fitriani, A.N. Fitrah, E. Hambali. Aplikasi asap cair pada lateks. *Jurnal PASTI* 9(1) (2012)
370 28-34.
371 [15] A. Jazbinšek, G. Viktor, L.F. Žilnik. *Isolation of phenol and phenolic compounds from fast pyrolysis*
372 *bio-oil of forestry residue*. Slovenia: National Institute of Chemistry (2008).
373 [16] S.V. Mantilla., A.M. Manrique, A. Gauthier-Maradei, Methodology for extraction of phenolic
374 compounds of bio-oil from agricultural biomass wastes, *Waste Biomass Valorization* 6 (2015) 371–383.
375 [17] Dahlia. *Pra rancangan pabrik pembuatan fenol dari tandan kosong kelapa sawit dengan proses*
376 *pirolisis dengan kapasitas produksi 10.000 ton/tahun*. Medan: Departemen Teknik Kimia Universitas
377 Sumatera Utara (2012).
378 [18] D. Hartanto, B. Triwibowo, Review model dan parameter interaksi pada korelasi kesetimbangan uap-
379 cair dan cair-cair sistem etanol (1) + air (2) + ionic liquids (3) dalam pemurnian bioetanol. *Jurnal*
380 *Rekayasa Proses* 8(1) (2014).
381 [19] D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Complex extraction of phenol, o-cresol, and p-cresol
382 from model coal tar using methanol and acetone solutions, *British J Appl. Sci.& Technol* 8(5) (2015)

12

13

383 427-436.

384 [20]J.M. Smith, H.C. Van Ness, M.M. Abbott, *Introduction to chemical engineering thermodynamics*,

385 5th edition, Mc Graw Hill International Book Company, New York (1996).

386 [21]D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Predicting the liquid phase equilibrium of multi-

387 components extraction by thermodynamic models, *Int. J. Thermodyn.* 19(2) (2015) 110-119.

388
389 **Table 1. Material Systems and Conditions for Equilibrium Extraction.**

	Quantity
feed	bio-oil
feed volume	2.5 mL
solvent	aqueous methanol
	aqueous acetic acid
mole fraction of water in solvent	0.2
solvent-feed mass ratio	1
shaking time	60 minutes
amplitudo of shaking	150, 200, 250 rpm
temperature	298, 313, 323 K.

390
391
392
393 **Table 2. Conditions of Analysis Using GC**

Column: Rastek RXi-5MS		
Column:		
Inner diameter	[m]	3.2×10^{-4}
Length	[m]	30
Carrier gas		He
Split ratio	[-]	153
Flow rate	[cm/sec]	26.6
Sample volume	m^3	1.10^{-9}
Injection temperature	[K]	553
Column temperature	[K]	313 – 573
Pressure column	kPa	10.0
Column flow	mL/min	0.54
Detector (FID) temperature	[K]	573

396
397
398
399
400
401

402
403 **Table 3. The Main Components of Bio-oil Produced by Pyrolysis of Coconut Shells**

Peak	Component	Percentage
1	Ethyl ester	37.60
2	Formic acid	4.02
3	1-Hydroxy-2-butanone	3.89
4	Furfural	5.45
5	Phenol	40.01
7	2-Methoxy-phenol	7.02

404
405
406
407 **Table 4. The Main Components of Bio-oil Produced by Pyrolysis of Coffee Shells**
408

Peak	Component	Percentage
1	Urea	5%
2	Acetic acid	26%
5	Furfural	6%
6	Phenol	34%
7	Phenol, 2-methoxy-	7%
8	Phenol, 2,6-dimethoxy	4%

409
410
411
412 **Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Methanol from Bio-**
413 **oil Produced from Coconut Shell**

Temperature	Speed	X_A	X_B	X_C	Y_A	Y_B	Y_D
	150	0.007	0.973	0.020	0.161	0.316	0.524
298 K	200	0.007	0.973	0.019	0.116	0.313	0.572
	250	0.009	0.967	0.024	0.094	0.488	0.418
	150	0.009	0.963	0.027	0.085	0.549	0.365
313 K	200	0.008	0.970	0.022	0.086	0.414	0.501
	250	0.010	0.963	0.027	0.062	0.555	0.383
	150	0.010	0.962	0.028	0.069	0.567	0.363
323 K	200	0.009	0.965	0.026	0.065	0.525	0.410
	250	0.012	0.959	0.029	0.029	0.615	0.356

414
415
416 **Table 6. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Acetic Acid from**

417 **Bio-oil Produced from Coffee Shell.**
418

Temperature	Speed	X_A	X_B	X_C	Y_A	Y_B	Y_D
	150	0.054	0.247	0.365	0.281	0.047	0.672
298 K	200	0.042	0.370	0.204	0.107	0.537	0.357
	250	0.024	0.551	0.093	0.019	0.878	0.104
	150	0.012	0.707	0.068	0.025	0.907	0.069
313 K	200	0.011	0.744	0.047	0.008	0.958	0.034
	250	0.010	0.764	0.036	0.003	0.979	0.019
	150	0.006	0.841	0.026	0.004	0.980	0.016
323 K	200	0.004	0.883	0.016	0.002	0.986	0.012
	250	0.004	0.903	0.012	0.001	0.947	0.007

419
420

Table 7. The Activity Coefficients were Calculated by UNIFAC Model.

Solution	Temperature	Speed	γ_A^I	γ_B^I	γ_C^I	γ_A^{II}	γ_B^{II}	γ_B^{III}
Methanol	298	150	0.176	0.769	0.037	2.360	2.063	1.025
		200	0.032	0.794	0.004	2.398	2.098	1.020
		250	0.019	0.799	0.003	2.435	2.143	1.015
	313	150	0.149	0.789	0.006	2.143	2.655	1.016
		200	0.119	0.791	0.003	2.215	2.700	1.012
		250	0.112	0.792	0.003	2.191	2.685	1.013
	323	150	0.049	0.788	0.007	2.181	2.504	1.007
		200	0.028	0.788	0.001	2.222	2.515	1.006
		250	0.034	0.788	0.001	2.191	2.519	1.006
Acetic Acid	298	150	0.199	1.191	0.020	3.108	1.980	1.011
		200	0.132	1.002	0.001	3.150	1.996	1.009
		250	0.073	1.015	0.001	3.198	2.0161	1.006
	313	150	0.196	1.000	0.003	2.798	1.805	1.005
		200	0.152	0.999	0.013	2.857	1.824	1.002
		250	0.141	0.999	0.014	2.836	1.815	1.003
	323	150	0.055	0.999	0.037	2.705	1.701	1.006
		200	0.035	0.999	0.004	2.728	1.701	1.004
		250	0.042	0.999	0.006	2.719	1.711	0.999

Table 8. The Activity Coefficients were Calculated by NRTL Model

Solution	Temperature	Speed	γ_A^I	γ_B^I	γ_C^I	γ_A^{II}	γ_B^{II}	γ_B^{III}
Methanol	298	150	0.077	0.926	0.381	0.265	2.037	0.655
		200	0.064	0.482	0.337	0.001	0.039	0.065
		250	0.063	0.283	0.387	1.3×10^{-6}	0.001	7.6×10^{-5}
	313	150	4.47×10^{6}	0.942	0.010	8.4×10^{-7}	1.050	0.044
		200	2.71×10^{6}	0.986	0.056	1.5×10^{-11}	1.014	1.1×10^{-5}
		250	1.80×10^{6}	0.944	0.039	4.9×10^{-39}	0.880	2.4×10^{-12}
	323	150	7.92×10^{6}	0.980	0.010	3.6×10^{-3}	1.028	0.025
		200	3.48×10^{6}	0.977	0.022	4.1×10^{-18}	1.006	4.1×10^{-12}
		250	9.44×10^{6}	0.972	0.024	3.5×10^{-22}	0.937	1.1×10^{-26}
Acetic Acid	298	150	0.045	0.644	0.218	0.432	1.087	0.678
		200	0.039	0.331	0.210	0.015	0.361	0.552
		250	0.036	0.193	0.232	9.5×10^{6}	0.017	0.027
	313	150	0.000	0.734	0.037	0.036	0.995	0.551
		200	0.003	0.732	0.050	0.030	0.999	0.444
		250	0.013	0.749	0.069	0.028	1.000	0.374
	323	150	0.000	0.734	0.037	0.035	1.139	0.011
		200	0.003	0.732	0.050	0.001	1.010	0.039
		250	0.013	0.749	0.069	8.9×10^{6}	0.694	9.6×10^{-7}

Table 8. Sum of the Square of the Error (SSE)

Model	Temperature	SSE	
		Methanol	Acetic Acid
UNIFAC	298	0.087	0.132
	313	0.065	0.083
	323	0.053	0.084
NRTL	298	0.024	0.065
	313	0.026	0.544
	323	0.015	0.077

Figure 2. Analysis Result by GC-MS for the Bio-oil Produced by Coconut Shells Pyrolysis

Figure 3. Analysis Result by GC-MS for the Bio-oil Produced by Coffee Shells Pyrolysis

Figure 4. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 298 K.

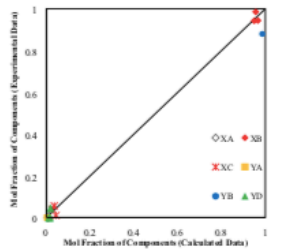Figure 5. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 313 K.

456 Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
457 Aqueous Methanol by UNIFAC Model at 323 K.

464 Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
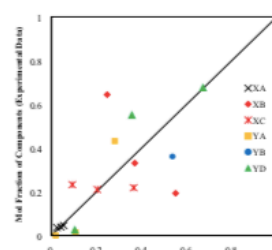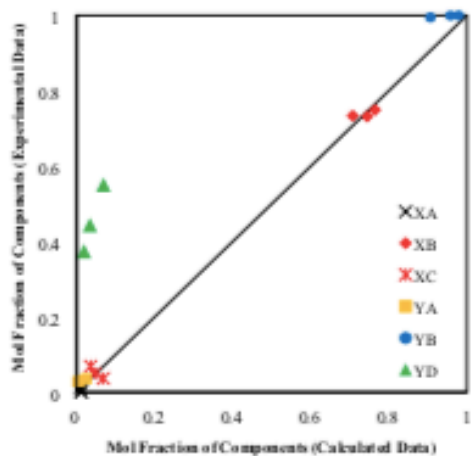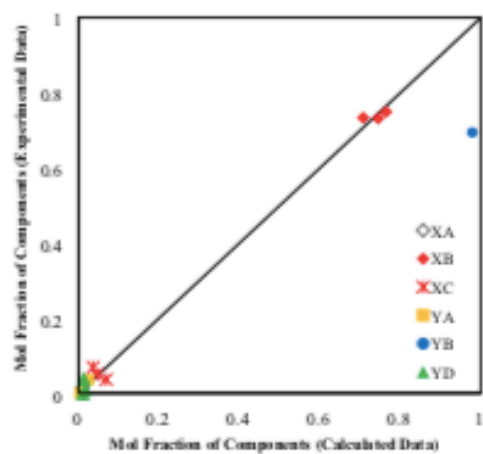465 Aqueous Acetic Acid by UNIFAC Model at 298 K.
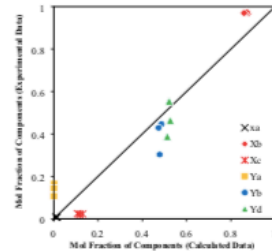
471 Figure 8. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
472 Aqueous Acetic Acid by UNIFAC Model at 313 K.
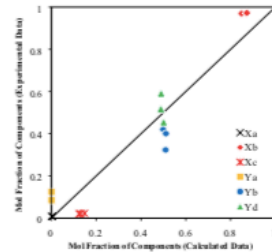
479 Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
480 Aqueous Acetic Acid by UNIFAC Model at 323 K.
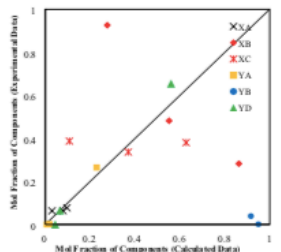
484 Figure 10. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
485 Aqueous Methanol by NRTL Model at 298 K

493 Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
494 Aqueous Methanol by NRTL Model at 313 K
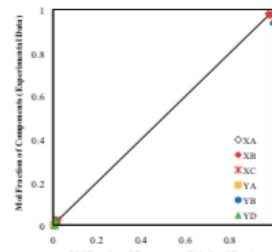
499 Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
500 Aqueous Methanol by NRTL Model at 323 K

508 Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using
509 Aqueous Acetic Acid by NRTL Model at 298 K

511
512
513 **Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using**
514 **Aqueous Acetic Acid by NRTL Model at 313 K**
515
516
517
518

519
520
521 **Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using**
522 **Acetic Acid by NRTL Model at 323 K**

6. Manuskrip siap untuk direview kembali

Your manuscript CJCHE_2018_233_R1 has been sent for review 🖨 ⤢

Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com>   Fri, May 18, 2018, 10:28 AM   ☆   ↩   ⋮

to me ▾

This message was sent automatically. Please do not reply.

