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 Penulis : Dewi Selvia Fardhyanti, Bayu Triwibowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani Fakultas Teknik, Universitas Negeri Semarang NIP. 197103161999032002

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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-dil. The correlation between experimental data and calculations shows that the UNIQUAC Functionalgroup 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) equilibriummodel can be used to predict liquid-liquid equilibrium in the extraction process of phenol form bio-oil pyrolysis of coffee shells.

Keywords	biomass, pyrolysis, bio-oil, UNIFAC, NRTL
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Corresponding Author	dewi selvia fardhyanti
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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: dewiselvis@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 pytolysis, to convert biomass into a more valuable product which is bio-oil. Bio-oil is a condensed liquid from vapors phase of biomass pytolysis such as cocount thelia and coffee shells. Biomass composition consisting of hemicellaluses, cellaluse, and lignin will oxidize to phenol which is the main content in bio-oil. Bio-oil from coffee shells contains 34% phenol, while 4001% as for phenol content of cocount 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 combastion system due to high viscosity, low calorific value, corosive, and unstable. Phenol compounds have some benefits as one of the compound for floor cleancer 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 coconat 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 faels 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 onrenewable 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 healthrow also convert it mis value-added end product.

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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], darian shell [6] and coconst 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 are a waste that has high lignocellabase content which have potential to be used as bio-oil. Bio-oil is a blackish liquid fael derived from biomass such as wood, coffee shells and ther biomas. Bio-oil contains lignin components (23.4%), cellalose (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 tors /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 shell waste as a base material in the manufacture of bio-oil. Characterization studies on coconut shell waste as a base material in the manufacture of bio-oil. Characterization studies on coconut shell havebeen 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 celluluse (34%), hemicelluluse (21%), lignin (27%) and ash (18%) [22].

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 caster to store and distribute than biomass in solid form. Bio-oil made from coconst 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 liquin derivative of phenol, acebal, organic acids and carboryl compounds such as ketones, addebydes and elses [13]. The nature of the acid is caused by the content of the dominant phenol compounds.

2

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, posticides, 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 Jazhimeck [15] on the isolation of phenol compounds from bio-oils from prodysis of forest waste and Manilla [16] on the extraction of phenol compounds from bio-oils from pryodysis 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 coconst 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, livuid lause 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 fael for engines, turbines and boilers. The bio-oil which processed further by liquidliquid 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 (Liquidliquid 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 UMIFAC. 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 off from coconst 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 coconatshell 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: Reset BV: 6145

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

Table I. 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 4.5 °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. 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 furnel, 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 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 Prausnite (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 nonelectrolyte 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 form the liquid mixture. If the value of the component activity coefficient has a value close to one, this indicates that form the liquid mixture. If the value of 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:

$ln \gamma_i = ln \gamma_i^c + ln \gamma_i^R$		(1)
$\ln \gamma_i^c = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{k}{L_i} + \ln \frac{J_i}{L_i}\right)$		(2)
$\ln \gamma_i^{R} = q_i \left[1 - \sum_k \left(\theta_{k,z_k}^{R_{ik}} - e_{ki} \ln \frac{\beta_{ii}}{z_k} \right) \right]$		(3)
$J_i = \frac{r_{,\kappa_i}}{\sum_j r_{,j}}$		(4)
$L_i = \frac{q_i r_i}{\sum_j q_i x_j}$		(5)
$r_i = \sum_k v_k^{(i)} R_k$		(6)
$q_i = \sum_k v_k^{(i)} Q_k$		(7)
$e_{ki} = \frac{n_k^{(i)}Q_k}{q}$	(8)	
$\beta_{ik} = \sum_m e_{mi} \tau_{mk}$		(9)

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 cocornat shell bio-oil. It shows that cocornat shell bio-oil contained total phenol for 40.01%. The results of GC-MS bio-oil analysis of cocornat 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 47.05% (coconst shell) and 45% (coffee shell). It was caused by the prodysis 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 temperatur, speed of stirring and type of solvents (aqueous methanol and aqueous acetic acid). Generally, 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 transferred 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.

_	
$\theta_k = \frac{\sum_i x_i q_i q_i}{\sum_i x_i q_i}$	(10)
$s_k = \sum_m \theta_m \tau_{mk}$	(11)
$\tau_{mk} = \exp \frac{-a_{nk}}{r}$	(12)

Where:

- $\ln \chi^{C}$ = Combinatorial compon
- ln γ^R = residual component
- J_i = component surface area component (i)
- Li = 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)
- $R_k = -parameter area for sub-group (k) (R_k = A_{vk}/(2.5 \ x \ 10^0), \ where \ A_{vk} \ is number of \ sub-group \ van der \ Walls surface area$
- $Q_k =$ number of parameter volume subgroup (k) (Q_k = V_{vk}/15.17, where V_{vk} is number of Van der Waals volume subgroup)
- area = 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{h}{L_i} + \ln \frac{h}{L_j}\right)\right] + \ln \left[q_i \left[1 - \sum_k \left(\frac{\sum_{i=1}^{r_i \neq i_i} z_{i_i} z_{i_i} e_{i_i}}{\sum_{j=1}^{r_i} q_i - \sum_{k=1}^{r_i} z_{i_k} e_{i_k} z_{i_k}}\right) \frac{z_{i_k} e_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} z_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_k \left(\frac{\sum_{j=1}^{r_i \neq i_i} z_{i_k} e_{i_k}}{\sum_{j=1}^{r_i} q_j}\right) \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k}}{z_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}}{z_{i_k} e_{i_k} e_{i_k}} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k}}}{z_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k} e_{i_k}}}{z_{i_k} e_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k}}}{z_{i_k} e_{i_k} e_{i_k} e_{i_k}}\right] + \ln \left[q_i \left[1 - \sum_{k=1}^{r_i} \frac{z_{i_k} e_{i_k}}}{z_{i_k} e_{i$$

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.

(13)

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 panameter 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 (a), which makes the equation applicable to different types of liquid-liquid mixture and equilibrium by choosing the appropriate a 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 a 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 (a) is estimated based on the state of the component and sometimes for certain substances the extreme number is obtained. The NRTL equation is expressed:

$\frac{G^2}{\pi kT} = \sum_{i=1}^{n} x_i \frac{\Sigma_{i=1}^{n} \tau_i G_{i_i} x_j}{Z_{i_{i=1}}^{n} G_{i_i} x_i}$	(14)
$\tau_{ij} = \frac{g_{ij} - g_{ii}}{g_T}$	(15)
$g_{ii} = g_{jj} = g_{kk} = 0$	(16)
$G_{ij} = \exp(- \propto_{ij} \tau_{ij})$	(17)
$\propto_{ij} \Rightarrow_{ji}$	(18)
$\ln \gamma_i = \frac{\sum_{k=1}^n \tau_{ij} d_{ik} x_i}{\sum_{k=1}^n d_{ik} x_k} + \sum_{j=1}^n \pi_j \frac{x_j d_{ij}}{\sum_{k=1}^n d_{ik} x_i} \tau_{ij} - \sum_{k=1}^n \frac{x_j \tau_{ik} d_{ijk}}{\sum_{k=1}^n d_{ijk} x_i}$	(19)
$X_{i} = e_{2p} \frac{z_{i+1}^{*} v_{i}^{*} d_{i} u_{i}}{z_{i+1}^{*} d_{i} u_{i}} + \sum_{j=1}^{n} z_{\frac{z_{j}^{*} u_{i}}{z_{1}^{*} - d_{i} u_{i}}}^{\frac{z_{j}^{*} u_{i}}{z_{1}^{*} - d_{i} u_{i}}} (t_{ij} - \sum_{i=1}^{n} \frac{z_{j}^{*} u_{i}^{*} d_{i} u_{i}}{z_{1}^{*} - d_{i} u_{i}})$	(20)
$Y_i = exp^{\frac{y_{i-1}^{i} - y_{i}^{i} + y_{i}^{i}}{\sum_{i=1}^{i} e_i x_i}} + \frac{y_{i+1}^{i} + \frac{x_{i+1}^{i}}{\sum_{i=1}^{i} e_i x_i}}{\sum_{i=1}^{i} e_i x_i} - \frac{y_{i+1}^{i} - y_{i+1}^{i}}{\sum_{i=1}^{i} e_i x_i}}$	(21)
Where:	
C ^E — malar Gibbs means	

- G^K = molar Gibbs
- 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
- 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 extinction 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 cocornut 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.

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

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 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.

 -			

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.

NRTL modeling gives a good correlation to liquid-liquid equilibrium data for ternary system on phenol extraction of bin-oil from pyrohysis 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.

ACKNOWLEDGMENTS

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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 x 10 ⁻⁴
Length	[m]	30
Carrier gas		He
Split mtio	[-]	153
Flow rate	[cm/sec]	26.6
Sample volume	m ³	1.10*
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	Furfunl	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	2.6%
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	$\mathbf{X}_{\mathbf{A}}$	Xa	$\mathbf{X}_{\mathbf{C}}$	YA	Ya	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	$\mathbf{X}_{\mathbf{A}}$	Xa	$\mathbf{x}_{\mathbf{c}}$	YA	Ya	Ya
	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	0,005	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

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Solution	Temperature	Speed	Y _A ¹	$\gamma_B{}^I$	γc ¹	$\gamma_A{}^{II}$	$\gamma_B{}^{II}$	$\gamma_D{}^{II}$
		150	0.176	0.769	0.037	2.360	2.063	1.025
	298	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
		150	0.149	0.789	0.006	2.143	2.655	1.016
Methanol	313	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	0.02.8	0.788	0.001	2 222	2.515	1.006
		250	0.034	0.788	0.001	2.191	2.519	1.006
	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
		150	0.196	1.000	0.003	2.798	1.805	1.005
etic Acid	313	200	0.152	0.999	0.013	2.857	1.824	1.002
		250	0.141	0.9.99	0.014	2.836	1.815	1.003
		150	0.055	0.999	0.037	2.705	1.701	1.006
	323	200	0.035	0.999	0.004	2.728	1.701	1.004
		250	0.042	0.999	0.005	2.719	1.711	0.999

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Solution	Temperature	Speed	$\gamma_A{}^I$	$\gamma_B{}^1$	γc ¹	γ_A^{II}	${\gamma_B}^{II}$	${\gamma_D}^{II}$
		150	0.077	0.926	0.381	0.265	2.037	0.655
	298	2.00	0.064	0.482	0.337	0.001	0.039	0.065
		2.50	0.063	0.283	0.387	1.3x10*	0.001	7.6x10 ⁻⁶
		150	4.47x10*	0.942	0.010	8.4x10 ⁻⁷	1.050	0.044
Methanol	313	2.00	2.71x10+	0.986	0.056	1.5x10-11	1.014	1.1x10 ⁻⁶
		2.50	1.80×10^{-5}	0.944	0.039	4.9x10 ⁻¹⁹	0.880	$2.4 x 10^{-12}$
		150	7.92x10*	0.980	0.010	3.6x10 ⁻³	1.02.8	0.025
	323	2:00	3.48x10+	0.977	0.022	4.1x10 ⁻¹⁴	1.006	4.1x10 ⁻¹²
		2.50	$9.44 \mathrm{x10^{-6}}$	0.972	0.024	$3.5 x 10^{-32}$	0.937	1.1x10 ⁻³⁰
		150	0.045	0.644	0.218	0.432	1.087	0.678
	298	200	0.039	0.331	0.210	0.015	0.361	0.552
		2.50	0.036	0.193	0.232	9.5x10 ⁻⁵	0.017	0.027
		150	0.000	0.734	0.037	0.036	0.995	0.551
Acetic Acid	313	200	0.003	0.732	0.050	0.030	0.999	0.444
		2.50	0.013	0.749	0.069	0.028	1.000	0.374
		150	0.000	0.734	0.037	0.035	1.139	0.011
	323	200	0.003	0.732	0.050	0.001	1.010	0.039
		250	0.013	0.749	0.069	8.9x10 ⁻⁶	0.694	9.6x10 ⁻⁷

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

M-4-1	T	SSE				
MINICI	1 emperature	Methanol	Acetic Acid			
	298	0.087	0.132			
UNIFAC	313	0.065	0.083			
	323	0.053	0.084			
	298	0,024	0,065			
NRTL	313	0.026	B-544			
	323	0,015	0,017			

Table 8. The Activity Coefficients were Calculated by NRTL Model



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.

