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Article

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

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

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

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1. Introduction

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

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

Indonesia is the third largest coffee producer in the world after Brazil and Vietnam by contributing about 6% of the world's total coffee production, also world's fourth largest coffee exporter with a market share of around 11% across the world. Coffee is one of the plantations with high economic value besides chocolate and tea. Based on data from the Indonesian Ministry of Forestry and Plantation, Indonesia's coffee production in 2013 reached 691160 tons with a plantation area of 47800 Ha [8]. Waste from coffee processing that is abundant and not utilized optimally is the coffee shell. A large percentage of waste from coffee shells derived from plantations amounts to approximately 11.08% which potentially causes environment hazard. Coffee shells are a waste that has high lignocellulose content which has a potential to be used as bio-oil. Bio-oil is a blackish liquid fuel derived from biomass such as wood, coffee shells and other biomass. Bio-oil contains lignin components (23.4%), cellulose (34.2%) and hemicellulose (24.5%) [8].

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

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

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

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

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

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

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

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

2. Experimental

2.1. Chemicals

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

2.2. Equilibrium procedure

Instruments used in this study:

a) Shaker bath, product by Memmert 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

	Quantity
Feed	Bio-oil
Feed volume	2.5 ml
Solvent	Aqueous methanol Aqueous acetic acid
Mole fraction of water in solvent	0.2
Solvent–feed mass ratio	1
Shaking time	60 min
Amplitude of shaking	150, 200, 250 $r \cdot min^{-1}$
Temperature	298, 313, 323 K

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

2.3. Analysis and characterization

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

Table 2
Conditions of analysis using GC

Column: Rastek RXi-5MS	
Column	
Inner diameter/m	3.2×10^{-4}
Length/m	30
Carrier gas	He
Split ratio	153
Flow rate/$cm \cdot s^{-1}$	26.6
Sample volume/m^3	1.10^{-9}
Injection temperature/K	553
Column temperature/K	313–573
Pressure column/kPa	10.0
Column flow/$ml \cdot min^{-1}$	0.54
Detector (FID) temperature/K	573

3. Results and Discussion

3.1. Bio-oil content

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

Tables 3 and 4 represent that bio-oil contains more than 6 main components. The percentage (%) of the compositions of the bio-oil analysis by GC–MS was obtained from the percentage area of the peak or the height of the peak in the 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 are 47.03% (coconut shell) and 45% (coffee shell). It was caused by the pyrolysis processing at 300–350 °C (low temperature carbonization) that produced more substances containing ester and phenolic compounds. The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil.

Table 3
The main components of bio-oil produced by pyrolysis of coconut shells

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

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

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

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

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

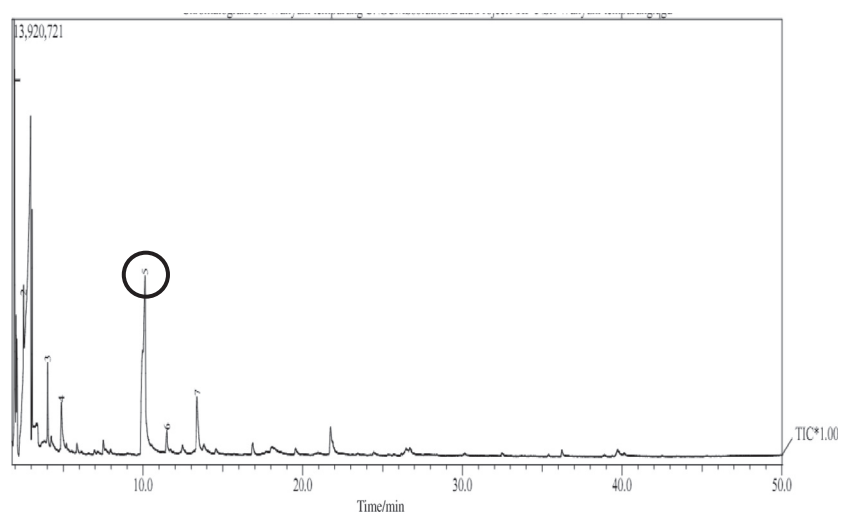

Fig. 1. Analysis result by GC–MS for the bio-oil produced by coconut shell pyrolysis.