Reference: CJCHE_2018_233_R1
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

I am currently identifying and contacting reviewers who are acknowledged experts in the field. Since peer review is a voluntary service it can take time to find reviewers who are both qualified and available. While reviewers are being contacted, the status of your manuscript will appear in EVISE® as 'Reviewer Invited'.

Once a reviewer agrees to review your manuscript, the status will change to 'Under Review'. When I have received the required number of expert reviews, the status will change to 'Ready for Decision' while I evaluate the reviews before making a decision on your manuscript.

To track the status of your manuscript, please log into EVISE® and go to 'My Submissions' via: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE

Kind regards,

Chinese Journal of Chemical Engineering

7. Reviews complete and decision pending for your manuscript CJCHE_2018_233_R1

Reviews complete and decision pending for your manuscript 🖨 ⬈
CJCHE_2018_233_R1 Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com>   Mon, Jun 4, 2018, 10:21 AM   ☆   ↩   ⋮
to me ▾

Reference: CJCHE_2018_233_R1
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

I am pleased to inform you that I have received all the required reviews, which I will now evaluate before making a decision on your manuscript referenced above.

In the event that I need to seek the opinion of an additional reviewer, you may see the status of your manuscript revert briefly from 'Ready for Decision' to 'Under Review'.

To track the status of your manuscript, please log into EVISE® http://www.evise.com/evise/faces/pages/navigation/ NavController.jspx?JRNL_ACR=CJCHE and go to 'My Submissions'.

I will inform you once I have made a decision.

Thank you again for submitting your manuscript to Chinese Journal of Chemical Engineering and for giving me the opportunity to consider your work.

Kind regards,

Chinese Journal of Chemical Engineering

8. Invitation to revise manuscript CJCHE_2018_233_R1

Invitation to revise manuscript CJCHE_2018_233_R1 [Inbox x]

Jianzhong Wu (Chinese Journal of Chemical Engineering) <EviseSuppor... Fri, Jun 8, 2018, 7:50 AM
to me

Ref: CJCHE_2018_233_R1
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. Fardhyanti,

I am enclosing further comments on your manuscript submitted to Chinese Journal of Chemical Engineering. The reviewer(s) recommended publication of your manuscript. However, additional revisions are required before acceptance. Therefore, I invite you to respond to the reviewers' comments and revise your manuscript accordingly.

To submit your revised manuscript:

- Log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE
- Locate your manuscript under the header 'My Submissions that need Revisions' on your 'My Author Tasks' view
- Click on 'Agree to Revise'
- Make the required edits
- Click on 'Complete Submission' to approve

What happens next?
After approving your submission you will receive a notification that the submission is complete. To track the status of your paper throughout the editorial process, log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE

Kind regards,

Jianzhong Wu
Associate editor
Chinese Journal of Chemical Engineering

Comments from the editors and reviewers:
-Reviewer 1

- Reviewer 1: The paper has been significantly improved.

-Reviewer 2

-
The modifications made in the revised manuscript are acceptable except for the following questions. The author does not explain or solve these problems positively. So the manuscript does not meet the requirements of publication at present.
1. In general, the speed of stirring has no effect on liquid-liquid equilibrium. So the speed of stirring should not appear in Table 5 and Table 6.
2. The experimental data were still not enough to obtain accurate and credible activity coefficient.
3. In the conclusion, the author pointed out that the UNIFAC modeling provides a good correlation to liquid-liquid equilibrium data under conditions of temperature of 323 K. However, the UNIFAC model or NRTL model should be used to describe the liquid-liquid equilibrium for different temperature rather than a specific temperature.
New problems in the revised manuscript:
4. The decimal point was wrongly written as a comma in Table 6 and Table 8.
5. Two tables were labeled as Table 8 in the revised manuscript.

9. Dalam proses revisi - CJCHE_2018_233_R2

Under Revision - CJCHE_2018_233_R2 for Chinese Journal of
Chinese Engineering Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com>   Sun, Jul 8, 2018, 11:13 AM
to me

This message was sent automatically. Please do not reply.

Ref: CJCHE_2018_233_R2
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

You kindly agreed to complete the following task: Under Revision. I would like to remind you to complete this task by 07/Aug/2018.

To view this request, log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE and click on the title of your manuscript, located under 'My Author Tasks' on your homepage.

Please complete the required steps and click on 'Complete Submission' to submit the manuscript.

What happens next?

After you submit your manuscript you will receive an email confirmation that your submission is complete. To track the status of your manuscript throughout the editorial process, log into EVISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=CJCHE and locate your submission under the header 'My Submissions with Journal' on your 'My Author Tasks' view.

Kind regards,

10. Submit revisi kedua oleh penulis

Received revision CJCHE_2018_233_R2 Inbox ×

Chinese Journal of Chemical Engineering <EviseSupport@elsevier.com>   Mon, Jul 23, 2018, 4:11 PM

to me

This message was sent automatically. Please do not reply.

Ref: CJCHE_2018_233_R2
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. fardhyanti,

Thank you for submitting your revised manuscript for consideration for publication in Chinese Journal of Chemical Engineering. Your revision was received in good order.

To track the status of your manuscript, please log into EVISE® http://www.evise.com/evise/faces/pages/navigation/ NavController.jspx?JRNL_ACR=CJCHE and locate the submission under the header 'My Submissions with Journal' on your 'My Author Tasks' view.

We appreciate your submitting your revision to this journal.

Kind regards,

Chinese Journal of Chemical Engineering

Have questions or need assistance?
For further assistance, please visit our Customer Support site. Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about EVISE® via interactive tutorials. You can also talk 24/5 to our customer support team by phone and 24/7 by live chat and email.

11. Manuskrip diterima (Accepted)

Your manuscript CJCHE_2018_233_R2 has been accepted Inbox ×

Jianzhong Wu (Chinese Journal of Chemical Engineering) <EviseSupp... Wed, Aug 1, 2018, 7:38 AM
to me

Ref: CJCHE_2018_233_R2
Title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Journal: Chinese Journal of Chemical Engineering

Dear Dr. Fardhyanti,

I am pleased to inform you that your paper has been accepted for publication. My own comments as well as any reviewer comments are appended to the end of this letter. Now that your manuscript has been accepted for publication it will proceed to copy-editing and production.

Thank you for submitting your work to Chinese Journal of Chemical Engineering. We hope you consider us again for future submissions.

Kind regards,

Jianzhong Wu
Associate editor
Chinese Journal of Chemical Engineering

Comments from the editors and reviewers:

Have questions or need assistance?
For further assistance, please visit our Customer Support site. Here you can search for solutions on a range of topics, find answers to frequently asked questions, and learn more about EVISE® via interactive tutorials. You can also talk 24/5 to our customer support team by phone and 24/7 by live chat and email.

12. Permintaan sedikit revisi format artikel

Chinese Journal of Chemical Engineering CJCHE_2018_233

Inbox ×

caomin70@gmail.com <caomin70@gmail.com>   Thu, Aug 30, 2018, 9:34 AM
to me

Dear Sir,
I want to check it with you before your article sent to production:
Which version of your article is the final version for publication because the zip file contains two versions of your article? I attached it for your confirmation. Please answer me as soon as possible! Thank you!

All the best,

Cao Min

caomin70@gmail.com

CJCHE_2018_233_...

caomin70@gmail.com <caomin70@gmail.com>   Aug 30, 2018, 12:43 PM
to me

Dear Sir,

I got it, thank you! However, there are two Table 9s in your article and there is no Table 7 in it. And there are also two Fig. 11s and two Fig.12s and there is lack of Fig.1. Could you check it again for me? I am looking forward to your answers. Thank you!

All the best,

Cao Min

caomin70@gmail.com

13. Track your article [CJCHE_1237] accepted in Chinese Journal of Chemical Engineering

Track your article [CJCHE_1237] accepted in Chinese Journal of Chemical Engineering   Inbox ×

Elsevier - Article Status <Article_Status@elsevier.com>   Tue, Sep 4, 2018, 10:05 AM
to me

Please note this is a system generated email from an unmanned mailbox.
If you have any queries we really want to hear from
you via our 24/7 support at http://help.elsevier.com

Article title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Reference: CJCHE1237
Journal title: Chinese Journal of Chemical Engineering
Corresponding author: Dr dewi selvia fardhyanti
First author: Dr dewi selvia fardhyanti
Dear Dr fardhyanti,

Your article Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models will be published in Chinese Journal of Chemical Engineering.

To track the status of your article throughout the publication process, please use our article tracking service:

Accepted Manuscript

Liquid phase equilibrium of phenol extraction from bio-oil produced by biomass pyrolysis using thermodynamic models

Dewi Selvia Fardhyanti, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani

Please cite this article as: Dewi Selvia Fardhyanti, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani , Liquid phase equilibrium of phenol extraction from bio-oil produced by biomass pyrolysis using thermodynamic models. Cjche (2018), doi:10.1016/j.cjche.2018.08.011

Liquid Phase Equilibrium of Phenol Extraction
from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models

Dewi Selvia Fardhyanti*, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati & Windy Oktaviani

Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang 50236, Indonesia.

ABSTRACT

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technology for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which contained in bio-oil.

The correlation between experimental data and calculations shows that the UNIQUAC Functional-group Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non Random Two Liquid (NRTL) equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

Keywords: biomass, pyrolysis, bio-oil, UNIFAC, NRTL.

1. INTRODUCTION

The role of fossil fuels still be crucial, but their effects will gradually be over taken by new and renewable energy sources. Along with the depletion of world oil reserves and environmental issues, various researches on renewable energy are being actively conducted by various parties. Therefore, technology needs be able to overcome the problem. One technology that can be used is pyrolysis technology where the material used comes from organic waste (biomass). Pyrolysis technology can overcome organic waste problems and make the environment healthy also convert it into value-added end product.

Biomass is an organic material derived from plants, algae, animal waste, industrial waste, forestry, and agricultural waste [1]. Biomass can be used as pyrolysis raw material to produce liquid (bio-oil), gas and solid products. Various kinds of biomass waste can be used as raw materials for the manufacture of bio-oils, such as corncobs [2], sawdust and wheat bran [3], castor [4], oak [5], durian shell [6] and coconut shell [7].

Indonesia is the third largest coffee producer in the world after Brazil and Vietnam by contributing about 6% of the world's total coffee production, also world's fourth largest coffee exporter with a market share of around 11% across the world. Coffee is one of the plantations with high economic value besides chocolate and tea. Based on data from Indonesian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 691,160 tons with a plantation area of 47,800 Ha [8]. Waste from coffee processing that abundant and not utilized optimally is the coffee shell. Large waste of coffee shells derived from plantations was approximately 11.08% which potentially cause environment hazard. Coffee shells are a waste that has high lignocellulose content which have potential to be used as bio-oil. Bio-oil is a blackish liquid fuel derived from biomass such as wood, coffee shells and other biomass. Bio-oil contains lignin components (23.4%), cellulose (34.2%) and hemicellulose (24.5%) [9].

In Indonesia, in addition to the coffee shell, one of the available biomass resources is coconut shell. Availability of coconut shell can be seen from the production of coconut fruit in Indonesia. Coconut is one of Indonesia's main commodities with an average production of 3,000,000 tons / year [10]. The utilization of coconut is very diverse, but for the utilization and way of handling waste is still limited. Coconut fruit can be used as food in daily life for the purpose of consumed directly. Coconut shells nowadays, lots of it become garbage that can not be utilized. One of the waste handling is to utilize coconut shell waste as a base material in the manufacture of bio-oil. Characterization studies on coconut shells have been done through proximate, ultimate, and Thermo Gravimetric (TG) analyzes.

The results of this analysis indicate that coconut shell has a high potential to produce fuel fluid by pyrolysis conversion process [11]. Chemical content of coconut shell is cellulose (34%), hemicellulose (21%), lignin (27%) and ash (18%) [12].