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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



The second secon

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









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

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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

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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

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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 the 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. However, before that, the following minor points should be carefully responded and revised.

Specific comments:

- 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.

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li r ti ti li	n thi esul he li o pr mpo iquio	is study, the author used the liquid-liquid extraction method to separate the phenol compounds from coconut shell pyrolysis bio-oils. T Its show that the correlation between experimental data and calculations shows that the UNIFAC equilibrium model can be used to pr quid-liquid equilibrium in the phenol extraction process of the coconut shell pyrolysis bio-oil. While the NRTL equilibrium model can be edict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis bio-oils. The NRTL equilibrium model can be edict liquid-liquid equilibrium in the extraction process of phenol from bio-oil pyrolysis of coffee shells. Generally, this study presents s trant data on the development of liquid-liquid equilibrium in the extraction process towards pyrolysis bio-oil. This paper fits into the so t-liquid equilibrium in the extraction process. However, before that, the following minor points should be carefully responded and revis	he edict e used ome ope of sed.			
5	Spec	ific comments:				
1	۱.	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 combustion system due to high viscosity"	the			
F	Plea	se give the full name for "UNIFAC equilibrium" and "NRTL equilibrium"				
2	2.	Introduction				
		Paragraph 1 Please add the related contents and references in this paragraph				
з	3.	2.2 Equilibrium Procedure				

"For the first stage, the agua 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 biooil."Please add the detection details

Reviewer 2

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 a

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.

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.

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4. Submit revisi oleh penulis

Received revision CJCHE_2018_233_R1 Inbox ×	Ð	ß	
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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 hemicolulose, 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 guite 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 Functionalgroup Activity Coefficients (UNIFAC) equilibrium model can be used to predic 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 prolysis 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 triwbowo, Heri Istanto, Muhammad Khusni Anajib, Amalia Larasati, Windy Oktaviani
Suggested reviewers	Catherine Peters, dhori hartanto, Ming-Jer Lee

Submission Files Included in this PDF

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

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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:

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

 According to the manning of context, "In Indonesia, in addition to the shell, one of the available biomass resources is coconst shell." should be replaced by "In Indonesia, in addition to the coffee shell, one of the 	 The manuscript has been revised. Line 56.
PART 3: Reviewer B (Green Highlight)	Authors' response to reviewer's comments
analysis used to determine total content of phenol in coconut shell bio- oil". Please add the detection details.	Line 145-155.
5. You mentioned "Gas Chromatography-Mass Spectrometry (GC-MS)	5. The manuscript has been revised.
 Prose revise the x-coordinate and y-coordinate activities, Figure 7- 11&0xff09;, and obtain the correct format. 	 The manuscript has been revised. Line 440-522.
"was conduct"should be "was conducted"	4. The manufacture law series of
What is "aquadest"? Error	
as a non-polar solvent." may be better	Line 129.

 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? 	 This operating temperature has not been y et used for industrial application. It is still used for laboratory system.
 In the section 3.1, "The results of GC-MS bis-oil analysis of coconst 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.
 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". 	 The manuscript has been revised. Line 152. Line 161 and 163.
5. In the section 3.1, there were two nontnees, "It shows that cocount shell bio-oil contained total phonol for 40.01%," and "The total phenolic compounds contained in bio-oil is 47.03% (cocount adult)". The percentages of total phenolic compounds pointed out in these sentnees should be comisent.	5. The manuscript has been revined. Line 155-156.

6. In general, the speed of stirring has no effect on liquid-liquid	6. In general, the speed of stirring has no effect for LLE. It
equilibrium. The speed of stirring has a significant effect on the	was showed from the Table 5 and Table 6 that almost all
composition of liquid-liquid equilibrium from the Table 5 and Table 6.	the compositions of the extract phase and raffinate phase
Why?	for each temperature has approaching the same value. For
	example: T=298 K, XA for speed 150 is 0.007, for speed
	200 is 0.007, and for speed 250 is 0.009, etc.
	Only e few data showed a big difference.
7. The data were too few to describe the liquid-liquid equilibrium well.	7. One of the important thing to describe the LLE is the
Enough datas are required.	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 that
	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.

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

liquid equilibrium under or up 323 K.

used to describe the liquid-liquid equilibrium under There is the same problem for the NRTL equation.

Liquid Phase Equilibrium of Phenol Extraction

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

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

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

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9 9 *Corresponding author Phone: +6282227611946; E-mail: <u>dewiselvia@mail.unnes.ac.id</u>

2 ABSTRACT

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- 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, prolysis such as coconut shells and coffee shells. Biomass composition comsisting of
- 18 hemicellulose, cellulose, and lignin will oxidize to phenol which is the main content in bio-oil. The totalic 19 phenolic compounds contained in bio-oil is 47.03% (coconut shell) and 45% (coffee shell). The content of
- 20 phenol compounds in corrosive bio-oils still quite high, the use of this bio-oil directly will cause various
- 21 difficulties in the combustion system due to high viscosity, low calorific value, corrosive, and unstable.
- 22 Phenol compounds have some benefits as one of the compound for floor cleaner and disinfectant which 23 contained in bio-oil.
- 24 The correlation between experimental data and calculations shows that the UNIQUAC Functional-group
- 25 Activity Coefficients (UNIFAC) equilibrium model can be used to predict the liquid-liquid equilibrium in
- 26 the phenol extraction process of the coconut shell pyrolysis bio-oil. While the Non Random Two Liquid
- 27 (NRTL) equilibrium model can be used to predict liquid-liquid equilibrium in the extraction process of
- 28 phenol from bio-oil pyrolysis of coffee shells.
- .

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

2 1. INTRODUCTION

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24 The role of fossil fuels still be crucial, but their effects will gradually be over taken by new and 25 renewable energy sources. Along with the depletion of world oil reserves and environmental issues.

36 various researches on renewable energy are being actively conducted by various parties. Therefore, 37 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 on overcome organic waste problems and make the environment health valso convert it into value-added

end product.

Biomass is an organic material derived from plants, algae, animal waste, industrial waste [10, Biomass can be used as pyrobysis raw material to produce liquid (hio-oil), gas and solid products. Various kinds of biomass waste can be used as raw materials for the manufacture of biooils, such as concobs [2], sawdast and wheat bran [3], castor [4], oak [5], durian shell [6] and cocornut shell [7].

Indenesia 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 basides chocolate and tea. Based on data from Indonesian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 69,160 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 lignocellalose content which have potential to be used as bio-oil. Bio-oil is a blackish liquid fael derived from biomass such as wook clifee shells and other biomass. Bio-oil contins figuin components (23.4%), cellalose (24.2%) and hemicellalose (24.5%) [9].

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

65 conversion process [11]. Chemical content of coconut shell is cellulose (34%), hemicellulose (21%), 66 lienin (27%) and ash (18%) [12].

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67 Before converted into bio-oil, coconut shell waste and coffee shell need to be treated first. It takes a

68 process before converting the waste of coffee shell into bio-oil which is pyrolysis. Pyrolysis is the

69 process of decomposition of a substance or material that is done at a relatively high temperature. 70 Pyrolysis results in the form of gas, liquid and solid. The solid result of this process is char (char). Gas

- 70 Pytolysis results in the rollin of gas, adjust and sould. The same result of this process is call (call), our and liquid products can be used as a source of bio-oil. Bio-oil can be used as an alternative fuel that is
- 72 easier to store and distribute than biomass in solid form. Bio-oil made from coconut shell material using
- riskow pyrohysis with pyrohysis 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
- 75 carbonyl compounds such as ketones, aldehydes and esters [13]. The nature of the acid is caused by the
- 76 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 83 84 solvent. This has been done by Jazbinsek [15] on the isolation of phenol compounds from bio-oils from 85 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 mpound from bio-oil of pyrolysis resulted of palm oil empty bunch using methanol solvent. The yield 87 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. 89 The purpose of phenol extraction is to improve the quality of bio-oil and reduce the corrosivity, so when 91 used as fuel, it will cause no damage to the engine.

82 Biomass pyrolysis converted to bio-oil studies have been conducted. Bio-oil produced from the 93 pyrolysis process can be used as fuel for engines, turbines and boilers. The bio-oil which processed 94 further by liquid-liquid extraction process will reduce the corrosive nature of bio-oil and obtained

95 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.

98 To design extraction columns required various information such as liquid-liquid equilibrium data 99 (Liquid-liquid Equilibrium). Thermodynamic models such as Equation of State or Activity Coefficient 100 are used to correlate the experimental data to obtain optimal interaction parameters. Optimal parameters 101 can be used to predict liquid-liquid equilibrium data to produce an equilibrium graph that is used to 102 design extraction columns [18]. The study on liquid-liquid equilibrium include NRTL, e-NRTL, 103 UNIOUAC, 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

112 2.1 Chemicals
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 114 All reagents v

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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 coconutshell 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-QP20108 Shimadra,
 column: Rastek RXi-5MS.

125 The material systems and experimental conditions for the equilibrium extraction are summarized in 126 Table 1.

127 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

132 this first stage are used as feeds on the second stage extraction. At the second stage extraction, each 133 extract was extracted using a methanol solvent under operating conditions shown in Table 1. 134

2.3 Analysis and Characterization

- 135 136 137 A fler equilibrium attained (60 minutes), the mixtures were poured into a separating funnel, settled for an
- 138 hour and separated into two phases. Then the two phases were weighed. The extract phase and the 139 raffinate phase of each extraction processes are analyzed by GC to obtain the concentration of each
- 140 component. The principal conditions of this analysis are shown in Table 2.
- 141 Table 2. Conditions of Analysis Using GC
- 142
- 3. RESULTS AND DISCUSSION 143

144 3.1 Rio-Oil Content

- The chromatograms of the GC-MS analysis are shown in Fig. 2 and 3. The results of the GC-MS 145
- nalysis of the bio-oil showed that they contained more than six chemical compounds such as ethyl ester, 146 147 phenol, furfural, acetic acid, and others.
- Figure 2. The Chromatogram of Bio-Oil Produced from Coconut Shell Pyrolysis 148
- Table 3. The Components of Bio-oil Produced from Coconut Shell Pyrolysis 149
- Figure 3. The Chromatogram of Bio-Oil Produced from Coffee Shell Pyrolysis 150
- Table 4. Component of Bio-oil Produced from Coffee Shell Pyrolysis 151
- Table 3 and 4 represent that bio-oil contains more than 6 main components. The percentage (%) of the 152
- mpositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the 151 154
- 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 47.00% 155
- (cocomat shell) and 45% (coffee shell). It was caused by the pyrolysis processing at 300-350°C (low 156
- 157 temperature carbonization) that produce more substances contain ester and phenolic compounds. The 158 composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main
- component of the bio-oil. 159
- 160 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 (aqueo 161
- methanol and aqueous acetic acid). Generaly, all extracts are rich of phenol but the mole fraction 162
- 163 significantly depends on extraction conditions; temperature, speed of stirring and type of solvents.
- 164 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].