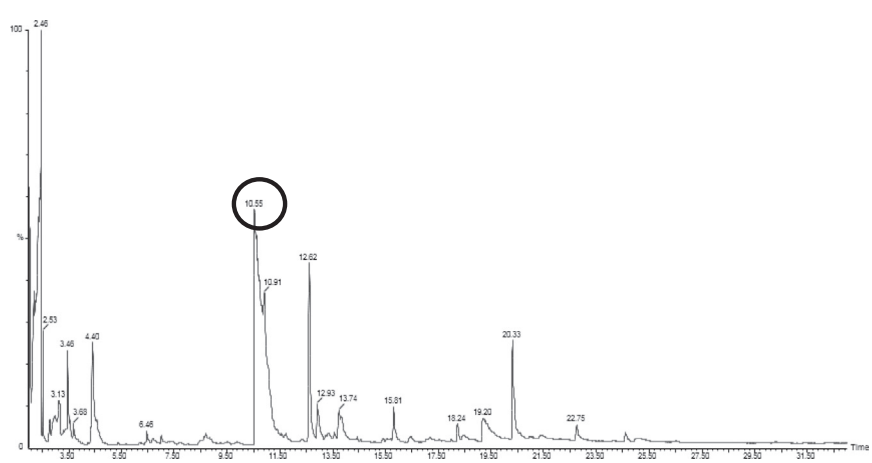

Fig. 2. Analysis result by GC–MS for the bio-oil produced by coffee shell pyrolysis.

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

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

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

Tables 5 and 6 show the equilibrium of multi-component 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 and coffee shell

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

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

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

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

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

a) UNIFAC: [18]

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

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

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

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

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

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

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

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

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

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

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

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

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

where:

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

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

The UNIFAC equation can be obtained to:

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

b) NRTL: [18]

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

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

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

$$\frac{G^E}{nRT} = \sum_{i=1}^{n} x_i \frac{\sum_{k=1}^{n}\tau_{ij}G_{ij}x_j}{\sum_{k=1}^{n}G_{ik}x_k} \quad (14)$$

$$\tau_{ij} = \frac{g_{ij} - g_{ii}}{RT} \quad (15)$$

$$g_{ii} = g_{jj} = g_{kk} = 0 \quad (16)$$

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

$$\alpha_{ij} = \alpha_{ji} \quad (18)$$

$$\ln\gamma_i = \frac{\sum_{j=1}^{n}\tau_{ij}G_{ij}x_j}{\sum_{k=1}^{n}G_{ik}x_k} + \sum_{j=1}^{n} x_i \frac{x_j G_{ij}}{\sum_{k=1}^{n}G_{ik}x_k}\tau_{ij} - \sum_{k=1}^{n}\frac{x_j\tau_{jk}G_{jk}}{\sum_{k=1}^{n}G_{jk}x_k} \quad (19)$$

$$X_i = \exp^{\frac{\sum_{j=1}^{n}\tau_{ij}G_{ij}x_j}{\sum_{k=1}^{n}G_{ik}x_k} + \sum_{j=1}^{n} x_i \frac{x_j G_{ij}}{\sum_{k=1}^{n}G_{ik}x_k}\left(\tau_{ij} - \sum_{k=1}^{n}\frac{x_j\tau_{jk}G_{jk}}{\sum_{k=1}^{n}G_{jk}x_k}\right)} \quad (20)$$

$$Y_i = \exp^{\frac{\sum_{j=1}^{n}\tau_{ij}G_{ij}x_j}{\sum_{k=1}^{n}G_{ik}x_k} + \sum_{j=1}^{n} x_i \frac{x_j G_{ij}}{\sum_{k=1}^{n}G_{ik}x_k}\left(\tau_{ij} - \sum_{k=1}^{n}\frac{x_j\tau_{jk}G_{jk}}{\sum_{k=1}^{n}G_{jk}x_k}\right)} \quad (21)$$