Before converted into bio-oil, coconut shell waste and coffee shell need to be treated first. It takes a process before converting the waste of coffee shell into bio-oil which is pyrolysis. Pyrolysis is the process of decomposition of a substance or material that is done at a relatively high temperature. Pyrolysis results in the form of gas, liquid and solid. The solid result of this process is char (char). Gas and liquid products can be used as a source of bio-oil. Bio-oil can be used as an alternative fuel that is easier to store and distribute than biomass in solid form. Bio-oil made from coconut shell material using slow pyrolysis with pyrolysis temperature 250-300 °C produces liquid which very acidic and corrosive. The largest organic component in bio-oil is the lignin derivative of phenol, alcohol, organic acids and carbonyl compounds such as ketones, aldehydes and esters [13]. The nature of the acid is caused by the content of the dominant phenol compounds.

Phenol compounds in addition to causing the smell of smoke in bio-oil, also showed antioxidant activity and corrosive [14]. Therefore, the use of this bio-oil will directly cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive and unstable [6].

Phenol needs to be extracted from bio-oil to reduce its corrosive properties. In addition, phenol is a compound that has a high economic value because of its expensive and widely used. Phenols have many important uses such as disinfectants, resins, pesticides, explosives, and drugs. The method that can be used to extract phenol compounds from bio-oil is by liquid-liquid extraction method using methanol solvent. This has been done by Jazbinsek [15] on the isolation of phenol compounds from bio-oils from pyrolysis of forest waste and Mantilla [16] on the extraction of phenol compounds from bio-oils from pyrolysis of agricultural waste. Dahlia [17] conducted research on liquid-liquid extraction of phenol compound from bio-oil of pyrolysis resulted of palm oil empty bunch using methanol solvent. The yield of phenol resulting from this extraction is 40%. In this study, it is expected that the liquid-liquid-extraction method can be used to separate the phenol compounds from coconut shell pyrolysis bio-oils. The purpose of phenol extraction is to improve the quality of bio-oil and reduce the corrosivity, so when used as fuel, it will cause no damage to the engine.

Biomass pyrolysis converted to bio-oil studies have been conducted. Bio-oil produced from the pyrolysis process can be used as fuel for engines, turbines and boilers. The bio-oil which processed further by liquid-liquid extraction process will reduce the corrosive nature of bio-oil and obtained chemicals which one of them is phenol. Research on extraction of phenol compounds from bio-oil is still very limited. In addition, thermodynamic modelling study on liquid-liquid equilibrium of phenol

extraction process from bio-oil still needs to be investigated further.

To design extraction columns required various information such as liquid-liquid equilibrium data (Liquid-Liquid Equilibrium). Thermodynamic models such as Equation of State or Activity Coefficient are used to correlate the experimental data to obtain optimal interaction parameters. Optimal parameters can be used to predict liquid-liquid equilibrium data to produce an equilibrium graph that is used to design extraction columns [18]. The study on liquid-liquid equilibrium include NRTL, e-NRTL, UNIQUAC, and UNIFAC.

Given the importance of thermodynamic modeling in this liquid-liquid extraction process and the price and benefits of phenol in the industrial world, this research becomes an important thing to do. From the equilibrium data, the optimum condition will be obtained where the highest yield of extract obtained in the extraction process of phenol compound from bio-oil from coconut pyrolysis. Liquid-liquid equilibrium data of the components of the system can be used in the design of the equipment in separation process.

2. EXPERIMENTAL SECTION

2.1 Chemicals

All reagents used here are A.R. grade and used as received without further purification. Methanol, acetic acid, and chloroform were purchased from e-Merck (Germany). The distilled water is available at the laboratory. Coffee shell and coconut shell were obtained from public market in Semarang.

2.2 Equilibrium Procedure

Instruments used in this study:

a) Shaker bath, product by Memmert WB14, SV1422, Scwabach, Germany.

b) Gas Chromatography (GC), product by GC 6820 Agilent Technologies, column: Rastek RXi-5MS002E.

c) Gas Chromatography-Mass Spectroscopy (GC-MS), product by GCMS-QP2010S Shimadzu, column: Rastek RXi-5MS.

The material systems and experimental conditions for the equilibrium extraction are summarized in Table 1.

Table 1. Material Systems and Conditions for Equilibrium Extraction

The bio-oil feed solution that containing phenol was extracted using two-stage extraction. The first stage uses distilled water as a polar solvent and chloroform as a non-polar solvent. Extraction was conducted with ice-bath method at 4-5°C, 200 rpm and stirring time for 2 hours. The extracts obtained

at this first stage are used as feeds on the second stage extraction. At the second stage extraction, each extract was extracted using a methanol solvent under operating conditions shown in Table 1.

2.3 Analysis and Characterization

After equilibrium attained (60 minutes), the mixtures were poured into a separating funnel, settled for an hour and separated into two phases. Then the two phases were weighed. The extract phase and the raffinate phase of each extraction processes are analyzed by GC to obtain the concentration of each component. The principal conditions of this analysis are shown in Table 2.

Table 2. Conditions of Analysis Using GC

3. RESULTS AND DISCUSSION

3.1 Bio-Oil Content

The chromatograms of the GC-MS analysis are shown in Fig. 1 and 2. The results of the GC-MS analysis of the bio-oil showed that they contained more than six chemical compounds such as ethyl ester, phenol, furfural, acetic acid, and others.

Figure 1. The Chromatogram of Bio-Oil Produced from Coconut Shell Pyrolysis

Table 3. The Components of Bio-oil Produced from Coconut Shell Pyrolysis

Figure 2. The Chromatogram of Bio-Oil Produced from Coffee Shell Pyrolysis

Table 4. Component of Bio-oil Produced from Coffee Shell Pyrolysis

Table 3 and 4 represent that bio-oil contains more than 6 main components. The percentage (%) of the compositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the height of the peak in the chromatograms. Using a method of GC-MS, this work presents a composition of the bio-oil generated in the experiment. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). It was caused by the pyrolysis processing at 300-350°C (low temperature carbonization) that produce more substances contain ester and phenolic compounds. The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil.

3.2 Equilibrium data on phenol extraction of bio-oil from coconut pyrolysis results

In this research the variables studied were temperature, speed of stirring and type of solvents (aqueous methanol and aqueous acetic acid). Generaly, all extracts are rich of phenol but the mole fraction significantly depends on extraction conditions: temperature, speed of stirring and type of

solvents. Methanol and acetic acid need to be mixed with water because their polarities are not strong enough to form immiscible mixture with bio-oil [19].

The mole fractions of any components in the raffinate phase and the extract phase are constant after 60 minutes, so the system is assumed to be in equilibrium. The amount of water transfered from the solvent into the raffinate phase was negligible [19].

In this work, we are reported experimental data for the phenol extraction from bio-oil produced from coconut shell and the phenol extraction from bio-oil produced from coffee shell.

Table 5 and 6 show the equilibrium of multi-components extraction data for aqueous acetone and aqueous methanol solvent in the extract phase and raffinate phase.

Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Methanol from Bio-oil Produced from Coconut Shell.

Table 6. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Acetic Acid from Bio-oil Produced from Coffee Shell.

3.3 Liquid-liquid Equilibrium for The Phenol Extraction Process using UNIFAC dan NRTL Models.

The UNIFAC and NRTL models were used to correlate the experimental data obtained for the systems under study. UNIFAC equation and NRTL equation (Smith, 1996) were used to correlate experimental phase equilibrium data. The activity coefficient models applied in this study are as follows:

a) UNIFAC: [20]

UNIFAC is a UNIQUAC Functional-group Activity Coefficients model based on the UNIQUAC equation by using functional groups of a molecule contained in the mixture to calculate the activity coefficients. This model was developed by Fredenslund, Jones, and Prausnitz (1975). The UNIFAC modeling is a continuation of the UNIQUAC modeling development. This model has the advantage of performing phase equilibrium estimation even in the absence of experimental data. This thermodynamic model is used to predict the estimation of non-electrolyte activity in non-ideal mixtures. The UNIFAC model calculates the activity coefficients by using functional groups present in the molecules that form the liquid mixture. If the value of the component activity coefficient has a value close to one, this indicates that the component is in the ideal state in the system [21]. The correlation in the UNIFAC model is used in order to reduce the number of binary interactions measured to predict the state of the system. The correlation for the UNIFAC model is shown as follows:

$$ln\,\gamma_i = ln\,\gamma_i^{\,c} + ln\,\gamma_i^{\,R} \tag{1}$$

$$ln\,\gamma_i^{\,c} = 1 - J_i + ln\,J_i - 5q_i\left(1 - \frac{J_i}{L_i} + ln\frac{J_i}{L_i}\right) \tag{2}$$

$$ln\,\gamma_i^{\,R} = q_i\left[1 - \sum_k\left(\theta_k\frac{\beta_{ik}}{s_k} - e_{ki}\,ln\frac{\beta_{ik}}{s_k}\right)\right] \tag{3}$$

$$J_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{4}$$

$$L_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{5}$$

$$r_i = \sum_k v_k^{(i)} R_k \tag{6}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{7}$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \tag{8}$$

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk} \tag{9}$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_i x_j q_j} \tag{10}$$

$$s_k = \sum_m \theta_m \tau_{mk} \tag{11}$$

$$\tau_{mk} = exp\frac{-a_{mk}}{T} \tag{12}$$

Where:

$ln\,\gamma_i^{\,C}$ = Combinatorial component

$ln\,\gamma_i^{\,R}$ = residual component

J_i = component surface area component (i)

L_i = component volume fraction (i)

r_i = pure component surface area parameter (i)

x_i = pure component mol fraction (i)

q_i = pure component volume parameter (i)

$v_k^{(i)}$ = number of sub-group (k) on component (i)

R_k = parameter area for sub-group (k) ($R_k = A_{wk}/(2.5 \times 10^9)$, where A_{wk} is number of sub-group van der Walls surface area)

Q_k = number of parameter volume subgroup (k) ($Q_k = V_{wk}/15.17$, where V_{wk} is number of Van der Waals volume subgroup)

a_{mk} = group of interaction parameter from group m and k [18]

x_i = liquid mol fraction of component (i)

UNIFAC equation can be obtained to :

$ln\,\gamma_i =$

$$ln\left[1 - J_i + ln\,J_i + 5q_i\left(1 - \frac{J_i}{L_i} + ln\frac{J_i}{L_i}\right)\right] +$$

$$ln\left\{q_i\left[1 - \sum_k\left(\frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \cdot \frac{\sum_m e_{mi}\tau_{mk}}{\sum_m \theta_m \tau_{mk}} - \frac{v_k^{(i)} Q_k}{q_i} \cdot ln\frac{\sum_m e_{mi}\tau_{mk}}{\sum_m \theta_m \tau_{mk}}\right)\right]\right\} \tag{13}$$

b) NRTL: [20]

Non Random Two Liquid (NRTL) is derived from the Scott two liquid model and it is assumed that randomness is the same as the model used on the Wilson model. The NRTL model has a non-random parameter (α_{12}) making it possible to use in a wide variety of mixtures. The NRTL model uses only binary parameters to calculate the phase equilibrium properties.

The NRTL (Non Random Two-Liquid) equation was first developed by Renon and Prausnitz (1968). The NRTL model is derived from the Scott two liquid model and it is assumed that the non-random parameter is the same as the model used in the Wilson Model. The NRTL equation is developed based on a two-fluid theory with the addition of a non-random parameter (α), which makes the equation applicable to different types of liquid-liquid mixture and equilibrium by choosing the appropriate α price. The parameter estimation for this equation is done by setting the α value at a certain value and subsequently optimizing the objective function to obtain two optimal parameter interactions. The recommended α value is 0.2 - 0.47. The value of α is often adjusted to certain conditions, but usually the value of $\alpha = 0.3$. Unlike the Wilson equation which contains two adjustable parameters, the NRTL equation contains three parameters, so the NRTL equation can be an alternative model if other models are inadequate. This equation can also estimate the equilibrium of multicomponent systems without additional parameters.