197	$J_i = \frac{\tau_i \varkappa_i}{\sum_{j' \in I} \varkappa_j}$		(4)
198	$L_i = \frac{q_i \kappa_i}{\sum_j q_j \kappa_j}$		(5)
199	$r_i = \sum_k v_k^{i}$	$^{(i)}R_k$	(6)
200	$q_i = \sum_k v_k$		(7)
201	12 ⁽¹⁾ Q	<u>.</u>	181
201	$e_{ki} = q$	_	(8)
202	$\beta_{ik} = \sum_{m} \epsilon$	mi ^r mk	(9)
203	$\theta_k = \frac{\sum_i x_i q_i}{\sum_j x_j q_i}$	ne: V	(10)
204	$s_k = \sum_m \theta_r$	n ^T mk	(11)
205	$\tau_{mk} = \exp(-i t r_{mk})$	$\frac{-a_{rel}}{T}$	(12)
206	Where:		
207	$\ln \gamma^{\rm C}$	= Combinatorial component	
208	In _N a	= residual component	
209	J_1	- component surface area component (i)	
210	Li	= component volume fraction (i)	
211	r,	= pure component surface area parameter (i)	
212	\mathbf{x}_{i}	- pure component mol fraction (i)	
213	qi	- pure component volume parameter (i)	
214	$v_k^{(i)}$	= number of sub-group (k) on component (i)	
215	$\mathbf{R}_{\mathbf{k}}$	= parameter area for sub-group (k) ($R_k = A_{uk}/(2.5 \ x \ 10^9)$), where A_{uk} is num	ber of sub-group
216		van der Walls surface arera	
217	Q_k	= number of parameter volume subgroup (k) ($Q_k = V_{vk}/15.17$, where V_{vk} is	s number of Van
218		der Waals volume subgroup)	
219	a _{rek}	- group of interaction parameter from group m and k [18]	
220	\mathbf{x}_{i}	= liquid mol fraction of component (i)	
221	UNIFAC o	equation can be obtained to :	
222	$\ln \gamma_i = \ln$	$\left[1 - J_i + \ln J_i + 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right)\right] + \ln \left[q_i \left[1 - \sum_k \left(\frac{\sum_i x_i q_i \cdot \mathbf{v}_i}{\sum_j q_i}, \frac{\sum_i a_i \mathbf{v}_i \cdot \mathbf{v}_i}{\sum_i a_i \mathbf{v}_i}, \frac{\mathbf{v}_i \cdot \nabla q_i}{q_i}, \frac{\mathbf{v}_i \cdot \nabla q_i}{q_i}\right)\right]$	$\ln \frac{\sum_{in} \sigma_{ini} \tau_{oni}}{\sum_{in} \theta_{ini} \tau_{oni}} \right]$
223		(13)	

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b) NRTL: [20]

- The mole fractions of any components in the raffinate phase and the extract phase are constant after 60 166 167 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]. 168
- 169 In this work, we are reported experimental data for the phenol extraction from bio-oil produced from 170 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.
- 172 Table 5. Equilibrium of Components Extraction Data for Phenol Extraction using Aqueous 174 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

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:

182 a) UNIFAC: [20]

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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 195 coefficients. This model was developed by Fredenslund, Jones, and Prausnitz (1975). The UNIFAC 186 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 190 the liquid mixture. If the value of the component activity coefficient has a value close to one, this indicates 191 that the component is in the ideal state in the system [21]. The correlation in the UNIFAC model is used 192 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:

194	$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R$	(1)
195	$ln \gamma_i^c = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{h}{L_i} + \ln \frac{h}{L_i}\right)$	(2)
196	$ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{z_{ik}} - e_{ki} ln \frac{\beta_{ik}}{z_{ik}} \right) \right]$	(3)

226 Non Random Two Liquid (NRTL) is derived from the Scott two liquid model and it is assumed that 227 randomness is the same as the model used on the Wilson model. The NRTL model has a non-random 228 parameter (q12) making it possible to use in a wide variety of mixtures. The NRTL model uses only binary parameters to calculate the phase equilibrium properties. 229

The NRTL (Non Random Two-Liquid) equation was first developed by Renon and Prausnitz (1968). 231 The NRTL model is derived from the Scott two liquid model and it is assumed that the non-random 232 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 (a), which makes the equation 233 applicable to different types of liquid-liquid mixture and equilibrium by choosing the appropriate a price. The parameter estimation for this equation is done by setting the a value at a certain value and subsequently optimizing the objective function to obtain two optimal parameter interactions. The 237 recommended a value is 0.2 - 0.47. The value of a is often adjusted to certain conditions, but usually the value of a = 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 241 additional parameters.

242 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 243 disadvantage because it contains three parameters for each pair of components. The third parameter (a) 244 is estimated based on the state of the component and sometimes for certain substances the extreme 245 246 number is obtained. The NRTL equation is expressed:

247	$\frac{\partial^{i}}{nkT} = \sum_{l=1}^{n} \frac{\overline{x}_{l=1}^{u} \overline{\tau}_{l} \overline{c}_{l=1}^{u}}{x_{l} \sum_{\substack{n=1\\ n=1}^{n}}^{u} c_{n} x_{n}}$	(14)
248	$\tau_{ij} = \frac{\theta_{ij} - \theta_{ii}}{RT}$	(15)
249	$g_{ii} = g_{jj} = g_{kk} = 0$	(16)
250	$G_{ij} = \exp(- \propto_{ij} \tau_{ij})$	(17)
251	$\propto_{ij} = \propto_{ji}$	
252	$(18)\ln \gamma_i = \frac{\sum_{i=1}^n t_{i/}G_i \kappa_i}{\sum_{k=1}^n G_i \kappa_i} + \sum_{j=1}^n x_{i_j} \frac{x_j G_j}{\sum_{k=1}^n G_i \kappa_k} t_{ij} - \sum_{k=1}^n \frac{x_j \tau_k G_{ik}}{\sum_{k=1}^n G_j \kappa_k}$	(19)
253	$\begin{array}{c} \frac{z_{j-1}^{\prime}c_{i}^{\prime}c_{i}^{\prime}c_{i}^{\prime}}{\sum_{i}-c_{i}c_{i}c_{i}}+\sum_{j=1}^{n}x_{j}\frac{z_{j}c_{i}}{z_{1}^{\prime}-c_{i}c_{i}}c_{i}+\sum_{i=1}^{n}\frac{z_{j}^{\prime}c_{i}c_{i}}{z_{1}^{\prime}-c_{i}c_{i}c_{i}})\\ X_{j}=\exp^{\sum_{i=1}^{n}\frac{z_{i}^{\prime}c_{i}c_{i}}{z_{1}^{\prime}-c_{i}c_{i}c_{i}}+\sum_{i=1}^{n}\frac{z_{i}^{\prime}c_{i}}{z_{1}^{\prime}-c_{i}c_{i}c_{i}})\end{array}$	(20)