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

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

Table 7
The activity coefficients were calculated by UNIFAC model

Solution	Temperature	Biomass	γ_a^I	γ_b^I	γ_c^I	γ_a^{II}	γ_b^{II}	γ_d^{II}
Methanol	298 K	Coconut shell	0.176	1.969	0.037	0.005	0.063	2.360
			0.032	1.994	0.004	0.008	0.098	2.398
			0.019	1.999	0.003	0.012	0.143	2.435
		Coffee shell	0.064	1.093	0.067	0.014	0.047	3.112
			0.040	1.024	0.038	0.017	0.063	3.215
			0.027	1.976	0.019	0.022	0.981	3.309
	313 K	Coconut shell	0.149	1.789	0.006	0.028	0.055	2.143
			0.119	1.791	0.003	0.027	0.070	2.215
			0.112	1.792	0.003	0.034	0.085	2.191
		Coffee shell	0.157	1.965	0.042	0.023	0.032	2.143
			0.161	1.983	0.029	0.025	0.056	2.215
			0.178	1.992	0.011	0.025	0.062	2.191
	323 K	Coconut shell	0.049	1.788	0.007	0.017	0.054	2.181
			0.028	1.831	0.001	0.017	0.052	2.222
			0.034	1.870	0.001	0.017	0.052	2.191
		Coffee shell	0.058	1.675	0.012	0.021	0.041	2.181
			0.063	1.780	0.021	0.036	0.064	2.222
			0.088	1.832	0.028	0.032	0.068	2.191
Acetic acid	298 K	Coconut shell	0.199	1.191	0.020	0.023	0.078	3.108
			0.132	1.002	0.018	0.035	0.081	3.150
			0.073	1.015	0.015	0.044	0.086	3.198
		Coffee shell	0.206	1.222	0.033	0.022	0.083	3.108
			0.325	1.123	0.042	0.043	0.087	3.150
			0.368	1.015	0.047	0.078	0.091	3.198
	313 K	Coconut shell	0.196	1.021	0.003	0.038	0.081	2.798
			0.152	1.319	0.013	0.040	0.087	2.857
			0.141	1.459	0.014	0.043	0.091	2.836
		Coffee shell	0.211	1.032	0.033	0.056	0.108	2.798
			0.278	1.804	0.037	0.069	0.115	2.857
			0.305	1.829	0.044	0.053	0.130	2.836
	323 K	Coconut shell	0.055	1.925	0.037	0.044	0.071	2.705
			0.035	1.967	0.004	0.044	0.076	2.728
			0.042	2.009	0.006	0.044	0.083	2.719
		Coffee shell	0.087	1.909	0.056	0.063	0.111	2.705
			0.090	1.921	0.067	0.067	0.135	2.728
			0.103	2.001	0.070	0.051	0.155	2.719

Note: γ_a^I mole fraction of component in extract phase
γ_b^I mole fraction of solvent in extract phase
γ_c^I mole fraction of water in extract phase
γ_a^{II} mole fraction of component in raffinate phase
γ_b^{II} mole fraction of solvent in raffinate phase
γ_d^{II} mole fraction of bio-oil in raffinate phase.