The NRTL equation can represent liquid-liquid equilibrium for both binary and multicomponent systems only with binary parameters. The equation is simpler than the UNIQUAC equation, but it has disadvantage because it contains three parameters for each pair of components. The third parameter (α) is estimated based on the state of the component and sometimes for certain substances the extreme number is obtained. The NRTL equation is expressed:

$$\frac{G^E}{nRT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} \tag{14}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{15}$$

$$g_{ii} = g_{jj} = g_{kk} = 0 \tag{16}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \tag{17}$$

$$\alpha_{ij} = \alpha_{ji} \tag{18}$$

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} x_j \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \sum_{k=1}^{n} \frac{x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k}\right) \tag{19}$$

$$X_i = \exp\frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} x_j \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \sum_{k=1}^{n} \frac{x_j \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k}\right) \tag{20}$$

9

$$Y_i = \exp\frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} x_j \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k} \left(\tau_{ij} - \sum_{k=1}^{n} \frac{x_j \tau_{kj} G_{kj}}{\sum_{k=1}^{n} G_{kj} x_k}\right) \tag{21}$$

Where:

G^E	=	molar Gibbs energy
R	=	gas constant
T	=	temperature
x	=	liquid phase mol fraction
i,j,k	=	component of 1, 2, 3, ..., n
α	=	non-random parameter for NRTL
g, G	=	component parameter
γ	=	activity coefficient
τ	=	empirical constant for NRTL

Table 7. The Activity Coefficients were Calculated by UNIFAC Model.

Table 8. The Activity Coefficients were Calculated by NRTL Model.

Table 7 and 8 shows the value of activity coefficient on phenol extraction using methanol solvent obtained from calculation with UNIFAC and NRTL modeling, from coefficient value of activity on each component shows that methanol and acetic acid component in the extract phase is in ideal condition because the value of activity coefficient obtained close to one. The activity coefficient value of phenol and water in the extract phase is not close to one, it means that phenol and water components are far from ideal conditions for the system. The ideal conditions of the components in the system show that the component is dominant, so the properties of the mixture are closer to the dominant component properties either in the extract or rafinate phase. In the raffinate phase, it is known that the bio-oil has a coefficient of activity close to the one, indicating that the bio-oil is in ideal conditions for the system, while the phenol and solvent (acetic acid or methanol) are far from ideal conditions. So non-ideality studies are very important for those systems [21].

Figure 3. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 298 K.

Where:

X_a: mole fraction of component in extract phase

X_b: mole fraction of solvent in extract phase

X_c: mole fraction of water in extract phase

Y_a: mole fraction of component in raffinate phase

10

Y_b: mole fraction of solvent in raffinate phase

Y_d: mole fraction of bio-oil in raffinate phase

Figure 4. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 313 K.

Figure 5. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 323 K.

Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 298 K.

Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 313 K.

Figure 8. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 323 K.

Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 298 K.

Figure 10. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 313 K.

Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 323 K.

Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 298 K.

Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 313 K.

Figure 14. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Acetic Acid by NRTL Model at 323 K.

Where:

γ_a^I: mole fraction of component in extract phase

γ_b^I: mole fraction of solvent in extract phase

γ_c^I: mole fraction of water in extract phase

γ_a^{II}: mole fraction of component in raffinate phase

γ_b^{II}: mole fraction of solvent in raffinate phase

γ_d^{II}: mole fraction of bio-oil in raffinate phase

11

The result of correlation of liquid-liquid equilibrium data by using UNIFAC and NRTL modeling gives good agreement between experimental data and calculation. This is shown by the value of SSE (Sum of the Square of the Error) is very small. The SSE values in UNIFAC and NRTL modeling can be seen in Table 9. The value of SSE is $0.015 - 0.554$.

Table 9. Sum of the Square of the Error (SSE)

Based on Table 9, it can be seen that extraction with methanol solvent for NRTL model has the smallest SSE value compared to the extraction with acetic acid solvent for UNIFAC model. The smaller the SSE values obtained show that the correlation between the experimental data and the calculation data indicates a better correlation. Good correlation results show that equilibrium modeling of UNIFAC and NRTL can be used to predict liquid-liquid equilibrium in phenol extraction process from coconut shell pyrolysis bio-oil and coffee shell using methanol solvent and acetic acid.

Figure 3-14 shows that the visual comparison of calculated and experimental mole fractions in the extract phase and the raffinate phase for the methanol solvent system by NRTL model are better than the other conditions (by UNIFAC model and acetic acid solvent).

4. CONCLUSION

NRTL modeling gives a good correlation to liquid-liquid equilibrium data for ternary system on phenol extraction of bio-oil using methanol solvent compared to the UNIFAC modeling using acetic acid solvent.

The activity coefficients of water and phenol in their phase are far from unity. It means that they are far from ideal condition. The activity coefficients of methanol, acetic acid, and bio-oil in their phases are close to one. It means that they are nearly ideal in their phases.

REFERENCES

[1] N. Sriram, *Renewable biomass energy*. Chicago: Illions Institute of Technology (2005).

12

39

[2] I. Demiral, A. Eryazici, S. Sensoz, S., Bio-oil production from pyrolysis of corncob (zea mays l.), *Biomass Bioenergy* 36 (2012) 43-49.

[3] M. Bertero, G. de la Puente, U. Sedran, Fuels from bio-oils: bio-oil production from different residual sources, characterization and thermal conditioning, *Fuel* 95 (2012) 263-271.

[4] V.C. Pandey, K. Singh, J.S. Singh, A. Kumar, B. Singh, R.P.Singh, Jatropha curcas: A potential bio-fuel plant for sustainable environmental development, *Renew. Sustain. Energy Rev.* 16 (2012) 2870-2883.

[5] C.J. Ellens, R.C. Brown, Optimization of a free-fall reactor for production of fast pyrolysis bio-oil, *Biores. Technol.* 103 (2012) 374-380.

[6] S. Ismadji, S., Kulit durian sebagai bahan baku pembuatan *bio-oil*: sumber energi terbarukan, *Prosiding Seminar Nasional Teknik Kimia Soehardjo Brotohardjono I*, Prodi Teknik Kimia UPN Veteran Jawa Timur (2012) 1-4.

[7] W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal Analytical Applied Pyrolysis.* 76 (2006) 230–237.

[8] Badan Pusat Statistik, 2015.

[9] C.E. Wyman, *Potential Synergies and Challenges in Refining Cellulosic Biomass to Fuels.* Biotechnol Progress (2002).

[10] Direktorat Jenderal Perkebunan. *Produksi Buah Kelapa di Indonesia* (2016).

[11] Joardder. *Pyrolysis of coconut shell for bio-oil.* Bangladesh: Department Of Mechanical Engineering Rajshahi University Of Engineering & Technology (2011).

[12] D. Tamado, E. Budi, R. Wirawan, H. Dwi, A. Tyaswuri, E. Sulistiani, E. Asma. Sifat termal karbon aktif berbahan arang tempurung kelapa, Seminar Nasional Fisika Universitas Negeri Jakarta (2013).

[13] S. Wang, *High Efficiency Separation of Bio-Oil.* InTech (2013).

[14] Kasim, Fitriani, A.N. Fitrah, E. Hambali. Aplikasi asap cair pada lateks. *Jurnal PASTI* 9(1) (2012) 28–34.

[15] A. Jazbinšek, G. Viktor, L.F. Žilnik. *Isolation of phenol and phenolic compounds from fast pyrolysis bio-oil of forestry residue.* Slovenia: National Institute of Chemistry (2008).

[16] S.V. Mantilla., A.M. Manrique, A. Gauthier-Maradei, Methodology for extraction of phenolic compounds of bio-oil from agricultural biomass wastes, *Waste Biomass Valorization* 6 (2015) 371–383.

[17] Dahlia. *Pra rancangan pabrik pembuatan fenol dari tandan kosong kelapa sawit dengan proses pirolisis dengan kapasitas produksi 10.000 ton/tahun.* Medan: Departemen Teknik Kimia Universitas Sumatera Utara (2012).

[18] D. Hartanto, B. Triwibowo, Review model dan parameter interaksi pada korelasi kesetimbangan uap-cair dan cair-cair sistem etanol (1) + air (2) + ionic liquids (3) dalam pemurnian bioetanol. *Jurnal Rekayasa Proses* 8(1) (2014).

13

[19] D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Complex extraction of phenol, o-cresol, and p-cresol from model coal tar using methanol and acetone solutions, *British J Appl. Sci & Technol.* 8(5) (2015) 427-436.

[20] J.M. Smith, H.C. Van Ness, M.M. Abbott, *Introduction to chemical engineering thermodynamics,* 5th edition, Mc Graw Hill International Book Company, New York (1996).

[21] D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Predicting the liquid phase equilibrium of multi-components extraction by thermodynamic models. *Int. J. Thermodyn.* 19(2) (2015) 110-119.

14

Table 1. Material Systems and Conditions for Equilibrium Extraction.

	Quantity
feed	bio-oil
feed volume	2.5 mL
solvent	aqueous methanol
	aqueous acetic acid
mole fraction of water in solvent	0.2
solvent-feed mass ratio	1
shaking time	60 minutes
amplitudo of shaking	150, 200, 250 rpm
temperature	298, 313, 323 K.

Table 2. Conditions of Analysis Using GC

Column: Rastek RXi-5MS

Column:		
Inner diameter	[m]	3.2×10^{-4}
Length	[m]	30
Carrier gas		He
Split ratio	[-]	153
Flow rate	[cm/sec]	26.6
Sample volume	m^3	1.10^{-6}
Injection temperature	[K]	553
Column temperature	[K]	313 – 573
Pressure column	kPa	10.0
Column flow	mL/min	0.54
Detector (FID) temperature	[K]	573

Table 3. The Main Components of Bio-oil Produced by Pyrolysis of Coconut Shells

15

Peak	Component	Percentage
1	Ethyl ester	37.60
2	Formic acid	4.02
3	1-Hydroxy-2-butanone	3.89
4	Furfural	5.45
5	Phenol	40.01
7	2-Methoxy-phenol	7.02

Table 4. The Main Components of Bio-oil Produced by Pyrolysis of Coffee Shells

Peak	Component	Percentage
1	Urea	5%
2	Acetic acid	26%
5	Furfural	6%
6	Phenol	34%
7	Phenol, 2-methoxy-	7%
8	Phenol, 2,6-dimethoxy	4%

16

Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Methanol from Bio-oil Produced from Coconut Shell and Coffee Shell.

Temperature	Biomass	X_a	X_b	X_c	Y_a	Y_b	Y_d
298 K	Coconut Shell	0.096	0.876	0.363	0.229	0.921	0.560
		0.078	0.852	0.370	0.219	0.916	0.653
		0.030	0.863	0.311	0.165	0.950	0.544
	Coffee Shell	0.076	0.926	0.333	0.259	0.891	0.540
		0.058	0.902	0.340	0.249	0.886	0.633
		0.016	0.913	0.281	0.195	0.920	0.524
313 K	Coconut Shell	0.077	0.949	0.043	0.085	0.549	0.365
		0.083	0.956	0.035	0.086	0.414	0.501
		0.071	0.967	0.026	0.062	0.555	0.383
	Coffee Shell	0.087	0.956	0.023	0.365	0.975	0.018
		0.093	0.963	0.025	0.343	0.982	0.014
		0.081	0.974	0.016	0.292	0.986	0.012
323 K	Coconut Shell	0.054	0.972	0.023	0.395	0.945	0.025
		0.051	0.978	0.017	0.373	0.952	0.021
		0.049	0.980	0.015	0.322	0.956	0.019
	Coffee Shell	0.044	0.922	0.033	0.235	0.988	0.010
		0.041	0.928	0.030	0.287	0.991	0.018
		0.039	0.930	0.026	0.343	0.992	0.017

Table 6. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous Acetic Acid from Bio-oil Produced from Coconut Shell and Coffee Shell.

Temperature	Biomass	X_a	X_b	X_c	Y_a	Y_b	Y_d
298 K	Coconut Shell	0.024	0.247	0.365	0.028	0.470	0.672
		0.024	0.370	0.204	0.011	0.537	0.457
		0.024	0.551	0.093	0.019	0.878	0.104
	Coffee Shell	0.033	0.707	0.375	0.033	0.431	0.687
		0.031	0.744	0.214	0.016	0.587	0.472
		0.030	0.764	0.103	0.022	0.832	0.119
313 K	Coconut Shell	0.012	0.707	0.068	0.025	0.907	0.687
		0.011	0.744	0.047	0.008	0.958	0.339
		0.010	0.764	0.036	0.003	0.979	0.019
	Coffee Shell	0.021	0.217	0.078	0.035	0.912	0.702
		0.021	0.340	0.057	0.003	0.963	0.354
		0.020	0.521	0.046	0.002	0.955	0.034
323 K	Coconut Shell	0.012	0.677	0.068	0.025	0.907	0.016
		0.011	0.714	0.047	0.008	0.958	0.012
		0.010	0.734	0.036	0.003	0.979	0.011
	Coffee Shell	0.022	0.677	0.078	0.030	0.896	0.031
		0.021	0.714	0.057	0.005	0.931	0.027
		0.023	0.734	0.046	0.008	0.944	0.026

Table 7. The Activity Coefficients were Calculated by UNIFAC Model.