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	-	1-19-177 + 5 th	285	to, more macron of solvent in farmate place
254	$Y_i = exp$	$\Sigma_{i=1}^{n} \bar{c}_{k} \bar{x}_{k}^{i} + \bar{a}_{j=1} \bar{a}_{\Sigma_{i=1}^{n}} \bar{c}_{i} \bar{c}_{k}^{i} \bar{c}_{k}^{i(j)} - \bar{a}_{k} = 3 \Sigma_{i=1}^{n} \bar{c}_{jk} \bar{x}_{k}^{j}$ (21)	286	Yd: mole fraction of bio-oil in raffinate phase
			367	Emer 5 Comparison of Coloristical and Experimental Male Experimental Male Experimental States
255	Where:		28)	Figure 5. Comparison of Calculated and Experimental store Fractions of the Friende Extraction
256	G^{E}	- molar Gibbs energy	288	using Aqueous Methanol by UNIFAC Model at 515 K.
257	R	= gas constant	289	Figure 6. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
258	Т	= temperature	290	using Aqueous Methanol by UNIFAC Model at 323 K.
259	х	- liquid phase mol fraction	291	Figure 7. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
260	i,j,k	- component of 1, 2, 3,, n	292	using Aqueous Acetic Acid by UNIFAC Model at 298 K.
261	α	 non-random parameter for NRTL 	202	Emer 9 Comparison of Coloristed and Examinantal Male Exactions of the Blood Extension
262	g, G	 component parameter 	293	Figure 8. Comparison of Calculated and Experimental store Fractions of the Friende Extraction
263	Y	- activity coefficient	294	using Aqueous Acetic Acid by UNIP AC Model at 515 K.
264	τ	= empirical constant for NRTL	295	Figure 9. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
265	Table 7. 1	The Activity Coefficients were Calculated by UNIFAC Model.	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
266	Table 8.	The Activity Coefficients were Calculated by NR TL Model	298	using Aqueous Methanol by NRTL Model at 298 K.
267	Table 7	and 8 shows the value of activity coefficient on phenol extraction using methanol solvent	200	Eigure 11 Comparison of Calculated and Experimental Male Eractions of the Dhand Extraction
268	obtained fi	rom calculation with UNIFAC and NRTL modeling, from coefficient value of activity on each	200	nging Aqueons Mathaned by NPTI Model at 212K
269	componen	t shows that methanol and acetic acid component in extract phase is in ideal condition because	500	using sequeous stemator by sterie stores in 515 K.
270	the value of	of activity coefficient obtained close to one. The activity coefficient value of phenol and water	301	Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
271	activity in	the extract phase is not close to one, it means that the phenol and water components are in less	302	using Aqueous Methanol by NRTL Model at 323 K.
272	than ideal	conditions in the system. The ideal conditions of the components in the system show that the	303	Figure 13. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
273	componen	t is dominant, so the properties of the mixture are closer to the dominant component properties	304	using Aqueous Acetic Acid by NRTL Model at 298 K.
274	cither in th	he extract or rafinate phase. In raffinate it is known that the solvent has a coefficient of activity	305	Figure 11, Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
275	close to th	e one, indicating that the solvent is in ideal conditions in the system, while the phenol and bio-	306	using Ameous Acriic Acid by NRTI, Model at 313 K.
276	oil compo	ments are in less than ideal conditions. So non-ideality studies are very important for those		and reference sector systems in size in
277	systems [2	211.	307	Figure 12. Comparison of Calculated and Experimental Mole Fractions of the Phenol Extraction
			308	using Acetic Acid by NRTL Model at 323 K.
278	Figure 4.	Comparison of Calculated and Experimental store Fractions of the Prienoi Extraction	309	The result of correlation of liquid-liquid equilibrium data by using UNIFAC and NRTL modeling gives
219	using Aqu	reous steinanoi by UNIFAC stonet at 258 K.	310	good agreement between experimental data and calculation. This is shown by the value of SSE (Sum of
280	Where:		311	the Square of the Error) is very small. The SSE values in UNIFAC and NRTL modeling can be seen in
281	Xa: mole	fraction of component in extract phase	312	Table 8. The value of SSE is 0.015 - 0.554.
282	Xb: mole	fraction of solvent in extract phase		Table 0. Come of the Constant of the Propert (CEP)
282 283	Xb: mole Xc: mole	fraction of solvent in extract phase fraction of water in extract phase	313	Table 8. Sum of the Square of the Error (SSE)
282 283 284	Xb: mole Xc: mole Ya: mole	fraction of solvent in extract phase fraction of water in extract phase fraction of component in taffinate phase	313 314	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
282 283 284	Xb: mole Xc: mole Ya: mole	fraction of solvent in extract phase fraction of water in extract phase fraction of component in taffinate phase 10	313 314	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 11
282 283 284	Xb: mole Xc: mole Ya: mole	fraction of solvent in extract phase fraction of water in extract phase fraction of component in inffinate phase 10	313 314	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 11
282 283 284	Xb: mole Xc: mole Ya: mole	fraction of solvent in extract phase fraction of water in extract phase fraction of component in mflinate phase 10	313 314	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 ii
282 283 284	Xb: mole Xc: mole Ya: mole	fraction of solvent in extract phase fraction of water in extract phase fraction of component in mflinate phase 10	313 314	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 ii
282 283 284	Xb: mole Xc: mole Ya: mole	fraction of solvent in extract phase fraction of water in extract phase fraction of component in mffinate phase 10	313 314	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 ii
282 283 284 315	Xb: mole Xc: mole Ya: mole the smalle	fraction of solvent in extract phase fraction of component in mffinate phase 10 st SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC model) and	313 314 348	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 II
282 283 284 315 316	Xb: mole Xc: mole Ya: mole the smalle 0.015 (for	fraction of solvent in extract phase fraction of component in affinate phase 10 set SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC modd) and r NRTL model). The smaller the SSE values obtained show that the correlation between the	313 314 348 349	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 11 [3] M. Bertero, G. de la Paente, U. Sedran, Faels from bio-oils: bio-oil production from different residual sources, characterization and thermal conditioning, Fael 95 (2012) 263-271.
282 283 284 315 316 317	Xb : mole Xc: mole Ya: mole the smalle 0.015 (for experimen	fraction of solvent in extract phase fraction of water in extract phase fraction of component in uffinate phase 10 est SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC model) and r NRTL model). The smaller the SSE value obtained show that the correlation between the tail data and the calculation data indicates a better correlation. Good correlation results show	313 314 348 349 350	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 11 [3] M. Bertero, G. de la Puente, U. Sedran, Fuels from bio-oile: bio-oil production from different residual sources, characterization and formal conditioning. Fuel 95 (2012) 263-271. [4] V.C. Pandey, K. Singh, J. S. Singh, A. Kumar, B. Singh, R.P. Singh, Jatropha curcus : A potential bio-
282 283 284 315 316 317 318	Xb : mole Xc: mole Ya: mole the smalle 0.015 (for experiment that equil	fraction of solvent in extract phase fraction of water in extract phase fraction of component in uffinate phase 10 est SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC model) and r NRTL models. The smaller the SSE values obtained show that the correlation between the tail data and the calculation data indicates a better correlation. Good correlation results show bruin modeling of UNIFAC and NRTL can be used to predict liquid-liquid equilibrium in	313 314 348 349 350 351	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 II [3] M. Bertero, G. de la Paente, U. Sedran, Faels from bio-oils: bio-oil production from different residual sources, characterization and thermal conditioning, Fael 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-
282 283 284 315 316 317 318 319	Xb : mole Xc: mole Ya: mole the smalle 0.015 (for experimen that equil phenol ex	fraction of solvent in extract phase fraction of water in extract phase fraction of component in affinate phase 10 est SSE value compared to other conditions with SSE value of 0.053 (for UNIFAC model) and r NRTL model). The smaller the SSE values obtained show that the correlation between the null data and the calculation data indicates a better correlation. Good correlation between the thil data mild the calculation data indicates a better correlation. Good correlation testuls show thrum modeling of UNIFAC and NRTL can be used to predict liquid-liquid equilibrium in traction process	313 314 348 349 350 351 352	 Table 8. Sum of the Square of the Error (SSE) Based on Table 8, it can be seen that extraction with inclunod solvent with temperature of 323 K has [3] M. Bertero, G. de la Puente, U. Sedran, Fuels from bis-oils: bis-oil production from different residual sources, characterization and thermal conditioning. <i>Fuel</i> 95 (2012) 263-271. [4] V.C. Pandcy, K. Singh, J.S. Singh, A. Kamar, B. Singh, R.P. Singh, Jatopha curcas: A potential bis-fuel plant for sustainable environmental development, <i>Renew. Sustain. Energy Rev.</i> 16 (2012) 2870-2883.
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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.

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388 389 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 298, 313, 323 K. temperature 390 391 392 393 Table 2. Conditions of Analysis Using GC 4 Column: Rastek R.Xi-5MS Column: [m] [m] Inner diameter 3.2 x 10⁻⁴ 30 Length Carrier gas He Splitratio [-] 153

Table 1. Material Systems and Conditions for Equilibrium Extraction.

[cm/sec]	26.6
m ³	1.10*
[K]	553
[K]	313 - 573
k Pa	10.0
mL/min	0.54
[K]	573
	[cm/sec] m ³ [K] [K] kPa mL/min [K]

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Peak	Component	Per	centage					
1	Ethyl ester	3	7.60					
2	Formic acid		4.02					
3 1-F	lydroxy-2-butanon	. 3	3.89					
4	Furfunl	-	5.45					
5	Phenol	4	0.01					
7 2	-Methoxy-phenol	1	7.02					
Table 4. The Peak	Main Component	of Bio-	oil Produce Percer	tage	ås of Coffee	Shells		
1	Urea		5%					
2	Acetic acid		269	6				
5	Furfunl		6%					
6	Phenol		349	6				
7	Phenol, 2-metho	αy-	7%					
7 8	Phenol, 2-metho Phenol, 2,6-dimet	a y- hoay	7% 4%					
7 8 Table 5. Equ oil Produced Temperatu	Phenol, 2-metho Phenol, 2,6-dimet illibrium of Compo- I from Coconut She re Speed	n y- hoxy nents Et II XA	7% 4% straction D Xa	ata for Pher	ol Extractio	n using Aq Ya	acous Meth	anoi from B —
7 8 Table 5. Equ oil Produced Temperatu	Phenol, 2-metho Phenol, 2,6-dimet allibrium of Compo If from Cocon ut She re Speed 150	xy- hoxy ments E: II X _A 0.007	7% 4% xtraction D Xa 0.973	ta for Pher X _C 0.020	ol Extractio	n using Aq Ya 0.316	Neth	an ei frem B
7 8 Table 5. Equ oil Produced Temperatu 298 K	Phenol, 2-metho Phenol, 2,6-dimet Allibrium of Compo- I from Coconut She re Speed 150	a y- hoay ments E X _A 0.007	7% 4% straction D Xa 0.973 0.973	ta for Pher X _c 0.020 0.019	ol Extractio Y _A 0.161 0.116	n using Aqu Ya 0.316 0.313	0.524 0.572	anoi from B — —
7 8 Table 5. Equ oil Produced Temperatu 298 K	Phenol, 2-metho Phenol, 2,6-dimet allbrium of Compo- I from Cocon ut She re Speed 150 200 250	xy- hoxy ments E X _A 0.007 0.007	7% 4% xtraction D Xa 0.973 0.973 0.967	X _c 0.020 0.019 0.024	el Extractio Y _A 0.161 0.116 0.094	n using Aqu Ya 0.316 0.313 0.488	Yp 0.524 0.572 0.418	an ol from B
7 8 Table 5. Equ oil Produced Temperatu 298 K	Phenol, 2-metho Phenol, 2-,6-dimet allbrium of Compo- from Coconut Sho re Speed 150 200 250	a y- hoxy ments E X 0.007 0.007 0.009	7% 4% xtraction D 0.973 0.973 0.967 0.963	xc 0.020 0.024 0.027	el Extractio Y _A 0.161 0.116 0.094 0.085	n using Aqu Ya 0.316 0.313 0.488 0.549	Y ₀ 0.524 0.572 0.418 0.365	and from B
7 8 Table 5. Equ oil Produced Temperatu 298 K 313 K	Phenol, 2-metho Phenol, 2-dimet allbrium of Compo- from Coconut Shu re Speed 150 200 250 150 200	a y- facaxy ments E: X _A 0.007 0.009 0.009 0.008	7% 4% straction D 0.973 0.973 0.967 0.963 0.970	xc 0.020 0.024 0.027 0.022	el Extractio Y _A 0.161 0.116 0.094 0.085 0.086	n using Aqu Ya 0.316 0.313 0.488 0.549 0.414	Y ₀ 0.524 0.572 0.418 0.365 0.501	and from B
7 8 Table 5. Eqn oil Produced Temperatu 298 K 313 K	Phenol, 2-metho Phenol, 2-6-dimet millerium of Comp- from Coconut Sho 200 250 150 200 250	a y- hoxy ments Ex	7% 4% xtraction D 0.973 0.973 0.967 0.963 0.970 0.963	xc 0.020 0.024 0.027 0.022 0.027	el Extractio Y _A 0.161 0.116 0.094 0.085 0.086 0.062	n using Aq1 Ya 0.316 0.313 0.488 0.549 0.414 0.555	Vo 0.524 0.524 0.572 0.418 0.365 0.501 0.383	and from B
7 8 Table 5. Equ oil Produced Temperatu 298 K 313 K	Phenol, 2-metho Phenol, 2-6-dimet millerium of Comp- from Coconut Sho 200 250 150 200 250 150 200 250	a y- fhoxy ments Ex model X A 0.007 0.009 0.009 0.009 0.008 0.010 0.010	7% 4% xtraction D 0.973 0.967 0.963 0.970 0.963 0.970 0.963	x _c 0.020 0.021 0.024 0.027 0.022 0.027 0.028	el Extractie Y _A 0.161 0.116 0.094 0.085 0.086 0.062 0.069	n using Aq1 Ya 0.316 0.313 0.488 0.549 0.414 0.555 0.567	Vo 0.524 0.572 0.418 0.365 0.501 0.383 0.363	anol from B
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Bio-oil Produce	d from Col	fee ShelL						
Temperature	Speed	\mathbf{X}_{A}	Xa	Xc	Ya	Ya	Yp	
	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	0.005	0.841	0.026	0.004	0.980	0.016	

15

0,883 0,016 0,002 0,986

0,001 0,947

0,903 0,012

17

Yp

0,012

0,007

419 420 _ 323 K

200 0,004

250 0,004

Solution	Temperature	Speed	Y _A ¹	$\gamma_B{}^1$	γc ¹	γ_A^{II}	$\gamma_B{}^{II}$	γp
		150	0.176	0.769	0.037	2.360	2.063	1.
	298	200	0.032	0.794	0.004	2.398	2.098	1.0
		250	0.019	0.799	0.003	2.435	2.143	1.5
		150	0.149	0.789	0.006	2.143	2.655	1.0
Methan ol	313	200	0.119	0.791	0.003	2.215	2.700	1.
		250	0.112	0.792	0.003	2.191	2.685	1.5
		150	0.049	0.788	0.007	2.181	2.504	1.0
	323	200	0.028	0.788	0.001	2.222	2.515	1.0
		250	0.034	0.788	0.001	2.191	2.519	1.9
		150	0.199	1.191	0.020	3.108	1.980	1.
	298	200	0.132	1.002	0.001	3.150	1.996	1.9
		250	0.073	1.015	0.001	3.198	2.0161	1.0
		150	0.196	1.000	0.003	2.798	1.805	1.
Acetic Acid	313	200	0.152	0.999	0.013	2.857	1.824	1.5
		250	0.141	0.999	0.014	2.836	1.815	1.0
		150	0.055	0.999	0.037	2.705	1.701	1.5
	323	200	0.035	0.999	0.004	2.728	1.701	1.0
		250	0.042	0.999	0.006	2.719	1.711	0.