Table 8
The activity coefficients were calculated by NRTL model

Solution	Temperature	Biomass	γ_a^I	γ_b^I	γ_c^I	γ_a^{II}	γ_b^{II}	γ_d^{II}
Methanol	298 K	Coconut shell	0.077	0.996	0.381	0.005	0.218	2.037
			0.064	0.982	0.337	0.001	0.222	2.037
			0.063	0.998	0.387	1.3×10^{-6}	0.345	2.045
		Coffee shell	0.132	1.003	0.289	0.001	0.468	1.903
			0.157	1.045	0.376	0.001	0.458	1.923
			0.221	1.067	0.401	0.001	0.312	2.007
	313 K	Coconut shell	4.47×10^{-8}	1.003	0.010	8.4×10^{-7}	0.278	1.050
			2.71×10^{-6}	1.009	0.056	1.5×10^{-11}	0.308	1.014
			1.80×10^{-5}	1.023	0.039	4.9×10^{-19}	0.347	0.880
		Coffee shell	0.004	1.000	0.067	0.017	0.280	0.999
			0.005	0.997	0.089	0.003	0.480	1.012
			0.007	1.035	0.100	0.020	0.308	1.003
	323 K	Coconut shell	7.92×10^{-8}	1.110	0.010	3.6×10^{-3}	0.111	1.028
			3.48×10^{-6}	1.098	0.022	4.1×10^{-14}	0.132	1.006
			9.44×10^{-6}	1.122	0.024	3.5×10^{-32}	0.133	0.937
		Coffee shell	0.001	1.333	0.054	0.004	0.167	1.012
			0.008	1.412	0.057	0.007	0.175	1.097
			0.008	1.389	0.055	0.103	0.175	1.032
Acetic acid	298 K	Coconut shell	0.045	1.209	0.218	0.002	0.210	1.087
			0.039	1.211	0.210	0.015	0.200	1.265
			0.036	1.309	0.232	9.5×10^{-5}	0.200	1.478
		Coffee shell	0.146	1.448	0.087	0.057	0.234	2.014
			0.155	1.443	0.075	0.059	0.247	2.004
			0.128	1.761	0.102	0.078	0.231	2.065
	313 K	Coconut shell	0.002	2.003	0.037	0.036	0.126	0.995
			0.003	2.032	0.050	0.030	0.119	0.999
			0.013	1.956	0.069	0.028	0.117	1.000
		Coffee shell	0.019	1.782	0.023	0.022	0.209	1.119
			0.018	1.834	0.026	0.025	0.211	1.118
			0.021	2.000	0.080	0.025	0.211	1.097
	323 K	Coconut shell	0.115	1.546	0.037	0.035	0.308	1.139
			0.138	1.690	0.050	0.001	0.311	1.010
			0.200	1.800	0.069	8.9×10^{-6}	0.289	1.021
		Coffee shell	0.054	1.906	0.046	0.013	0.267	1.290
			0.093	2.035	0.067	0.016	0.234	1.317
			0.093	2.088	0.099	0.021	0.222	1.320

Note: γ_a^I mole fraction of component in extract phase
γ_b^I mole fraction of solvent in extract phase
γ_c^I mole fraction of water in extract phase
γ_a^{II} mole fraction of component in raffinate phase
γ_b^{II} mole fraction of solvent in raffinate phase
γ_d^{II} mole fraction of bio-oil in raffinate phase.

the system, while the phenol and solvent (acetic acid or methanol) are far from ideal conditions. So non-ideality studies are very important for those systems [19].

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), which 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)

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

Based on Table 9, it can be seen that extraction with methanol solvent for the NRTL model has the smallest SSE value compared to the extraction with acetic acid solvent for the UNIFAC model.

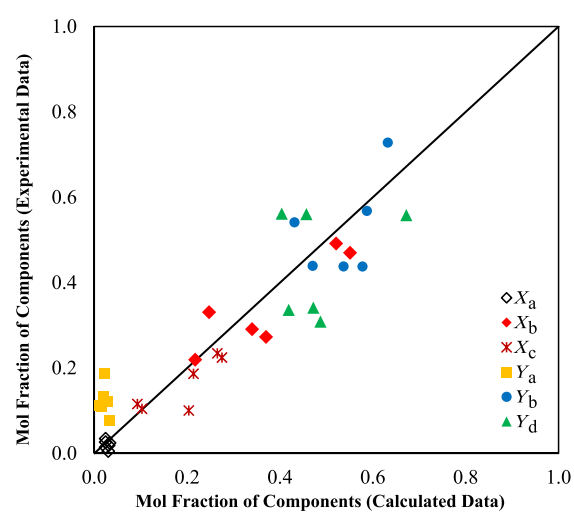

Fig. 3. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous methanol by UNIFAC model at 298 K.
where:
X_a mole fraction of component in extract phase
X_b mole fraction of solvent in extract phase
X_c mole fraction of water in extract phase
Y_a mole fraction of component in raffinate phase
Y_b mole fraction of solvent in raffinate phase
Y_d mole fraction of bio-oil in raffinate phase.

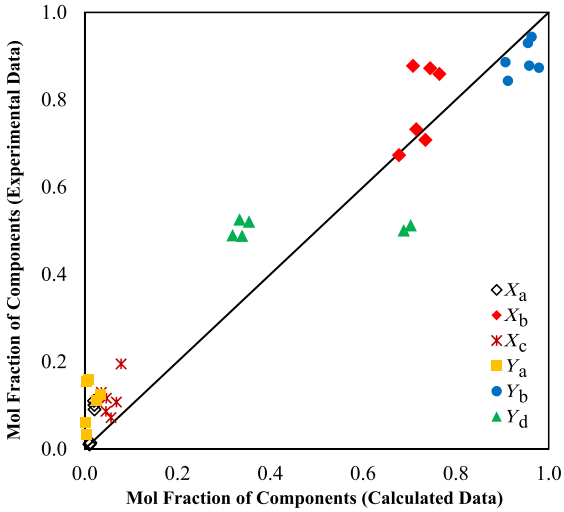

Fig. 4. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous methanol by UNIFAC model at 313 K.