Solution	Temperature	Biomass	γ_a^i	γ_b^i	γ_c^i	γ_a^{iii}	γ_b^{ii}	γ_d^{iii}
Methanol	298 K	Coconut Shell	0.176	1.969	0.037	0.005	0.063	2.360
			0.032	1.994	0.004	0.008	0.098	2.398
			0.019	1.999	0.003	0.012	0.143	2.435
		Coffee Shell	0.064	1.093	0.067	0.014	0.047	3.112
			0.040	1.024	0.038	0.017	0.063	3.215
			0.027	1.976	0.019	0.022	0.981	3.309
	313 K	Coconut Shell	0.149	1.789	0.006	0.028	0.055	2.143
			0.119	1.791	0.005	0.027	0.070	2.215
			0.112	1.792	0.003	0.034	0.085	2.191
		Coffee Shell	0.157	1.965	0.042	0.023	0.032	2.143
			0.161	1.983	0.029	0.025	0.056	2.215
			0.178	1.992	0.011	0.025	0.062	2.191
	323 K	Coconut Shell	0.049	1.788	0.007	0.017	0.054	2.181
			0.028	1.831	0.001	0.017	0.052	2.222
			0.034	1.870	0.001	0.017	0.052	2.191
		Coffee Shell	0.058	1.625	0.012	0.021	0.041	2.181
			0.063	1.780	0.021	0.036	0.064	2.222
			0.088	1.832	0.028	0.032	0.068	2.191
Acetic Acid	298 K	Coconut Shell	0.199	1.191	0.020	0.023	0.078	3.108
			0.132	1.002	0.018	0.035	0.086	3.150
			0.073	1.015	0.013	0.044	0.086	3.198
		Coffee Shell	0.206	1.222	0.033	0.022	0.083	3.108
			0.325	1.123	0.042	0.043	0.087	3.150
			0.368	1.015	0.047	0.078	0.091	3.198
	313 K	Coconut Shell	0.196	1.021	0.003	0.038	0.081	2.798
			0.152	1.319	0.013	0.040	0.087	2.857
			0.141	1.459	0.014	0.043	0.091	2.836
		Coffee Shell	0.211	1.032	0.033	0.056	0.108	2.798
			0.278	1.804	0.037	0.069	0.115	2.857
			0.305	1.829	0.044	0.053	0.130	2.836
	323 K	Coconut Shell	0.055	1.925	0.037	0.044	0.071	2.705
			0.035	1.967	0.004	0.044	0.076	2.728
			0.042	2.009	0.006	0.044	0.083	2.719
		Coffee Shell	0.087	1.909	0.056	0.063	0.111	2.705
			0.090	1.921	0.067	0.067	0.135	2.728
			0.103	2.001	0.070	0.051	0.155	2.719

Table 8. The Activity Coefficients were Calculated by NRTL Model

Solution	Temperature	Biomass	γ_a^{ii}	γ_b^{ii}	γ_c^{ii}	γ_a^{iii}	γ_b^{iii}	γ_d^{iii}
Methanol	298 K	Coconut Shell	0.077	0.996	0.381	0.005	0.218	2.037
			0.064	0.982	0.337	0.001	0.222	2.037
			0.063	0.998	0.387	1.3×10^{-6}	0.345	2.045
		Coffee Shell	0.132	1.003	0.289	0.001	0.468	1.903
			0.157	1.045	0.376	0.001	0.458	1.923
			0.221	1.067	0.401	0.001	0.312	2.007
	313 K	Coconut Shell	4.47×10^{-5}	1.003	0.010	8.4×10^{-5}	0.278	1.050
			2.71×10^{-6}	1.009	0.056	1.5×10^{-11}	0.308	1.614
			1.80×10^{-5}	1.023	0.039	4.9×10^{-10}	0.347	0.880
		Coffee Shell	0.004	1.000	0.067	0.017	0.280	0.999
			0.005	0.997	0.049	0.003	0.480	1.012
			0.007	1.035	0.006	0.020	0.308	1.003
	323 K	Coconut Shell	7.92×10^{-5}	1.110	0.010	3.6×10^{-5}	0.111	1.028
			3.48×10^{-6}	1.098	0.022	4.1×10^{-16}	0.132	1.006
			9.44×10^{-6}	1.822	0.024	3.5×10^{-12}	0.133	0.937
		Coffee Shell	0.001	1.333	0.054	0.004	0.167	1.012
			0.008	1.412	0.057	0.007	0.175	1.097
			0.008	1.399	0.055	0.103	0.175	1.032
Acetic Acid	298 K	Coconut Shell	0.045	1.209	0.218	0.002	0.210	1.087
			0.039	1.211	0.210	0.015	0.200	1.265
			0.036	1.309	0.232	9.5×10^{-5}	0.200	1.478
		Coffee Shell	0.146	1.448	0.087	0.057	0.234	2.014
			0.155	1.443	0.075	0.059	0.247	2.004
			0.128	1.761	0.102	0.078	0.231	2.065
	313 K	Coconut Shell	0.002	2.069	0.037	0.036	0.126	0.995
			0.003	2.032	0.050	0.030	0.119	0.999
			0.013	1.956	0.069	0.028	0.117	1.000
		Coffee Shell	0.019	1.782	0.023	0.022	0.209	1.119
			0.018	1.834	0.026	0.025	0.211	1.118
			0.021	2.000	0.080	0.025	0.211	1.097
	323 K	Coconut Shell	0.115	1.546	0.037	0.035	0.308	1.139
			0.138	1.690	0.050	0.008	0.311	1.010
			0.200	1.800	0.069	8.9×10^{-5}	0.289	1.021
		Coffee Shell	0.054	1.906	0.046	0.013	0.267	1.290
			0.093	2.035	0.067	0.016	0.234	1.317
			0.093	2.088	0.099	0.021	0.222	1.320

17

Table 9. Sum of the Square of the Error (SSE)

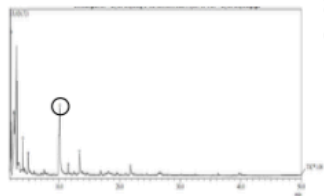| Model	Temperature	SSE	
		Methanol	Acetic Acid
UNIFAC	298	0.087	0.132
	313	0.065	0.083
	323	0.053	0.084
NRTL	298	0.024	0.065
	313	0.026	0.054
	323	0.015	0.077

Figure 1. Analysis Result by GC-MS for the Bio-oil Produced by Coconut Shells Pyrolysis

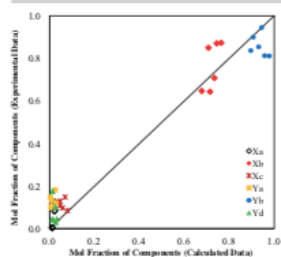Figure 2. Analysis Result by GC-MS for the Bio-oil Produced by Coffee Shells Pyrolysis
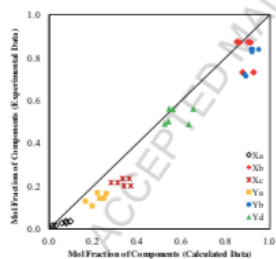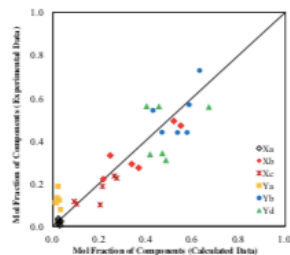
Figure 3. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 298 K.

Figure 4. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 313 K.

Figure 5. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by UNIFAC Model at 323 K.

Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 298 K.

Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 313 K.

Figure 8. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by UNIFAC Model at 323 K.

Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 298 K

Figure 11. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 323 K

Figure 10. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Methanol by NRTL Model at 313 K

Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 298 K

43

Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Aqueous Acetic Acid by NRTL Model at 313 K

Figure 14. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction using Acetic Acid by NRTL Model at 323 K

14. Production has begun on your article [CJCHE_1237] in Chinese Journal of Chemical Engineering

Production has begun on your article [CJCHE_1237] in Chinese Journal of Chemical Engineering Inbox ×

z.espadilla@elsevier.com <z.espadilla@elsevier.com>   Tue, Sep 4, 2018, 10:41 AM

to me

P-authoracknl-v12

Dr Dewi Selvia Fardhyanti
Universitas Negeri Semarang
Faculty of Engineering
Department of Chemical Engineering
Semarang 50236
Indonesia
Phone: +6282227611946
Fax: not available
E-mail: dewiselvia@mail.unnes.ac.id

, 04 September 2018

Our reference: CJCHE 1237
Editorial reference: CJCHE_2018_233

Re: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil
Produced by Biomass Pyrolysis using Thermodynamic Models

To be published in: Chinese Journal of Chemical Engineering

Dear Dr Fardhyanti,

Thank you for choosing to publish in Chinese Journal of Chemical
Engineering.

Please read this e-mail carefully and check that your details are
correct so we can contact you if needed. Please also note your
article's reference number (CJCHE 1237) and quote it in all future
correspondence so we can provide you with the best service.

JOURNAL PUBLISHING AGREEMENT

We are proceeding with the publication of your article on the
understanding that you will complete the 'Journal Publishing
Agreement', which is now available online. To complete the online
form please go to

http://authors.elsevier.com/authorforms/CJCHE1237/42b834bacd98a8f974f37f396b606706

If this link does not work, please copy the entire URL (noting that
it may run on to a second line in this message) into your browser.

Please note if you are an Australian, Canadian, US or UK government
employee and one of your co-authors is not a government employee,
they can complete the form if you forward this e-mail to them.

Please note if you are an Australian, Canadian, US or UK government employee and one of your co-authors is not a government employee, they can complete the form if you forward this e-mail to them.

For further assistance, please visit our customer support site at www.elsevier.com/supportcen. Here you can search for solutions on a range of topics. You will also find our 24/7 support contact details should you need any help from one of our customer support representatives.

Yours sincerely,

Zeneth Espadilla

Elsevier
E-Mail: z.espadilla@elsevier.com
Fax: not available

↩ Reply   ➡ Forward
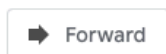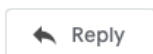
15. Rights and Access form completed for your article [CJCHE_1237]

Rights and Access form completed for your article [CJCHE_1237]

Elsevier - Author Forms <Article_Status@elsevier.com>
to me

Tue, Sep 4, 2018, 12:25 PM

ELSEVIER

Dear Dr Fardhyanti,

Thank you for completing the Rights and Access Form for your article *Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models* on September 04, 2018.

The Order Summary is attached to this email.
Your article will be available to subscribers as soon as it is published.
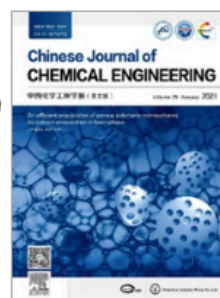
If you have any questions, please do not hesitate to contact us. To help us assist you, please quote our article reference CJCHE1237 in all correspondence.

Now that your article has been accepted, you will want to maximize the impact of your work. Elsevier facilitates and encourages authors to share their article responsibly. To learn about the many ways in which you can share your article whilst

respecting copyright, visit: www.elsevier.com/sharing-articles.

Kind regards,
Elsevier Researcher Support

Have questions or need assistance?
Please do not reply to this automated message.
For further assistance, please visit our Elsevier Support Center where you search for solutions on a range of topics and find answers to frequently asked questions.
You can also talk to our researcher support team by phone 24 hours a day from Monday-Friday and 24/7 by live chat and email.

© 2018 Elsevier Ltd | Privacy Policy http://www.elsevier.com/privacypolicy
Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, United Kingdom, Registration No. 1982084. This e-mail has been sent to you from Elsevier Ltd. To ensure delivery to your inbox (not bulk or junk folders), please add article_status@elsevier.com to your address book or safe senders list.