18

425 426 Table 8. The Activity Cod NRTL M

Solution	Temperature	Speed	$\gamma_A^{\ 1}$	$\gamma_B{}^1$	γc ¹	$\gamma_A{}^{II}$	$\gamma_B{}^B$	$\gamma_D{}^{11}$
		150	0.077	0.926	0.381	0.265	2.037	0.655
	298	200	0.064	0.482	0.337	0.001	0.039	0.065
		250	0.063	0.283	0.387	1.3x10 ⁻⁶	0.001	7.6x10 ⁻⁵
		150	$4.47 x 10^{ 8}$	0.942	0.010	8.4x10 ⁻⁷	1.050	0.044
Methanol	313	200	2.71x 10 ⁴	0.986	0.056	1.5x10 ⁻¹¹	1.014	1.1x10 ⁻¹
		250	$1.80 \mathrm{x} 10^4$	0.944	0.039	4.9x10 ⁻¹⁰	0.880	2.4x10 ⁻¹
		150	7.92x 10*	0.980	0.010	3.6x10-3	1.028	0.025
	323	200	3.48x 104	0.977	0.022	4.1x10 ⁻¹⁴	1.006	4.1x10 ⁻¹
		250	9.44x10*	0.972	0.02.4	$3.5 x 10^{-32}$	0.937	1.1x10 ⁻³
		150	0.045	0.644	0.218	0.432	1.087	0.678
	298	200	0.03.9	0.331	0.210	0.015	0.361	0.552
		250	0.03-6	0.193	0.232	9.5x10 ^c	0.017	0.027
		150	0.000	0.734	0.037	0.036	0.995	0.551
Acetic Acid	313	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
		150	0.000	0.734	0.037	0.035	1.139	0.011
	323	200	0.003	0.732	0.050	0.001	1.010	0.039
		250	0.013	0.749	0.069	8.9x10 ⁶	0.694	9.6x10 ⁻¹

427 428 429 Table 8. Sum of the Square of the Error (SSE)

		SSE		
Model	Temperature	Methanol	Acetic Acid	
	298	0.087	0.132	
UNIFAC	313	0.065	0.083	
	323	0.053	0.084	
	298	0,024	0,065	
NRTL	313	0.026	19 0,544	
	323	0,015	0,077	



20







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

21





512 513 514 515

517 518





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



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	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

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:

5 and Table 6.

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.

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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

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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.



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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 obase, industrial waste, forestry, and agricultural waste [1]. Biomass can be used as psyrolysis 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 concobs [2], sawdust and wheat bran [3], caster [4], oak [5], durian shell [6] and ecconut shell [7].

Indenesia 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 ori 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 production in 2013 reached 691,160 tons with a plantation area of 47,800 Ha [8]. Waste from coffee production in 2013 reached 691,160 tons with a plantation area of 47,800 Ha [8]. Waste from coffee production in 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 biorol. 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 shells wave as a base material in the manufacture of bio-vil. Characterization studies on coconut shells have been done through proximate, utilimate, and Thermo Gravimetric (TG) analyzes.

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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 plase of biomass pyrolysis such as cocount shells and coffee shells. Biomass comparison consisting of hemicellulose, calldose, 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% (cocount 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 combution system due to high viscosity, low calorfic value, corrosive, and unstable. Phenol compounds have some benefits as one of the compound for Those cleaner and disinfectant which contained inbio-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 cocornt shell profysis blood. 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 pyrobysis of coffee shells.

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

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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 casier to store and distribute than biomass in solid form. Bio-oil made from coconst shell material using slow pyrolysis with pyrolysis temperature 250-300 °C producer liquid which very acidic and corrosive. The largest organic component in bio-oil is the lignin derivative of phenol, akohol, organic acids and carbonyl compounds such as ketones, aldehydes and estens [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 yake because of its expensive and widely used. Phenols have many important uses such as disinfecting, resins, pesticides, explosives, and drugs. The method that can be used to extract thenol 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 arcicultural waste. Dahlia [17] conducted research on liquid-liquid extraction method not liquid-liquid extraction method not for physics of arcicultural 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 sepante the phenol compounds from colour 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 the 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, tarthines and bollets. 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-liquid equilibrium of phenol

ACCEPTED MANUSCRIPT xtraction 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, UNRU/AC, 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 the oil from oceanit pyrolysis. Liquidliquid 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 coopting 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

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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 transferred 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 cocorat 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-1201

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 fredershand, Jones, and Praumitz (1975). The UNIFAC modeling is a continuation of the UNIQUAC modeling development. This model has the advantage of performing phase equilibrium groups immation of non-electrolyte activity in non-ideal mixtures. The UNIFAC 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 toring interactions measured to predict the state of the toring the state of the toring toring toring toring toring the state of the toring toring toring toring toring toring the state of the toring to

$ln \gamma_i = ln \gamma_i^c + ln \gamma_i^R$	(1)
$ln y_i^c = 1 - J_i + ln J_i - 5q_i \left(1 - \frac{l_i}{L_i} + ln \frac{l_i}{L_i}\right)$	(2)
$ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right]$	(3)

system. The correlation for the UNIFAC model is shown as follows:

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at this first stage are used as feeds on the second stage extraction. At the second stage extraction, ea 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

Figure 2. The Chromatogram of bio-Off Froduced from Conce Snea Fyroryse

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 chormatograms. 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% (eccount 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



 $\ln \left\{q_{i}\left[1-\sum_{k}\left(\frac{\sum_{j}x_{i}q_{i}\sigma_{kj}}{\sum_{j}x_{j}q_{j}},\frac{\sum_{m}x_{mi}r_{mk}}{\sum_{m}\theta_{m}r_{mk}}-\frac{x_{k}^{(i)}Q_{k}}{q_{i}},\ln\frac{\sum_{m}x_{mk}r_{mk}}{\sum_{m}\theta_{m}r_{mk}}\right)\right\}\right\}$ (13)

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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 (a), which makes the equation applicable to different types of liquid-liquid mixture and equilibrium by choosing the appropriate a price. The parameter estimation for this equation is done by setting the value at a certain value and subsequently optimizing the objective function to obtain two optimal parameter interactions. The recommended evalue is 0.2 - 0.47. The value of a is tolen 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 (a) is estimated based on the sche of the component and sometimes for certain substances the extreme number is obtained. The NRTL equation is expressed:

$\frac{c^2}{ntr} = \sum_{l=1}^{n} x_l \frac{\sum_{k=1}^{l} x_k c_k x_k}{\sum_{k=1}^{l} d_k x_k}.$	(14)
$\tau_{ij} = \frac{S_{ij} - S_{ij}}{kT}$	(15)
$g_{ii} = g_{jj} = g_{kk} = 0$	(16)
$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$	(17)
$\propto_{ij} = \propto_{\mu}$	(18)
$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ij} (\mathcal{L}_{ij} \mathbf{z}_i)}{\sum_{i=1}^n \mathcal{L}_{ii} \mathbf{z}_i} + \sum_{j=1}^n \mathbf{z}_i \frac{\mathbf{z}_j \mathcal{L}_{ij}}{\sum_{i=1}^n \mathcal{L}_{ii} \mathbf{z}_i} \mathbf{\tau}_{ij} - \sum_{k=1}^n \frac{\mathbf{z}_j \tau_{ik} \mathcal{L}_{ik}}{\sum_{i=1}^n \mathcal{L}_{ij} \mathbf{z}_{ik}}$	(19)
$x_i = e^{\frac{X_{i=1}^{n} \gamma_i c_i x_i}{2\xi_{i=1}^{n} c_i x_i} + \sum_{i=1}^{n} x_i \frac{X_{i=1}^{i}}{\xi_{i=1}^{n} c_i x_i} (x_i - \sum_{i=1}^{n} \frac{x_i \gamma_i c_i a_i}{2\xi_{i=1}^{n} c_i x_i})}$	(20)

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Y_b: mole fraction of solvent in raffinate phase Y_c: 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 1.3. 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:

ya: mole fraction of component in extract phase

- yb1: mole fraction of solvent in extract phase
- γ_c^{I} : mole fraction of water in extract phase
- $\gamma_a^{II}:$ mole fraction of component in raffinate phase
- $\gamma_b^{\mbox{\tiny III}}$ mole fraction of solvent in raffinate phase
- γ_d^{II} : mole fraction of bio-oil in raffinate phase

$\frac{\frac{2^{\mu}_{c1}x_1^{c_1}c_2^{\mu_2}}{2^{\mu}_{c1}c_2^{\mu_2}+\sum_{i=1}^{n}x_i\frac{x_ic_i}{2^{\mu}_{c1}c_ix_i}(x_i-\sum_{i=1}^{n}\frac{x_ix_i}{2^{\mu}_{c1}c_ix_i}x_i)}}{y_i = \exp\left(\frac{x_i}{2^{\mu}_{c1}c_ix_i}+\sum_{i=1}^{n}x_i\frac{x_i}{2^{\mu}_{c1}c_ix_i}}\right)$

(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 cakulation with UNIFAC and NRTE modeling, from coefficient value of activity on each component shows that methanol and acets 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 phases 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 coefficient calue (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:

X₄: mole fraction of component in extract phase X₆: mole fraction of solvent in extract phase X₄: mole fraction of water in extract phase Y₄: mole fraction of component in raffinate phase

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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 ecconut shell pyrolysis bio-oil and coffee shell using methanol solvent and precic 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 temary system on phenol extinction 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.