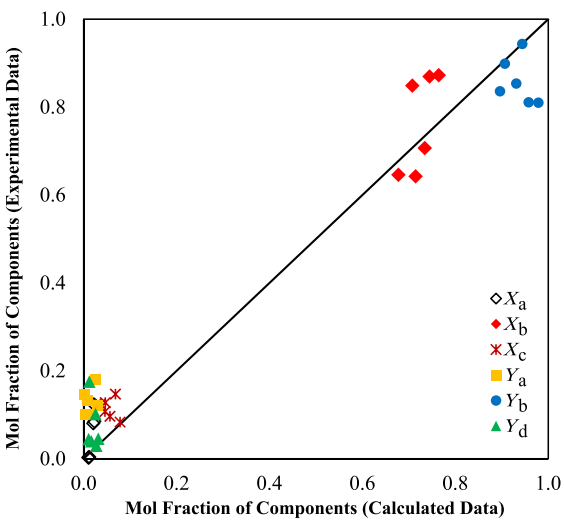

Fig. 5. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous methanol by UNIFAC model at 323 K.

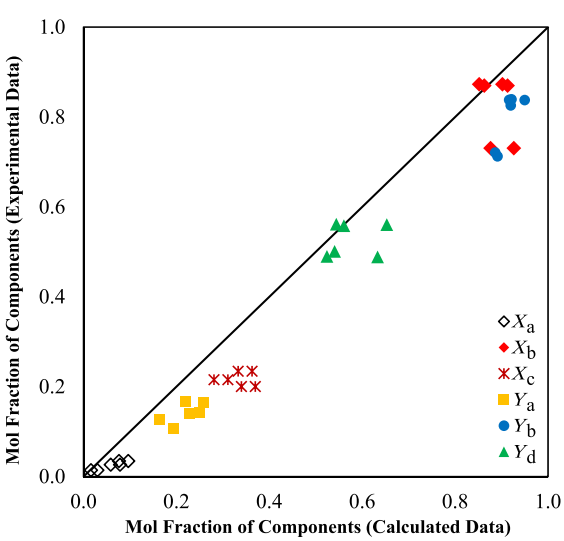

Fig. 6. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous acetic acid by UNIFAC model at 298 K.

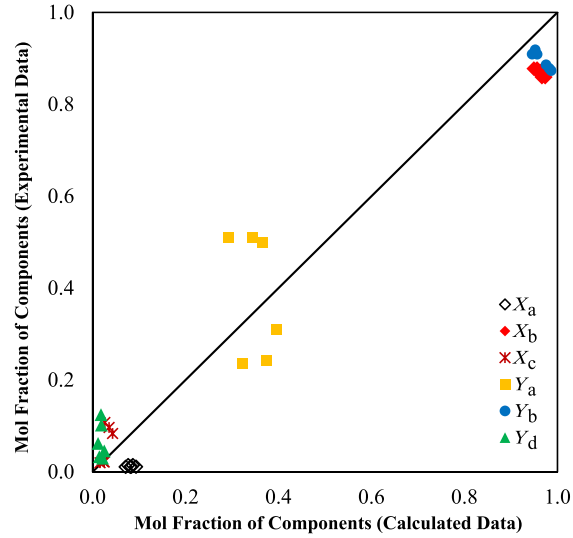

Fig. 7. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous acetic acid by UNIFAC model at 313 K.