< />

📄 Order Confirmation...
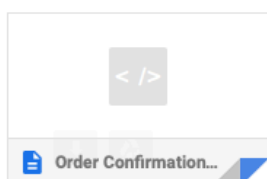
16. Publishing Agreement completed for your article [CJCHE_1237]

Publishing Agreement completed for your article [CJCHE_1237]

Inbox ×

Elsevier - Author Forms <Article_Status@elsevier.com>   Tue, Sep 4, 2018, 12:30 PM
to me

Please note this is a system generated email from an unmanned mailbox.
If you have any queries we really want to hear from
you via our 24/7 support at http://service.elsevier.com

Article title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Article reference: CJCHE1237
Journal title: Chinese Journal of Chemical Engineering
Corresponding author: Dr Dewi Selvia Fardhyanti
First author: Dr Dewi Selvia Fardhyanti

Dear Dr Fardhyanti,

Thank you for completing the Rights and Access Form. Please find attached a copy of the "Journal Publishing (License) Agreement" which you completed online on 4-SEP-2018.

If you have any questions, please do not hesitate to contact us. To help us assist you, please quote our article reference CJCHE1237 in all correspondence.

Now that your article has been accepted, you will want to maximize the impact of your work. Elsevier facilitates and encourages authors to share their article responsibly. To learn about the many ways in which you can share your article whilst respecting copyright, visit: www.elsevier.com/sharing-articles.

We are committed to publishing your article as quickly as possible.

Kind regards,
Elsevier Author Support

HAVE QUESTIONS OR NEED ASSISTANCE?
For further assistance, please visit our Customer Support site where you search for solutions on a range of topics and find answers for frequently asked questions. You can also talk to our customer support team by hone 24 hours a day from Monday-Friday and 24/7 by live chat and email.
Get started at > http://service.elsevier.com

© 2018 Elsevier Ltd | Privacy Policy http://www.elsevier.com/privacypolicy
Elsevier Limited, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, United Kingdom, Registration No. 1982084.
This e-mail has been sent to you from Elsevier Ltd. To ensure delivery to your inbox (not bulk or junk folders), please add article_status@elsevier.com to your address book or safe senders list.

[T-5a-20180404]

Chinese Journal of Chemical Engineering
Transfer of Copyright Agreement

Scientific publishers and authors share a common interest in the protection of copyright: authors principally because they want their creative work to be protected from plagiarism and other unlawful uses, publishers because they need to protect their work and investment in the publication, marketing and distribution of the article written by the author(s) for each article being published. We therefore would like you to complete and return this form promptly, retaining a copy for your records. Your co-operation is essential and appreciated.

Article title: LIQUID PHASE EQUILIBRIUM OF PHENOL EXTRACTION FROM BIO-OIL PRODUCED BY BIOMASS PYROLYSIS USING THERMODYNAMICS MODELS

Author(s): DEWI SELVIA FARDHYANTI, BAYU TRIWIBOWO, HERI ISTANTO, MUHAMMAD KHUSNI ANAJIB, AMALIA LARASATI & WINDY OKTAVIANI.

Company or institution: UNIVERSITAS NEGERI SEMARANG

To be published in the *Chinese Journal of Chemical Engineering*.

Effective upon acceptance for publication, copyright (including all rights thereunder and the right to obtain copyright registration in the name of the publisher, where separately or as a part of proceedings or otherwise) in the above article is hereby transferred throughout the world and for the full term and all extensions and renewals thereof, to Chemical Industry Press.

This transfer includes the right to adapt the article for use in conjunction with computer systems and programs, including reproduction or publication in machine-readable form and incorporation in retrieval systems.

Rights of authors

The publisher recognizes the retention of the following rights by the author(s):
1. Paten and trademark rights and any process or procedure described in the article.
2. The right to photocopy or make single electronic copies of the article for their own personnel use, including for their own classroom use, or for the personal use of colleagues, provided the copies are not offered for sale and are not distributed in a systematic way outside for their employing institution (e.g. via an e-mail list or public file server). Posting of the article on a secure network (not accessible to the public) within the author's institution is permitted.
3. The right, subsequently to publication, to use the article or any part thereof free of charge in a printed compilation of works of their own, such as collected writing or lecture notes.

Note

◆ All copies, paper or electronic or other use of the information must include an indication of

the copyright and a full citation of the proceeding source.

◆ Please refer requests for all uses not included above, including the authorization of other parties to reproduce or otherwise use all or part of the article (including figures and tables), to Editorial Office of   Chinese Journal of Chemical Engineering

Authorship

If the article was prepared jointly with author(s), the signing author has informed the coauthor(s) of the terms of this copyright transfer and is signing on their behalf as their agent and represents that he or she is authorized to do so. Please confirm by ticking the appropriate item following the signature line. The signing author shall bear responsibility for designating the coauthor(s) and must inform the publisher of any changes in authorship.

If copyright is held by the employer, the employer or an authorized representative of the employer must sign. If the author signs, it is understood that this is with the authorization of the employer and the employer's acceptance of the terms of the transfer. Please confirm by ticking the appropriate item following the signature line.
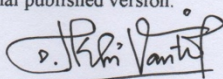
Warranties

The author(s) warrant(s) that the article is the author's original work and has not been submitted or published elsewhere. The author(s) warrant(s) that the article contains no libelous or other unlawful statements, and does not infringe on the rights of others. If except from copyright works are included, the author(s) has (have) obtained or will obtain written permission from the copyrights owners and will credit the sources in the article.
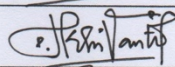
Preprints

The author(s) must agree that if a prior version of this work (normally a preprint) has been posted to an electric public server, they will not update and/or replace the prior version in order to make it identical in contents to the final published version.

First author signature: _____

Corresponding author signature: _____ E-mail address: dewiselvia@mail.unnes.ac.id.

Co-contributor's signature: _____

Date : 05 / 15 / 2018

17. Publication of your article [CJCHE_1237] in Chinese Journal of Chemical Engineering is on hold due to file problems

Publication of your article [CJCHE_1237] in Chinese Journal of Chemical Engineering is on hold due to file problems Inbox x

z.espadilla@elsevier.com <z.espadilla@elsevier.com>
to me

Wed, Sep 5, 2018, 11:57 AM

P-fileproblems-v3

Our reference: CJCHE 1237
Editorial reference: CJCHE_2018_233
To be published in: Chinese Journal of Chemical Engineering
Re: Problems with the files for "Liquid Phase Equilibrium of
Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis
using Thermodynamic Models"

Dear Dr Fardhyanti,

We are pleased to inform you that we have received your
accepted manuscript in Production and now wish to begin the
typesetting process.

Unfortunately we have encountered a problem with the
electronic files you provided and cannot process your article
further until these problems are resolved:

* Multiple manuscript was provided "2018_233.docx and DS
Fardhyanti - Indonesia.docx". Please advise correct version
to be use. Thank you.

Please quote the reference for your article, CJCHE 1237,
in all correspondence. Thank you for your help; I look
forward to hearing from you soon.

Yours sincerely,

Zeneth Espadilla
Elsevier
E-Mail: z.espadilla@elsevier.com
Fax:

18. Your accepted manuscript [CJCHE_1237] is now available online

Your accepted manuscript [CJCHE_1237] is now available online Inbox ×

Elsevier - Article Status <Article_Status@elsevier.com>   Fri, Sep 7, 2018, 9:56 PM
to me

Article title: Liquid Phase Equilibrium of Phenol Extraction from Bio-oil Produced by Biomass Pyrolysis using Thermodynamic Models
Article reference: CJCHE1237
Journal title: Chinese Journal of Chemical Engineering
Corresponding author: Dr Dewi Selvia Fardhyanti
First author: Dr Dewi Selvia Fardhyanti
Accepted manuscript available online: 7-SEP-2018
DOI information: 10.1016/j.cjche.2018.08.011

Dear Dr Fardhyanti,

We are pleased to inform you that your accepted manuscript (unformatted and unedited PDF) is now available online at:

https://doi.org/10.1016/j.cjche.2018.08.011

You might like to bookmark this permanent URL to your article. Please note access to the full text of this article will depend on your personal or institutional entitlements.
This version of your article has already been made available at this early stage to provide the fastest access to your article. It is not intended to be the final version of
your article. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note changes to the

Liquid phase equilibrium of phenol extraction from bio-oil produced by biomass pyrolysis using thermodynamic models

Dewi Selvia Fardhyanti ⚲ ✉, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani

⊞ Show more

Get rights and content

Abstract

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technology for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The totalic phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which contained in bio-oil.

The correlation between experimental data and calculations shows that the UNIQUAC Functional-group Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid–liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non Random Two Liquid (NRTL) equilibrium model can be used to predict liquid–liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

Keywords

biomass; pyrolysis; bio-oil; UNIFAC; NRTL

Recommended articles   Citing articles (0)

View full text

19. Permintaan proof reading dari Elsevier

Proofs of [CJCHE_1237] Inbox ×

Elsevier <corrections.esch@elsevier.spitech.com>   Mon, Sep 10, 2018, 11:23 PM
to me ▾

PLEASE DO NOT ALTER THE SUBJECT LINE OF THIS E-MAIL ON REPLY

Dear Dr Dewi Selvia Fardhyanti,

Thank you for publishing with Chinese Journal of Chemical Engineering . We are pleased to inform you that the proof for your upcoming publication is ready for review via the link below. You will find instructions on the start page on how to make corrections directly on-screen or through PDF.

https://live1.elsevierproofcentral.com/authorproofs/SPIN2695ae0ae3217abfc302705bd3c04b947

Please open this hyperlink using one of the following browser versions:
• Mozilla Firefox 35+
• Microsoft Internet Explorer 11
• Google Chrome 40+
(Note: Mac OS Safari and Microsoft Edge are not supported.)

We ask you to check that you are satisfied with the accuracy of the typesetting, copy-editing, and with the completeness and correctness of the text, tables and figures. To assist you with this, copy-editing changes have been highlighted.

You can save and return to your article at any time during the correction process. Once you make corrections and hit the SUBMIT button you can no longer make further corrections. When multiple authors are expected to make corrections, it important to note that each person does not click the SUBMIT button at the end of their corrections.

20. Corrections received (Elsevier)

Corrections received Inbox ×

optteam@elsevierproofcentral.com via amazonses.com Wed, Sep 12, 2018, 8:27 PM
to me

This is an automatically generated message. Please do not reply because this mailbox is not monitored.

Dear Dr. Dewi Selvia Fardhyanti,

Thank you very much for using the Proof Central application for your article "Liquid phase equilibrium of phenol extraction from bio-oil produced by biomass pyrolysis using thermodynamic models" in the journal "CJCHE"

All your corrections have been saved in our system. Please find attached the PDF summary of your corrections generated from the Proof Central application for your immediate reference.

To track the status of your article throughout the publication process, please use our article tracking service:

http://authors.elsevier.com/TrackPaper.html?trk_article=CJCHE1237&trk_surname=

For help with article tracking:
http://support.elsevier.com/app/answers/detail/a_id/90

Kindly note that now we have received your corrections, your article is considered finalised and further amendments are no longer possible.

For further assistance, please visit our customer support site at http://support.elsevier.com. Here you can search for solutions on a range of topics. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

21. Your article [CJCHE_1237] - is now available online (Elsevier)

https://doi.org/10.1016/j.cjche.2018.08.011
Please note that access to the full text of this article will depend on your personal or institutional entitlements.
This article can already be cited using the year of online availability and the DOI as follows: Author(s), Article Title, Journal (Year), DOI.

WHAT HAPPENS NEXT
You will be automatically notified by e-mail once the full bibliographic details are available.

To track the status of your article throughout the publication process, please use our article tracking service:
https://authors.elsevier.com/tracking/article/details.do?aid=1237&jid=CJCHE&surname=Fardhyanti

Kind regards,
Elsevier Author Support

ADVANCING WOMEN
Advancing women in science and libraries in the developing world:
Every year, the Elsevier Foundation provides grants to institutions around the world, with a focus on support for the world's libraries and for scholars in the early stages of their careers. Since 2002, The Elsevier Foundation has awarded more than 60 grants worth millions dollars to non-profit organizations focusing on helping the world's libraries, nurse faculties, and women scholars during their early and mid-careers. Maybe we can help you.

See the latest call for funding applications at: www.elsevierfoundation.org

HAVE QUESTIONS OR NEED ASSISTANCE?
For further assistance, please visit our Customer Support site where you search for solutions on a range of topics and find answers for frequently asked questions. You can also talk to our customer support team by hone 24 hours a day from Monday-Friday and 24/7 by live chat and email.