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

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rak	Component	Percentage
1	Ethyl ester	37.60
2	Formic acid	4.02
3	1-Hydroxy-2-butanon e	3.89
4	Furfural	5.45
5	Phenol	40.01
7	2-Methoxy-phenol	7.02
Peak	Component	Perc
1	Urea	5
2	Acetic acid	2
5	Furfaral	6
6	Phenol	3
7	Phenol, 2-methoxy-	7
8	Phenol, 2,6-dimethox	y _4
		Æ

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

Temperature	Biomass	Xa	$\mathbf{X}_{\mathbf{b}}$	\mathbf{X}_{c}	Ya	$\mathbf{Y}_{\mathbf{b}}$	Ye
		0.096	0.876	0.363	0.229	0.921	0.56
	Coconut Shell	0.078	0.852	0.370	0.219	0.916	0.65
		0.03.0	0.863	0.311	0.165	0.950	0.54
298 K		0.076	0.926	0.333	0.259	0.891	0.54
	Coffee Shell	0.058	0.902	0.340	0.249	0.886	0.63
		0.016	0.913	0.281	0.195	0.920	0.52
		0.077	0.949	0.043	0.085	0.549	0.36
	Coconut Shell	0.083	0.956	0.035	0.086	0.414	0.50
		0.071	0.967	0.026	0.062	0.555	0.38
313 K		0.087	0.956	0.023	0.365	0.975	0.01
	Coffee Shell	0.093	0.963	0.025	0.343	0.982	0.01
		0.081	0.974	0.016	0.292	0.986	0.01
	1	6.054	0.972	0.023	0.395	0.945	0.02
	Coconut Shell	0.051	0.978	0.017	0.373	0.952	0.02
	18	0.049	0.980	0.015	0.322	0.956	0.01
323 K	CV.	0.044	0.922	0.033	0.235	0.988	0.01
C	Coffee Shell	0.041	0.928	0.030	0.287	0.991	0.01
5		0.03.9	0.930	0.026	0.343	0.992	0.01

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		Xa	X _b	\mathbf{X}_{c}	Ya	Y _b	Ya
		0.024	0.247	0.365	0.028	0.470	0.672
	Co conut Shell	0.024	0.370	0.204	0.011	0.537	0.457
		0.024	0.551	0.093	0.019	0.878	0.104
298 K		0.033	0.707	0.375	0.033	0.431	0.687
	Coffee Shell	0.031	0.744	0.214	0.016	0.587	0.472
		0.030	0.764	0.103	0.022	0.832	0.119
		0.012	0.707	0.068	0.025	0.907	0.687
	Co conut Shell	0.011	0.744	0.047	0.008	0.958	0.339
		0.010	0.764	0.036	0.003	0.979	0.019
313 K		0.021	0217	0.078	0.035	0.912	0.702
	Coffee Shell	0.021	0.340	0.057	0.003	0.963	0.354
		0.020	0.521	0.046	0.002	0.955	0.034
		0.012	0.677	0.068	0.025	0.907	0.016
	Co conut She ll	0.011	0.714	0.047	0.008	0.958	0.012
171 K	$\overline{\mathbf{G}}$	0.010	0.734	0.036	0.003	0.979	0.011
ALC R	Y	0.022	0.677	0.078	0.030	0.896	0.031
	Coffee Shell	0.021	0.714	0.057	0.005	0.931	0.027
		0.023	0.734	0.046	0.008	0.944	0.026

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

Solution	Te mper at ure	Biomass	Yal	$\gamma_{\rm b}{}^{\rm i}$	$\gamma_c^{\ i}$	¥a ^{III}	$\gamma_{\rm b}{}^{\rm H}$	$\gamma_d^{\rm III}$
		C	0.176	1.969	0.037	0.005	0.063	2.360
	204.2	Coconat	0.032	1.994	0.004	0.008	0.098	2.398
		Shell	0.019	1.999	0.003	0.012	0.143	2.435
	250 K		0.064	1.093	0.067	0.014	0.047	3.112
		Shell	0.040	1.024	0.038	0.017	0.063	3.215
			0.027	1.976	0.019	0.022	0.981	3.309
		Constant	0.149	1.789	0.006	0.028	0.055	2.143
		Coconut	0.119	1.791	0.003	0.027	0.070	2.215
Mathemat	212.8	onen	0.112	1.792	0.003	0.034	0.085	2.191
stemator	313 K	Coffee	0.157	1.965	0.042	0.023	0.032	2.143
		Shall	0.161	1.983	0.029	0.025	0.055	2.215
		Junca	0.178	1.992	0.011	0.025	0.062	2.191
			0.049	1.788	0.007	0.017	0.054	2.181
		Coconut	0.028	1.831	0.001	0.017	0.052	2.222
	222.8	Shell	0.034	1.870	0.001	0.017	0.052	2.191
	343 %	0.00	0.058	1.675	0.012	0.021	0.041	2.181
		COLEC	0.063	1.780	0.021	0.036	0.064	2.222
		Sheii	0.088	1.832	0.028	0.032	0.068	2.191
		C	0.199	1.191	0.020	0.023	0.078	3.108
		Shall	0.132	1.002	0.018	0.035	0.081	3.150
	704 1	Shen	0.073	1.015	0.015	0.044	0.086	3.198
	250 K	Coffee	0.206	1.222	0.033	0.022	0.083	3.108
			0.725	1.123	0.042	0.043	0.087	3.150
		Suca	0.368	1.015	0.047	0.078	0.091	3.198
		Coconst	0.196	1.021	0.003	0.038	0.081	2.798
		Shall	0.152	1.319	0.013	0.040	0.087	2.857
Acatio Acid	212.8	onell	0.141	1.459	0.014	0.043	0.091	2.836
755 5115 756 16	2124	Coffee /	0.211	1.032	0.033	0.056	0.108	2.798
		Shell	0.278	1.804	0.037	0.069	0.115	2.857
			0.305	1.829	0.044	0.053	0.130	2.836
		Cocomit	0.055	1.925	0.037	0.044	0.071	2.705
		Shell	0.035	1.967	0.004	0.044	0.076	2.728
	323 K	1.4000	0.042	2.009	0.006	0.044	0.083	2.719
		Giffer	0.087	1.909	0.056	0.063	0.111	2.705
	()	Shell	0.090	1.921	0.067	0.067	0.135	2.728
		1.545 C	0.103	2.001	0.070	0.051	0.155	2.719
	()							
	\sim							
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Methanol 2	298 K 113 K	Coonut Shell Coffee Shell Coffee Shell Coffee Shell Coonut Shell	0.077 0.064 0.063 0.152 0.157 0.221 4.47x10 ⁻⁹ 2.71x10 ⁻⁴ 1.80x10 ⁻⁵ 0.064 0.065 0.067 7.92x10 ⁻³ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	0.996 0.982 0.998 1.003 1.045 1.067 1.003 1.009 1.023 1.000 0.997 1.035 1.110 1.088 1.122	0.381 0.337 0.387 0.387 0.387 0.397 0.376 0.401 0.010 0.056 0.067 0.067 0.089 0.067 0.089 0.067	0.005 0.001 1.3x10 ⁴ 0.001 0.001 0.001 0.001 13x10 ⁴ 13x10 ⁴ 45x10 ⁴ 0.017 0.003 0.020 3.6x10 ⁴ 41x10 ⁴	0.218 0.222 0.345 0.468 0.458 0.312 0.278 0.308 0.347 0.280 0.480 0.308 0.3147 0.280 0.440 0.308	2.02 2.03 1.90 1.92 1.03 1.03 0.99 1.04 1.04 1.04 1.04 1.04 1.04	
2 Methanol	198 K 113 K	Coonst Shell Coffee Shell Coonst Shell Coffee Shell Coonst Shell	0.064 0.063 0.132 0.157 0.221 4.47x10 ⁻⁹ 2.71x10 ⁻⁶ 1.30x10 ⁻⁵ 0.004 0.005 0.007 7.52x10 ⁻⁹ 3.48x10 ⁻⁶ 5.44x10 ⁻⁶	0.982 0.998 1.003 1.045 1.067 1.003 1.009 1.023 1.009 1.035 1.010 1.035 1.110 1.038 1.122	0.337 0.387 0.289 0.376 0.401 0.010 0.056 0.039 0.067 0.089 0.000 0.010 0.022	0.001 1.3x10 ⁴ 0.001 0.001 0.001 0.001 0.4x10 ⁴ 15x10 ⁴ 15x10 ⁴ 0.017 0.003 0.020 3.6x10 ⁴ 41x10 ⁴	0222 0345 0468 0458 0312 0278 0308 0347 0280 0480 0480 0308 0111 0132	2.02 2.04 1.90 1.92 2.00 1.02 0.99 1.01 0.99 1.00 1.00 1.00	
Methanol	198 K 113 K	Coffee Shell Coconut Shell Coffee Shell Coconut Shell	0.063 0.132 0.157 0.221 4.47xt0 ⁻³ 2.71x10 ⁻⁴ 1.80x10 ⁻⁵ 0.004 0.005 0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 5.44x10 ⁴ 0.007	0.998 1.003 1.045 1.067 1.003 1.009 1.023 1.000 0.997 1.035 1.110 1.098 1.122	0.387 0.289 0.376 0.401 0.056 0.056 0.057 0.067 0.067 0.089 0.060 0.010 0.022	1.3x10* 0.001 0.001 0.001 3.4x10* 13x10* 4.9x16* 0.017 0.003 0.020 3.6x10* 4.1x16*	0.345 0.468 0.458 0.312 0.278 0.308 0.347 0.280 0.480 0.308 0.308 0.111 0.132	2.04 1.90 1.92 2.00 1.02 0.99 1.00 1.00 1.00 1.00	
 Methanol 	998 K 113 K 223 K	Coffee Shell Coconut Shell Coffee Shell Coconut Shell	0.132 0.157 0.221 447x10 ³ 2.71x10 ⁴ 1.80x10 ⁻⁵ 0.004 0.005 0.007 7.92x10 ³ 3.48x10 ⁴ 8.44x10 ⁴	1.003 1.045 1.067 1.003 1.009 1.023 1.000 0.997 1.035 1.110 1.098 1.422	0.289 0.376 0.401 0.010 0.056 0.039 0.067 0.089 0.000 0.010 0.010 0.022	0.001 0.001 0.001 8.4k10 ⁴ 15x10 ⁴¹ 4.9x16 ⁴⁸ 0.017 0.003 0.020 3.6k10 ⁴ 4.1x16 ⁴⁸	0.468 0.458 0.312 0.278 0.308 0.347 0.230 0.430 0.308 0.308 0.3111 0.132	1.90 1.92 2.00 1.09 1.00 0.99 1.00 1.00 1.00	
Methanol :	113 K 123 K	Coffee Shell Coconut Shell Coffee Shell Coconut Shell	0.157 0.221 4.47x10 ⁻⁹ 2.71x10 ⁻⁶ 1.80x10 ⁻⁵ 0.005 0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.94x10 ⁻⁶	1.045 1.067 1.003 1.009 1.023 1.000 0.997 1.035 1.110 1.098 1.422	0.376 0.401 0.010 0.056 0.039 0.067 0.089 0.000 0.010 0.022 0.022	0.001 0.001 8.4x10 ⁴ 13x10 ¹¹ 4.9x10 ¹⁸ 0.017 0.003 0.020 3.6x10 ⁴ 4.1x10 ¹⁸	0.458 0.312 0.278 0.308 0.347 0.230 0.430 0.308 0.308 0.111 0.132	1.92 2.00 1.02 0.99 1.00 1.00 1.00 1.00	
Methanol :	113 K 123 K	Shell Coconut Shell Coffee Shell Coconut Shell	0.221 4.47x10 ⁻⁸ 2.71x10 ⁻⁶ 1.80x10 ⁻⁵ 0.004 0.005 0.007 7.92x10 ⁻³ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	1.067 1.003 1.009 1.023 1.000 0.997 1.035 1.110 1.098 1.422	0.401 0.010 0.056 0.039 0.067 0.089 0.006 0.000 0.010 0.010 0.022	0.001 8.4x10 ⁴ 1.5x10 ¹⁰ 4.9x16 ¹⁸ 0.007 0.003 0.020 3.6x10 ⁴ 4.1x16 ¹⁸	0.312 0.278 0.308 0.347 0.280 0.480 0.308 0.111 0.132	2.00 1.09 1.01 0.38 0.99 1.01 1.00 1.02	
Methanol :	113 K.	Coconut Shell Coffee Shell Coconut Shell	4.47x10 ⁻⁹ 2.71x10 ⁻⁶ 1.30x10 ⁻³ 0.004 0.005 0.007 7.92x10 ⁻³ 3.43x10 ⁻⁶ 9.44x10 ⁻⁶	1.003 1.009 1.023 1.000 0.997 1.035 1.110 1.098 1.422	0.010 0.056 0.039 0.067 0.089 0.000 0.010 0.010 0.022	8.4c10 ⁴ 13x10 ¹⁰ 49x10 ¹⁰ 0.007 0.003 0.020 3.6c10 ³ 4.1x10 ¹⁰	0.278 0.308 0.347 0.280 0.480 0.308 0.111 0.132	1.0 1.0 0.3 0.9 1.0 1.0 1.0	
Methanol :	113 K 123 K	Coconut Shell Coffee Shell Coconut Shell	2.71x10 ⁻⁶ 1.80x10 ⁻⁵ 0.004 0.005 0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.44x10 ⁴	1.009 1.023 1.000 0.997 1.035 1.110 1.098 1.422	0.056 0.039 0.067 0.089 0.090 0.000 0.010 0.010 0.022 0.021	13x10" 49x10" 0.017 0.003 0.020 3.6x10" 4.1x16"	0.308 0.347 0.280 0.480 0.308 0.111 0.132	1.0 0.8 0.9 1.0 1.0 1.0	
-	113 K 123 K	Shell Coffee Shell Coconut Shell	1.80x10 ⁻⁵ 0.004 0.005 0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	1.023 1.000 0.997 1.035 1.110 1.098 1.422	0.039 0.067 0.089 0.090 0.000 0.010 0.022 0.022	49x16 ¹⁸ 0.017 0.003 0.020 3.6x10 ² 4.1x10 ¹⁸	0.347 0.280 0.480 0.308 0.111 0.132	0.89 0.99 1.01 1.02 1.02	
	113 K 123 K	Coffee Shell Coconut Shell	0.004 0.005 0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	1.000 0.997 1.035 1.110 1.098 1.422	0.067 0.089 0.090 0.000 0.010 0.022 0.021	0.017 0.003 0.020 3.6x10 ⁹ 4.1x10 ¹⁰	0.280 0.480 0.308 0.111 0.132	0.99	
	23 K	Coffee Shell Coconut Shell	0.005 0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	0.997 1.035 1.110 1.098 1.422	0.089	0.003 0.020 3.6x10 ³ 4.1x10 ³⁴	0.480 0.308 0.111 0.132	1.0	
	23 K	Shell Coconut Shell	0.007 7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	1.035 1.110 1.098 1.422	0,000	0.020 3.6x10 ³ 4.1x10 ¹⁸	0.308	1.0	
	23 K	Coconut Shell	7.92x10 ⁻⁸ 3.48x10 ⁻⁶ 9.44x10 ⁻⁶	1.093 1.110 1.098 1.422	0.000	3.6x10 ³ 4.1x10 ¹⁸	0.111 0.132	1.0	
1	23 K	Coconut Shell	3.48x10 ⁻⁶ 9.44x10 ⁻⁶	1.098	0.022	4.1x10 ⁻¹⁰	0.132	1.04	
3	23 K	Shell	9.44x10 ⁴	1.098	0.022	4.1X10	0.1.5.2		
3	123 K		2.44310	1.122		7.0.1022	0.177	1.0	
					0.024	3.3410	0.133	0.9	
		Coffee Shell	0.000	1.00	0.054	0.004	0.16/	1.0	
			0.008	1.412	0.057	0.007	0.175	1.08	
			0.008	1.389	0.055	0.109	0.1/5	1.0	
		Coconut	0.040	1.209	0.218	0.002	0.210	1.08	
		Shell	0.035	1.200	0.210	0.013	0.200	1.47	
-	298 K.	98 K	0.046	1.349	0.087	0.057	0.200	2.01	
		Coffee	Coffee	0.155	1.443	0.075	0.0.99	0.247	2.00
		Shell	0.128	1.761	0.102	0.078	0.231	2.06	
			0.002	2.003	0.037	0.036	0.126	0.99	
		Coconig	0.003	2.032	0.050	0.030	0.119	0.99	
		Silen	0.013	1.956	0.069	0.028	0.117	1.00	
Accele Aces	1.5 K	Cattor	0.019	1.782	0.023	0.022	0.209	1.11	
		Shell	0.018	1.834	0.026	0.025	0.211	1.11	
		~	0.021	2.000	0.080	0.025	0.211	1.09	
		Coconst	0.115	1.546	0.037	0.035	0.308	1.13	
		Shell	0.138	1.690	0.050	0.008	0.311	1.01	
3	23 K	-	0.200	1.800	0.069	8.9x10	0.289	1.02	
	~~	Coffee	0.054	1.906	0.046	0.013	0.267	1.29	
	C \	Shell	0.093	2.035	0.067	0.016	0.234	1.31	