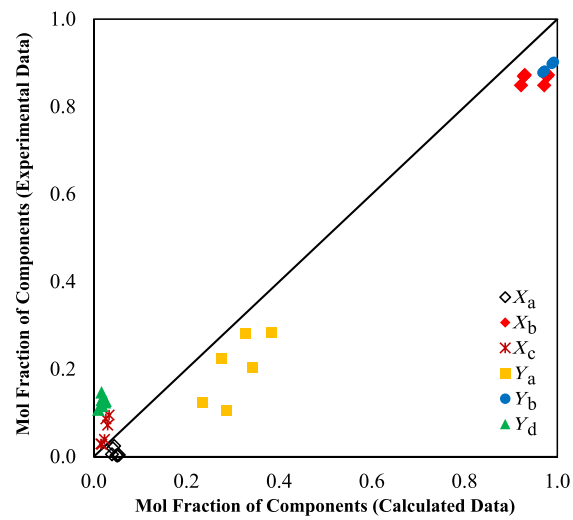

Fig. 8. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous acetic acid by UNIFAC model at 323 K.

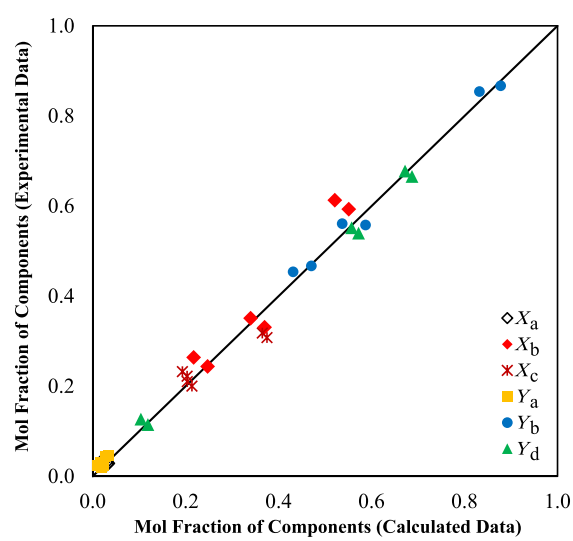

Fig. 9. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous methanol by NRTL model at 298 K.

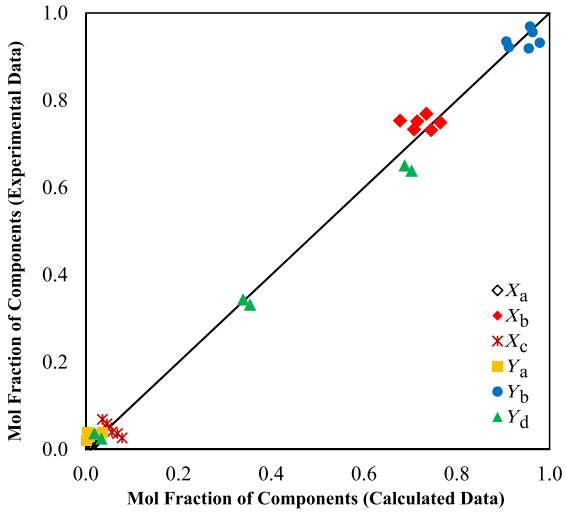

Fig. 10. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous methanol by NRTL model at 313 K.

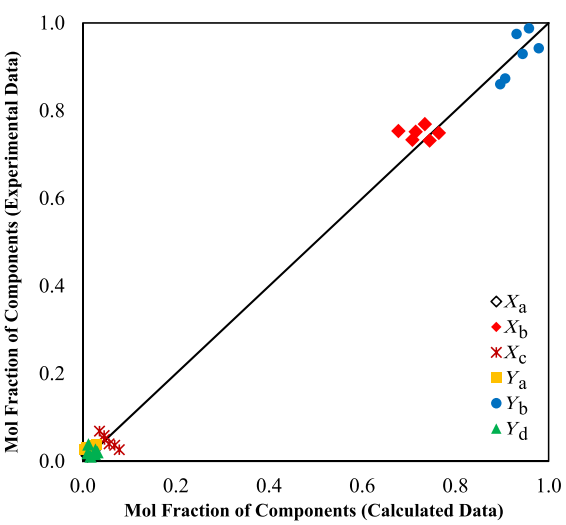

Fig. 11. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous methanol by NRTL model at 323 K.