Article

Liquid phase equilibrium of phenol extraction from bio-oil produced by biomass pyrolysis using thermodynamic models

Dewi Selvia Fardhyanti *, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib,
Amalia Larasati, Windy Oktaviani

Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang 50229, Indonesia

ABSTRACT

Utilization of biomass as a new and renewable energy source is being actively conducted by various parties. One of the technologies for utilizing or converting biomass as an energy source is pyrolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from the vapor phase of biomass pyrolysis such as coconut shells and coffee shells. Biomass composition consisting of hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The total phenolic compound contained in bio-oil are 47.03% (coconut shell) and 45% (coffee shell). The content of phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosivity, and instability. Phenol compounds have some benefits as one of the compounds for floor cleaners and disinfectants which are contained in bio-oil.

The correlation between experimental data and calculations shows that the UNIQUAC Functional-group Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non-Random Two Liquid (NRTL) equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells.

© 2018 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

The role of fossil fuels is still crucial, but their effects will gradually be overtaken by new and renewable energy sources. Along with the depletion of world oil reserves and environmental issues, various researches on renewable energy are being actively conducted by various parties. Therefore, technology needs be able to overcome the problem. One technology that can be used is pyrolysis technology where the material used comes from organic waste (biomass). Pyrolysis technology can overcome organic waste problems and make the environment healthy by converting waste into value-added end product.

Biomass is an organic material derived from plants, algae, animal waste, industrial waste, forestry, and agricultural waste [1]. Biomass can be used as pyrolysis raw material to produce liquid (bio-oil), gas and solid products. Various kinds of biomass waste can be used as raw materials for the manufacture of bio-oils, such as corncobs [2], sawdust and wheat bran [3], castor [4], oak [5], durian shell [6] and coconut shell [7].

Indonesia is the third largest coffee producer in the world after Brazil and Vietnam by contributing about 6% of the world's total coffee production, also world's fourth largest coffee exporter with a market share of around 11% across the world. Coffee is one of the plantations with high economic value besides chocolate and tea. Based on data from the Indonesian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 691160 tons with a plantation area of 47800 Ha [8]. Waste from coffee processing that is abundant and not utilized optimally is the coffee shell. A large percentage of waste from coffee shells derived from plantations amounts to approximately 11.08% which potentially causes environment hazard. Coffee shells are a waste that has high lignocellulose content which has a potential to be used as bio-oil. Bio-oil is a blackish liquid fuel derived from biomass such as wood, coffee shells and other biomass. Bio-oil contains lignin components (21.4%), cellulose (34.2%) and hemicellulose (24.5%) [8].

In Indonesia, in addition to the coffee shell, one of the available biomass resources is coconut shell. Availability of coconut shell can be seen from the production of coconut fruit in Indonesia. Coconut is one of Indonesia's main commodities with an average production of 3000000 tons per-year [9]. The utilization of coconut is very diverse, but the utilization and way of handling waste are still limited. Coconut fruit can be used as food in daily life for the purpose of direct consumption. Nowadays, lots of coconut shells become garbage that cannot be utilized. One of the waste handling is to utilize coconut shell waste as a base material in the manufacture of bio-oil. Characterization studies

* Corresponding author.
  E-mail address: dewiselvia@mail.unnes.ac.id (D.S. Fardhyanti).

on coconut shells have been done through proximate, ultimate, and Thermo Gravimetric (TG) analyses. The results of this analysis indicate that coconut shell has a high potential to produce fuel fluid by pyrolysis conversion process [10]. Chemical content of coconut shell is cellulose (34%), hemicellulose (21%), lignin (27%) and ash (18%) [11].

Before converted into bio-oil, coconut shell waste and coffee shell need to be treated first. It takes a process before converting the waste of coffee shell into bio-oil which is pyrolysis. Pyrolysis is the process of decomposition of a substance or material that is done at a relatively high temperature. Pyrolysis results in the form of gas, liquid and solid. The solid result of this process is char (char). Gas and liquid products can be used as a source of bio-oil. Bio-oil can be used as an alternative fuel that is easier to store and distribute than biomass in solid form. Bio-oil made from coconut shell material using slow pyrolysis with pyrolysis temperature 250–300 °C produces a liquid which is very acidic and corrosive. The largest organic component in bio-oil is the lignin derivative of phenol, alcohol, organic acids and carbonyl compounds such as ketones, aldehydes and esters [12]. The nature of the acid is caused by the content of the dominant phenol compounds.

Phenol compounds in addition to causing the smell of smoke in bio-oil, also showed antioxidant activity and corrosivity [13]. Therefore, the use of this bio-oil directly cause various difficulties in the combustion system due to high viscosity, low calorific value, corrosivity and instability [6].

Phenol needs to be extracted from bio-oil to reduce its corrosive properties. In addition, phenol is a compound that has a high economic value because it is expensive and widely used. Phenols have many important uses such as disinfectants, resin, pesticides, explosives, and drugs. The method that can be used to extract phenol compounds from bio-oil is by liquid–liquid extraction method using methanol solvent. This has been done by Jazbinšek [14] on the isolation of phenol compounds from bio-oils from pyrolysis of forest waste and Mantilla [15] on the extraction of phenol compounds from bio-oils from pyrolysis of agricultural waste. Dahlia [16] conducted research on liquid–liquid extraction of phenol compound from bio-oil of pyrolysis on salted oil palm oil empty bunch using methanol solvent. The yield of phenol resulting from this extraction is 40%. In this study, it is expected that the liquid–liquid extraction method can be used to separate the phenol compounds from coconut shell pyrolysis bio-oils. The purpose of phenol extraction is to improve the quality of bio-oil and reduce the corrosivity, so when used as fuel, it will cause no damage to the engine.

Biomass pyrolysis converted to bio-oil studies have been conducted. Bio-oil produced from the pyrolysis process can be used as fuel for engines, turbines and boilers. Further processing by the liquid–liquid extraction process will reduce the corrosive nature of bio-oil and obtained chemicals, in which one of them is phenol. Research on extraction of phenol compounds from bio-oil is still very limited. In addition, the thermodynamic modelling study on liquid–liquid equilibrium of the phenol extraction process from bio-oil still needs to be investigated further.

To design extraction columns required much information such as liquid–liquid equilibrium data (liquid–liquid equilibrium). Thermodynamic models such as Equation of State or Activity Coefficient are used to correlate the experimental data to obtain optimal interaction parameters. Optimal parameters can be used to predict liquid–liquid equilibrium data to produce an equilibrium graph that is used to design extraction columns [17]. The study on liquid–liquid equilibrium includes NRTL, e-NRTL, UNIQUAC, and UNIFAC.

Given the importance of thermodynamic modeling in this liquid–liquid extraction process and the price and benefits of phenol in the industrial world, this research becomes an important thing to do. From the equilibrium data, the optimum condition will be obtained where the highest yield of extract is obtained in the extraction process of phenol compound from bio-oil from coconut pyrolysis. Liquid–liquid equilibrium data of the components of the system can be used in the design of the equipment in the separation process.

2. Experimental

2.1. Chemicals

All reagents used here are of A.R. grade and used as received without further purification. Methanol, acetic acid, and chloroform were purchased from e-Merck (Germany). The distilled water is available at the laboratory. Coffee shell and coconut shell were obtained from public market in Semarang.

2.2. Equilibrium procedure

Instruments used in this study:

a) Shaker bath, product by Memmert W814, SV1422, Scwabach, Germany.
b) Gas Chromatography (GC), product by GC 6420 Agilent Technologies, column: Rastek RXi-5MS 0028.
c) Gas Chromatography-Mass Spectroscopy (GC-MS), product by GCMS-QP2010S Shimadzu, column: Rastek RXi-5MS.

The material systems and experimental conditions for the equilibrium extraction are summarized in Table 1.

Table 1
Material systems and conditions for equilibrium extraction

	Quantity
Feed	Bio-oil
Feed volume	2.5 ml
Solvent	Aqueous methanol, Aqueous acetic acid
Mole fraction of water in solvent	0.2
Solvent-feed mass ratio	1
Shaking time	60 min
Amplitude of shaking	150, 200, 250× min⁻¹
Temperature	298, 313, 323 K

The bio-oil feed solution that contains phenol was extracted using two-stage extraction. The first stage uses distilled water as a polar solvent and chloroform as a non-polar solvent. Extraction was conducted with the ice-bath method at 4–5 °C, 200× min⁻¹ and stirring time for 2 h. The extracts obtained at this first stage are used as feeds on the second stage extraction. At the second stage extraction, each extract was extracted using a methanol solvent under operating conditions shown in Table 1.

2.3. Analysis and characterization

After equilibrium was attained (60 min), the mixtures were poured into a separating funnel, settled for an hour and separated into two phases. Then the two phases were weighed. The extract phase and the raffinate phase of each extraction processes are analyzed by GC to obtain the concentration of each component. The principal conditions of this analysis are shown in Table 2.

Table 2
Conditions of analysis using GC

Column: Rastek RXi-5MS	
Column	
Inner diameter/m	3.2 × 10⁻⁴
Length/m	30
Carrier gas	He
Split ratio	155
Flowratio/cm·s⁻¹	26.6
Sample volume/m³	1.10⁻⁶
Injection temperature/K	553
Column temperature /K	313–573
Pressure column/kPa	83.0
Column flow /ml·min⁻¹	0.54
Detector (FID) temperature/K	573

3. Results and Discussion

3.1. Bio-oil content

The chromatograms of the GC-MS analysis are shown in Figs. 1 and 2. The results of the GC-MS analysis of the bio-oil showed that they contained more than six chemical compounds such as ethyl ester, phenol, furfural, acetic acid, and others.

Tables 3 and 4 represent that bio-oil contains more than 6 main components. The percentage (%) of the compositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the height of the peak in the chromatogram. Using a method of GC-MS, this work presents a composition of the bio-oil generated in the experiment. The totally phenolic compounds contained in bio-oil are 47.01% (coconut shell) and 43% (coffee shell). It was caused by the pyrolysis processing at 300–350 °C (low temperature carbonization) that produced more substances containing ester and phenolic compounds. The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil.

3.2. Equilibrium data on phenol extraction of bio-oil from coconut pyrolysis results

In this research the variables studied were temperature, speed of stirring and type of solvents (aqueous methanol and aqueous acetic acid). Generally, all extracts are rich in phenol but the mole fraction significantly depends on extraction conditions: temperature, speed of stirring and type of solvents. Methanol and acetic acid need to be
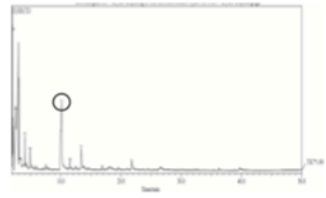
Table 3
The main components of bio-oil produced by pyrolysis of coconut shells

Peak	Component	Percentage
1	Ethyl ester	37.60%
2	Formic acid	4.02%
3	1-Hydroxy-2-butanone	3.69%
4	Furfural	5.45%
5	Phenol	40.03%
7	2-Methoxy-phenol	7.02%

Table 4
The main components of bio-oil produced by pyrolysis of coffee shells

Peak	Component	Percentage
1	Urea	5%
3	Aceticacid	26%
5	Furfural	6%
6	Phenol	34%
7	Phenol, 2-methoxy-	7%
8	Phenol, 2,6-dimethoxy	4%

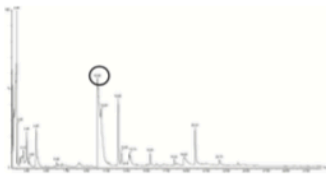**Fig. 1.** Analysis result by GC-MS for the bio-oil produced by coconut shell pyrolysis.

Fig. 2. Analysis result by GC-MS for the bio-oil produced by coffee shell pyrolysis.

mixed with water because their polarities are not strong enough to form an immiscible mixture with bio-oil [17].

The mole fractions of any components in the raffinate phase and the extract phase are constant after 60 min, so the system is assumed to be in equilibrium. The amount of water transferred from the solvent into the raffinate phase was negligible [17].

In this work, we report experimental data for the phenol extraction from bio-oil produced from coconut shell and the phenol extraction from bio-oil produced from coffee shell.

Tables 5 and 6 show the equilibrium of each component extraction data for aqueous acetone and aqueous methanol solvent in the extract phase and raffinate phase.