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



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

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Liquid phase equilibrium of phenol extraction from bio-oil produced by biomass pyrolysis using thermodynar	nic
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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

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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, University, Nativersity, Nativersity, Semanang, Semanang, Sci206, Jackowski

ARTICLE INFO Á B S T B Á C T Article Datage: Recti and 22 February 2018 Utilization of biomam as a new and renewable energy source is being actively conducted by various parties. One of the technologies for at lizing or converting biomass as an energy source is pyrodysis, to convert biomass into a more valuable product which is bio-of. Bio-of is a condensed liquid From the vapor phase of biomass pyrolysis Rept and increased for m25 (say 2018) Acopted 1 August 2018 Available online 7 Septem such as coconat shells and office shells. Biomass composition consisting of homicefuloue, orligin w, and Egsin will oxidize to phonol which is the main content in bio-oil. The total phonolic compound scontained in bio-oil alter 2018 are 47.033 (second shell) and 435 (sofflee shell). The content of phonol compounds in corrosive bio oftentill quite high, the use of this bio oil directly will once various difficulties in the combaction system due to high vis-Distant recalerific value, menoivity, and instability. Phonal compounds have some box offs as one of the comcontry la Parabolis pough for floor cleaners and disinfectants which are contained in his-cill lio-ol UNEX tereon experimental data and calculations shows that the UNQUACFunctional-group Activity The o

Coefficients (UNEAC) equilibrium model can be used to predict the liquid -liquid equilibrium in the phenol entraction process of the commut shell pyrelpis bio-oil. While the Nan-Bandom Two Liquid (NEE) equilibrium modelcan be used to predict liquid-liquid equilibrium in the extraction process of phenolfro of college-sheets

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1. Introduction

NO.

The role of the all facts is still crucial, but their effects will endually be overtaken by new and mnewable 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 he 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 a gricultural waste [1]. Bomass 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

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production, also world's fourth largest coffee exporter with a market share of around 11% across the world. Coffee is one of the plast ations with high economic value besides chocolate and tea. Rased on data from the Indone sian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 691 160 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 shelk derived from plast ations a mounts to approximately 11.08% which potentially causes environment hazard. Goffee shells are a waste that has high lignocellulose contest which has a potential to he used as bio-oil. Bio-oil is a blackish liquid fuel derived from biomass such as wood, soffice shells and other biomass. Bio-oil contains lignin components (23.40), cellulose (34.25) and hemicellulose (24.50) [8].

In Indonesia, in addition to the coffee the L one of the available biomass resources is coconut shell. Availability of costonat shell can be seen from the production of coconut fruit in Indonesia. Goconut 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 coconat shells become garbage that cannot be utilized. One of the wate handling is to utilize coconut shell waste as a base material in the manufacture of bio-oil. Characterization studies

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phenoi extraction purcess from files of sufficient to be investigated further. To de sign extractions columns required much shadness in such as pland-signed equiphers, the sum of the sum of the sum such as the sum of the equilibrium data to produce an explain layer to the sum of the induction of the sum of the design of the sum of the sum of the sum of the sum of the design of the sum of the sum of the sum of the sum of the design of the sum of the sum of the sum of the sum of the design of the sum of the design of the sum of the sum

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Table 1 Equil b from b

	Quartery
lived	lio-of
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Salvera	Aqueona resthaned Aqueona acetic with
Mole Baction of water in solwest	0.2
Solwest-Beedman ratio	1
Starking time	GD min
Jempilikale of shaking	150 200,250 r-min ⁻¹
Temperature	296 313, 323 K

After equilibrium was attained (40 min), the minture sweet into a coparating faunch, settled for an hear and esparated phases. Then the two phases were weighed. The extract phase radifiance phase of each estraction processes are assigned to obtain the concentration of each component. The principal co officia analysis are shown in Table 2.

Columns: Rastels R36-5NES	
Critaren	
ister discuster)m	3.2×10^{-1}
Larageth, ins.	30
Carrier gas	18
Split ratio	103
Row natalone a	26.6
Sample volume/m ²	1.107-1
Injection temperature/C	20
Cohamo termperatar e%	343-573
Provinger column/APa	10.0
Column/flow init-min-1	0.54
Detector (FD) itemperature/K	53