Table 5
Equilibrium of component extraction data for phenol extraction using aqueous methanol from bio-oil produced from coconut shell and coffee shell

Temperature	Biomass	x_a	x_b	x_c	y_a	y_b	y_c
298 K	Coconut shell	0.030	0.075	0.165	0.220	0.023	0.590
		0.030	0.052	0.170	0.219	0.034	0.555
		0.030	0.063	0.311	0.105	0.050	0.546
	Coffee shell	0.035	0.026	0.155	0.259	0.001	0.540
		0.078	0.002	0.340	0.240	0.003	0.553
		0.036	0.013	0.281	0.105	0.003	0.524
313 K	Coconut shell	0.077	0.040	0.165	0.085	0.040	0.565
		0.040	0.056	0.165	0.006	0.404	0.501
		0.035	0.067	0.026	0.062	0.055	0.585
	Coffee shell	0.035	0.067	0.016	0.023	0.015	0.058
		0.090	0.063	0.025	0.045	0.082	0.014
		0.030	0.074	0.016	0.202	0.086	0.025
323 K	Coconut shell	0.094	0.072	0.026	0.215	0.085	0.025
		0.030	0.070	0.017	0.373	0.052	0.021
		0.040	0.080	0.015	0.322	0.050	0.003
	Coffee shell	0.046	0.022	0.055	0.235	0.088	0.010
		0.046	0.028	0.030	0.287	0.001	0.058
		0.030	0.030	0.026	0.345	0.092	0.017

Table 6
Equilibrium of component extraction data for phenol extraction using aqueous acetic acid from bio-oil produced from coconut shell and coffee shell

Temperature	Biomass	x_a	x_b	x_c	y_a	y_b	y_c
298 K	Coconut shell	0.024	0.247	0.165	0.028	0.470	0.072
		0.024	0.370	0.206	0.031	0.537	0.457
		0.024	0.551	0.065	0.003	0.470	0.104
	Coffee shell	0.031	0.707	0.375	0.031	0.451	0.007
		0.031	0.744	0.214	0.016	0.587	0.072
313 K	Coconut shell	0.030	0.764	0.165	0.022	0.452	0.110
		0.032	0.307	0.068	0.025	0.007	0.087
		0.031	0.744	0.047	0.008	0.058	0.320
	Coffee shell	0.032	0.764	0.016	0.005	0.070	0.016
		0.021	0.217	0.078	0.003	0.012	0.702
		0.021	0.340	0.057	0.003	0.003	0.354
323 K	Coconut shell	0.020	0.521	0.046	0.002	0.005	0.054
		0.012	0.577	0.068	0.025	0.007	0.016
		0.031	0.714	0.047	0.008	0.058	0.012
	Coffee shell	0.030	0.734	0.030	0.005	0.070	0.011
		0.032	0.077	0.078	0.030	0.006	0.003
		0.021	0.714	0.057	0.005	0.031	0.027
		0.025	0.734	0.046	0.006	0.046	0.026

3.3. Liquid–liquid equilibrium for the phenol extraction process using UNIFAC and NRTL models

The UNIFAC and NRTL models were used to correlate the experimental data obtained for the systems under study. The UNIFAC equation and NRTL equation [18] were used to correlate experimental phase equilibrium data. The activity coefficient models applied in this study are as follows:

a) UNIFAC [18]

UNIFAC is a UNIQUAC Functional-group Activity Coefficients model based on the UNIQUAC equation by using functional groups of a molecule contained in the mixture to calculate the activity coefficients. The UNIFAC modeling is a continuation of the UNIQUAC modeling development. This model has the advantage of performing phase equilibrium estimation even in the absence of experimental data. This thermodynamic model is used to predict the estimation of non-electrolyte activity in non-ideal mixture. The UNIFAC model calculates the activity coefficients by using functional group present in the molecules that form the liquid mixture. If the value of the component activity coefficient has a value close to one, this indicates that the component is in the ideal state in the system [19]. The correlation in the UNIFAC model is used in order to reduce the number of binary interactions measured to predict the state of the system. The correlation for the UNIFAC model is shown as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{1}$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \tag{2}$$

$$\ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right] \tag{3}$$

$$J_i = \frac{r_i}{\sum_j r_j x_j} \tag{4}$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \tag{5}$$

$$r_i = \sum_k v_k^{(i)} R_k \tag{6}$$

$$q_i = \sum_k v_k^{(i)} Q_k \tag{7}$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \tag{8}$$

$$\beta_{ik} = \sum_{m} e_{mi} \tau_{mk} \tag{9}$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \tag{10}$$

$$s_k = \sum_m \theta_m \tau_{mk} \tag{11}$$

$$\tau_{mk} = \exp\left(-\frac{a_{mk}}{T}\right) \tag{12}$$

where:

$\ln \gamma_i^C$ combinatorial component
$\ln \gamma_i^R$ residual component
J_i component surface area component (i)
L_i component volume fraction (i)
r_i pure component surface area parameter (i)
x_i pure component mol fraction (i)
q_i pure component volume parameter (i)
$v_k^{(i)}$ number of sub-group (k) on component (i)
R_k parameter area for sub-group (k) ($R_k = A_{wk}/(2.5 \times 10^9)$; where A_{wk} is number of sub-group van der Waals surface area)

Q_k number of parameter volume subgroup (k) ($Q_k = V_{wk}/15.17$, where V_{wk} is number of van der Waals volume subgroup)
a_{mk} group of interaction parameter from groups m and k [17]
x_i liquid mol fraction of component (i)

The UNIFAC equation can be obtained to:

$$\ln \gamma_i = \ln\left[1 - J_i + \ln J_i + 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right)\right] + \ln\left[q_i\left(1 - \sum_k\left(\frac{\sum_i \theta_k \tau_{ik}}{s_k} - \frac{\sum_m \theta_m \tau_{mk}}{s_m} - \frac{v_k^{(i)} Q_k}{q_i} \ln \frac{\sum_m \theta_m \tau_{mk}}{s_m}\right)\right)\right] \tag{13}$$

b) NRTL [18]

Non-Random Two Liquid (NRTL) is derived from the Scott two liquid model and it is assumed that randomness is the same as the model used on the Wilson model. The NRTL model has a non-random parameter (α_{12}) making it possible to use a wide variety of mixtures. The NRTL model uses only binary parameters to calculate the phase equilibrium properties.

The NRTL model is derived from the Scott two liquid model and it is assumed that the non-random parameter is the same as the model used in the Wilson Model. The NRTL equation is developed based on a two-fluid theory with the addition of a non-random parameter (α_i), which makes the equation applicable to different types of liquid–liquid mixture and equilibrium by choosing the appropriate α price. The parameter estimation for this equation is done by setting the α value at a certain value and subsequently optimizing the objective function to obtain two optimal parameter interactions. The recommended α value is 0.2–0.47. The value of α is often adjusted to certain conditions, but usually the value of α = 0.3. Unlike the Wilson equation which contains two adjustable parameters, the NRTL equation contains three parameters, so the NRTL equation can be an alternative model if other models are inadequate. This equation can also estimate the equilibrium of multicomponent systems without additional parameters.

The NRTL equation can represent liquid–liquid equilibrium for both binary and multicomponent systems only with binary parameters. The equation is simpler than the UNIQUAC equation, but it has a disadvantage because it contains three parameters for each pair of components. The third parameter (α) is estimated based on the state of the component and sometimes for certain substances the extreme number is obtained. The NRTL equation is expressed:

$$\frac{G^E}{nRT} = \sum_{i=1}^{c} x_i \frac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{c} G_{li} x_l} \tag{14}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{15}$$

$$g_{ij} = g_{ji} = g_{ii} = 0 \tag{16}$$

$$G_{ij} = \exp(-\alpha_i \tau_{ij}) \tag{17}$$

$$\alpha_{ij} = \alpha_{ji} \tag{18}$$

$$\ln \gamma_i = \frac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{c} G_{li} x_l} + \sum_{j=1}^{c} x_j \frac{G_{ij}}{\sum_{l=1}^{c} G_{lj} x_l}\left(\tau_{ij} - \frac{\sum_{m=1}^{c} x_m \tau_{mj} G_{mj}}{\sum_{l=1}^{c} G_{lj} x_l}\right) \tag{19}$$

$$X_i = \exp \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_l x_l G_{li}} - \sum_j \frac{x_j G_{ij}}{\sum_l x_l G_{lj}}\left(\tau_{ij} - \frac{\sum_l x_l G_{lj} \tau_{lj}}{\sum_l G_{lj} x_l}\right) \tag{20}$$

$$Y_i = \exp \frac{\sum_j y_j G_{ji} \tau_{ji}}{\sum_l y_l G_{li}} - \sum_j \frac{y_j G_{ij}}{\sum_l y_l G_{lj}}\left(\tau_{ij} - \frac{\sum_l y_l G_{lj} \tau_{lj}}{\sum_l G_{lj} y_l}\right) \tag{21}$$

where:

G^E molar Gibbs energy
R gas constant
T temperature
x liquid phase mol fraction
i,j,k component of 1, 2, 3, …, n
α_i non-random parameters for NRTL
g, G component parameter
γ activity coefficient
τ empirical constant for NRTL.

Tables 7 and 8 show the value of activity coefficient on phenol extraction using methanol solvent obtained from calculation with UNIFAC and NRTL modeling, and the coefficient value of activity on each component shows that methanol and acetic acid component in the extract phase is in ideal condition because the value of activity coefficient obtained is close to one. The activity coefficient value of phenol and water in the extract phase is not close to one, it means that phenol and water components are far from ideal conditions for the system. The ideal conditions of the components in the system show that the components is dominant, so the properties of the mixture are closer to the dominant component properties either in the extract or raffinate phase. In the raffinate phase, it is known that the bio-oil has a coefficient of activity close to the one, indicating that the bio-oil is in ideal conditions to

Table 7
The activity coefficients were calculated by UNIFAC model

Solution	Temperature	Biomass	γ_1^s	γ_2^s	γ_3^s	γ_1^r	γ_2^r	γ_3^r
Methanol	298 K	Coconut shell	0.176	1.060	0.037	0.005	0.063	2.340
			0.052	1.004	0.004	0.008	0.098	2.366
		Coffee shell	0.019	1.000	0.005	0.012	0.145	2.435
			0.004	1.001	0.067	0.014	0.047	3.132
			0.040	1.024	0.058	0.017	0.063	3.235
			0.027	1.076	0.010	0.032	0.065	3.389
	313 K	Coconut shell	0.110	1.700	0.006	0.028	0.055	2.146
			0.110	1.761	0.005	0.027	0.070	2.235
			0.112	1.792	0.005	0.085	0.200	2.284
		Coffee shell	0.157	1.985	0.042	0.021	0.052	2.146
			0.161	1.983	0.020	0.025	0.056	2.235
			0.191	1.962	0.011	0.025	0.062	2.284
	323 K	Coconut shell	0.049	1.768	0.007	0.017	0.054	2.118
			0.028	1.831	0.005	0.017	0.052	2.222
			0.035	1.870	0.005	0.017	0.052	2.318
		Coffee shell	0.058	1.675	0.012	0.021	0.041	2.118
			0.063	1.780	0.011	0.036	0.064	2.222
			0.088	1.832	0.058	0.052	0.068	2.318
Acetic acid	298 K	Coconut shell	0.109	1.101	0.020	0.023	0.078	3.130
			0.132	1.082	0.016	0.035	0.065	3.135
			0.116	1.015	0.015	0.044	0.086	3.168
		Coffee shell	0.200	1.222	0.051	0.022	0.085	3.108
			0.325	1.123	0.042	0.043	0.087	3.135
			0.168	1.015	0.047	0.078	0.091	3.168
	313 K	Coconut shell	0.130	1.021	0.005	0.038	0.051	2.708
			0.152	1.310	0.013	0.040	0.087	2.857
			0.141	1.450	0.014	0.045	0.093	2.636
		Coffee shell	0.211	1.052	0.015	0.050	0.198	2.708
			0.278	1.004	0.057	0.040	0.115	2.857
			0.305	1.820	0.044	0.053	0.130	2.636
	323 K	Coconut shell	0.055	1.025	0.017	0.044	0.073	2.708
			0.035	1.067	0.004	0.044	0.100	2.857
			0.042	2.009	0.006	0.044	0.063	2.705
		Coffee shell	0.087	1.009	0.056	0.063	0.111	2.705
			0.080	1.021	0.007	0.037	0.112	2.708
			0.105	2.001	0.070	0.051	0.155	2.706

Note: γ_1^s mole fraction of component in extract phase
γ_2^s mole fraction of solvent in extract phase
γ_3^s mole fraction of water in extract phase
γ_1^r mole fraction of component in raffinate phase
γ_2^r mole fraction of solvent in raffinate phase
γ_3^r mole fraction of bio-oil in raffinate phase.