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	e Bonas		х,	X4	Х,	π.	¥ _k	Y4
218 K	Corners# 1	will .	DINK	0.876	0.363	0.229	0.521	0.560
			0.078	0.852	0.370	0.219	0.596	0.653
			0.030	0.863	0.311	0.165	0.950	0.544
	Collee she	8	0.0%	0.126	0.332	0.259	0,893	0.540
			0.0%	0.5852	0.340	0,249	0.88G	0.622
			DDE	0.913	0.281	0.195	0.520	0.524
313K	COURSE 1	wii i	0.077	0.949	0.045	0.085	0.549	0.365
			0.078	0.007	0.035	0.000	0.555	0.565
	Collected at		0.007	0.056	0.005	0.505	0.075	0.005
			DOTE	0.963	0.025	0.343	0.562	0.014
			0.08	0.074	0.016	0.252	0.586	0.012
323 K	Course al	lul l	0.0%	0.972	0.023	0.305	0.045	0.025
			0.0%	0.97\$	0.017	0.373	0.952	0.021
			0.040	0.560	0.015	0.322	0.956	0.019
	Colline shat		D.D.W	0.102	0.033	0.225	0.566	0.010
			0.04	0.125	0,030	0.287	0.991	0,018
			0.030	0.530	0,026	0.343	0.962	0.017
alain 6								
out being of	componentito es	anai	er dete Br	r pheres	d estrati	ionusing		aretic add
ran bio-cilp	roduced from a	cons.	shell an	1 coller	Baller			
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respected	*	γ_i	- 14		· · · · · · · · · · · · · · · · · · ·	T 4	τ_k	14
216K 0	line taroo	0.024	6 0.24	(7 E	1365	0.025	0.470	0.672
		0.024	6 0.33	10 0	1,204	0.011	0.537	0.457
		0.024	0.55	1 6	0.065	0.019	0.875	0.104
0	dec dall	0.033	0.76	17 6	1375	0.033	0.431	0.687
		0.031	0.74	H 0	1214	0.036	0.547	0.472
		0.034	0.76	и с	1102	0.022	0.832	0.119
313K O	occurat shell	0.01	2 0.76	17 6	0.0628	0.025	0.5607	0.687
		0.011	0.74	н	3.D47	0.006	0.154	0.339
		0.031	0.78	н с	0.036	0.003	0.979	0,019
	dee dad!	0.021	0,21	7 6	0.079	0.035	0.912	0.702
0		0.021	0.34	60 6	3485.7	DIRG	0.1853	0.354
0				1 6	ND4G	DIRG	0.955	0.034
0		0.025	9 0.54		STR2D	0.025	0.5857	0.016
0 323.K 0	iomat shell	0.020	0.52			0.006	0.954	0.012
о 323К О	ionnut shell	0.020 0.012 0.012	0.52	4 0	ND47		10.00716	mpii
0 323.K 0	ionnat shell	0.020 0.012 0.011 0.011	0.52 0.67 0.71 0.71 0.71 0.71 0.71 0.71 0.71 0.7	4 0	NEMET NETGEG	DURG	0.000	
о 323К О О	ionnat shell idheeshdil	0,120 0,012 0,011 0,010 0,020	0.52 0.67 0.67 0.67 0.67 0.67 0.67 0.67 0.67	14 E 14 E 17 E	0.0467 0.0546 0.0778	0.003	0,896	0.051
о 323К О О	inconut shell infloc shell	0,120 0,011 0,011 0,011 0,011 0,012	9 0.52 2 0.67 1 0.77 2 0.67 1 0.77 1 0.77	14 E 14 E 17 E	ND417 ND345 ND778 ND577	0.003	0,896	0.051 0.027
а 329.К О О	isconst shell isffee shell	0.020 0.011 0.011 0.021 0.021 0.021 0.021	9 0.52 0.67 0.77 0.677 0.677 0.677 0.677 0.677 0.77 0.77	14 0 14 0 17 0 14 0 14 0	NDMI7 NDS45 ND578 ND577 NDM65	0.003 0.005 0.005	0,8%	0.051 0.027 0.026
323-K 0	inconst shell influe shell	0.021 0.011 0.011 0.021 0.021 0.021 0.021	9 0.52 0.67 0 0.77 0 0.77 0 0.67 1 0.77 1 0.77		x047 x036 x079 x057 x046	0.003 0.030 0.005 0.008	0,896 0,951 0,944	0.051 0.027 0.026
323.K 0	occenat shell office shell	0.021 0.011 0.011 0.021 0.021 0.021 0.021	9 0.52 0.67 0 0.77 0 0.77 0 0.67 1 0.77 1 0.77		1047 1056 1079 1057 1046	0.005 0.050 0.005 0.008	0,896 0,951 0,944	0.031 0.027 0.026
0 323.K O	occenat shell office shaft	0.021 0.011 0.021 0.021 0.021 0.021	0 0.52 0 0.62 0 0.71 0 0.72 0 0.62 1 0.71 0 0.73		x0407 x0536 x0778 x0757 x07465	0.005 0.005 0.006	0,896 0,951 0,944	0.031 0.027 0.026
а 323К О О	occenat shell office shall	0.021 0.011 0.021 0.021 0.021 0.021	0 0.52 0 0.67 0 0.77 0 0.77 0 0.77 1 0.77 1 0.77 1 0.77		1047 1056 1078 1057 1046	0.005 0.005 0.006	0,896 0,951 0,944	0.031 0.027 0.026
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0 323 K 0 0	oconst shell office shell diqueid equal	0.012 0.011 0.011 0.021 0.021 0.021 0.021	n for d	he ph	0007 0036 0078 0057 0046	0.003 0.030 0.005 0.006	0,896 0,951 0,944	ortsi ortsi ortso ortso
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0 323.K 0 0 1.J. Liquid INFAC and The UN	oconst shell offee shell -liquid equil INRTL mode EAC and NRC	bitta bitta bitta bitta bitta bitta bitta bitta bitta	n for d	14 0 14 0 14 0 14 0 14 0	enol en	ones ones ones ones ones draction metate	nano nano nano nano nano the exp	o.031 o.027 o.026 ss asing
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 $\label{eq:second} Distribution of the analysis of the second se$

<text><text><text><text><text> Tables 7 and 8 show the value of activity coeffic traction using methanol solvest distant of low UNEX Carl NVER to the coefficient of the coefficient of the extern ghave in index coefficient with our the coefficient distant of carls or not. The activity coeffic and source in the extern ghave in index coefficient with your distant of the extern ghave in the coefficient of the next of coefficient of the extern of the solution activity and the extern of the extern of the extern of the next of coefficient of the extern of the extern action coefficient of the index of the low of the ac-tion of distant of the properties of the instant on the extern of the extern of the extern of the low of the extern of the extern of the extern of the low of the ex-erise of the extern of the extern of the low of the ex-erise of the extern of the extern of the low of the ex-tern of the extern of the extern

The third parameter (n) is estimated based on nent and sometimes for certain substance obtained. The NRTL equation is expressed:		323 K	Cocur studi	
$\frac{G^{i}}{aB^{i}} = \sum_{i=1}^{n} \chi_{i} \frac{\sum_{i=1}^{n} T_{i} G_{i} \chi_{i}}{\sum_{i=1}^{n} C_{i} \chi_{i}}$	(14)			Coffee shell
R R.		Acutic acid	298 K	Cocon shell
$\tau_i = \frac{c_i - c_i}{RT}$	(15)			Coffee shell
$g_{\rm X}=g_{\rm X}=g_{\rm int}=0$	(16)		313K	Cocum a Tadil
$G_{ij} = \exp(-\gamma_i \tau_{ij})$	(17)			

wason equation which contains two adjustance parameter:	s, une	Methanice	258 K	COCTEME	0.17%	1.0622	0.057	0.005	0.0822	2.340
NRTL equation contains three parameters, so the NRTL equ	ation			a faul l	0.052	1.994	0.004	0.008	0.006	2.5/8
can be an alternative model if other models are inadequate	This				0.019	1,999	0.005	0.012	0.145	2,435
equation can also estimate the equilibrium of multicomponent	# 134			Coffee	0.064	1.005	0.067	0.014	0.047	2112
e quaction can also e soumate che equinaria num o composient	e sys-			s fael L	0.040	1.024	0.058	0.017	0.065	3.215
cents wroto de accessar parameters.					0.027	1.976	0.019	0.022	0.981	2,2489
The NRTL equation can represent inquid-liquid equilibrium to	c (30 Ch		313K	COCURAN	0.140	1,789	0.005	0.028	0.055	2,149
binary and multicomponent systems only with binary parameter	s The			s fuel L	0.119	1,291	0.002	0.027	0.070	2,215
equation is simpler than the UNIQUAC equation, but it has a disa	dwan-				0.112	1.752	0.002	0.034	0.085	2,118
tage because it contains there parameters for each pair of commo-	avents.			Coffee	0.157	1.065	0.042	0.023	0.052	2,149
The third is second as I of is action and haved on the state of the co-				a fad f	0.161	1.985	0.029	0.025	0.056	2.215
The time parameter (reprisesumates under un une wate or une to	and a				0.179	1.002	0.011	0.025	0.062	2,118
neme and sometimes for certain substances the extreme many	Detr in		323 K	COCIEME	0.040	1,788	0.007	0.017	0.054	2,108
obtained. The NRTL equation is expressed:				11461	0.028	1,851	0.001	0.017	0.052	2.228
				0.00	0.054	1,870	0.001	0.017	0.052	2,108
6 - 5 - 564				-loti	0.007	1,000	0.0712	0.000	0.064	1.100
$\frac{dr}{dt} = \sum_{i=1}^{n} \chi_i \frac{g_{ij}g_{i-1}(r) p_i(p_i)}{\sum_{i=1}^{n} q_i}$	(14)			11001	0.085	1.000	0.000	0.077	0.000	1.1.1
11A2 2			Terrar Inc.		0.000	1.00.04	0.000	0.000	111000	4,110
		on the	2088	- Defi	0.150	1.0007	0.016	0.025	0.001	5.1.70
g g.		20.00		11001	0.0775	1.000	0.015	0.044	0.086	3.1.00
$T_{ij} = \frac{r_{ij}}{r_{ij}}$	(15)			College.	0.2005	1,222	0.0755	0.000	0.087	3.108
- ai				a field f	0.205	1175	0.047	0.045	0.087	3.170
	18.00				0.3425	1015	0.047	0.07%	0.001	3.100
$g_4 = g_8 = g_{16} = 0$	(16)		313.6	Courses	0.196	1.021	0.005	0.018	0.061	2.758
				studi	0.152	1.319	0.015	0.040	0.087	2.877
6					0.141	1.459	0.014	0.045	0.091	2.835
$c_{ij} = \exp(-\gamma_i \tau_{ij})$	(3.7)			Other	0.211	1.052	0.075	0.0%6	0.108	2.7%
				a fad l	0.278	1.004	0.027	0.060	0.115	2.817
					0.305	1.829	0.044	0.055	0.130	2.835
*i = *j	(18)		323 K	Correct	0.055	1.025	0.057	0.044	0.071	2.705
				a fad I	0.025	1.067	0.004	0.044	0.07%	2.728
N#					0.042	2.009	0.005	0.044	0.085	2.788
$\ln u = \frac{\lambda_{ij+1}T_{ij}G_{ij}X_{j}}{\sum i} + \frac{\nabla v}{\sum i} + \frac{X_{ij}G_{ij}}{\sum i} + \frac{X_{ij}T_{ij}G_{ij}}{\sum i} + \frac{X_{ij}T_{ij}G_{ij}}{\sum i}$	/100			Coffee	0.087	1.000	0.056	0.063	0.111	2.765
$f_1 = \sum_{k=1}^{n} G_k X_k$, $f_{k=j-1}^{n} \sum_{k=1}^{n} G_k X_k$, $f_{k=k-1}^{n} \sum_{k=1}^{n} G_k X_k$	(*.0)			a faul l	0.090	1.921	0.067	0.067	0.125	2.728
					0.105	2.001	0.070	0.051	0.155	2.788
		Notes of an	de l'autiens effe	and the second second second second	-	-			_	_
$(\gamma_1 - \gamma_{n-1}^{*}) (\beta_{n-1} - \gamma_{n-1}^{*}) (\beta_{n-1}$		record you have	our resonance of a	and an and	diam.	fame.				
$X_i = 0.30 \frac{12}{12} \frac{160}{12} \frac{1}{12} \frac{1}{$	(20)	3 milette	tion of solver	a secondaria	and a					
		The second	control values		-					

 $\begin{array}{c} \frac{12\pi_{12}h_{12}}{r_{12}} (\Sigma_{11}^{-1}, \Lambda_{12}^{-1}, \Sigma_{12}^{-1}, \Lambda_{12}^{-1}, \Gamma_{12}^{-1}, \Gamma_{12}^{-$

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