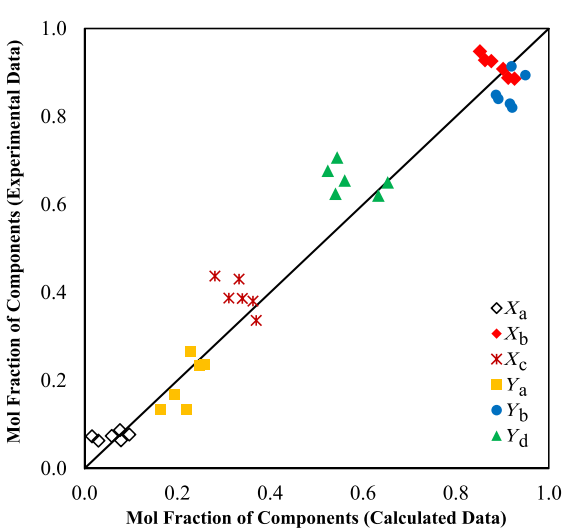

Fig. 12. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous acetic acid by NRTL model at 298 K.

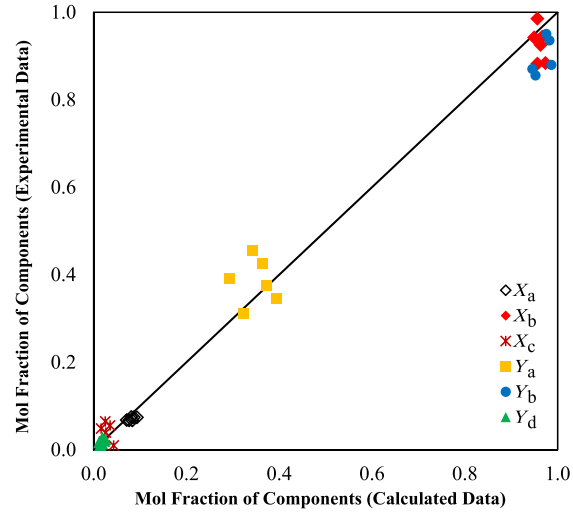

Fig. 13. Comparison of calculated and experimental mole fractions of the phenol extraction using aqueous acetic acid by NRTL model at 313 K.

The smaller 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 the phenol extraction process from coconut shell pyrolysis bio-oil and coffee shell using methanol solvent and acetic acid.

Figs. 3–14 show the visual comparison in which the calculated and experimental mole fractions in the extract phase and the raffinate phase for the methanol solvent system by the NRTL model are better than the other conditions (by UNIFAC model and acetic acid solvent).

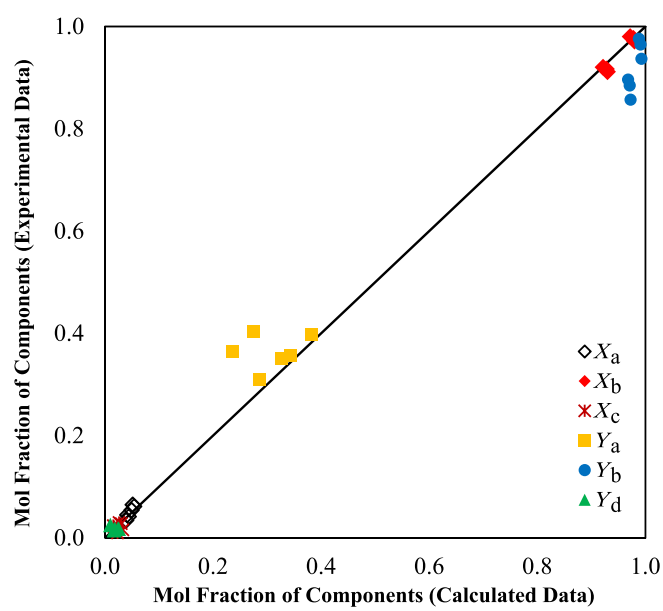

Fig. 14. Comparison of calculated and experimental mole fractions of the phenol extraction using acetic acid by NRTL model at 323 K.

4. Conclusions

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

The activity coefficients of water and phenol in their phase are far from unity. It means that they are far from the 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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References

[1] N. Sriram, Renewable Biomass Energy, Illions Institute of Technology, Chicago, 2005.
[2] I. Demiral, A. Eryazici, S. Sensoz, Bio-oil production from pyrolysis of corncob (*Zea mays* L.), *Biomass Bioenergy* 36 (2012) 43–49.
[3] M. Bertero, G. de la Puente, U. Sedran, Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning, *Fuel* 95 (2012) 263–271.
[4] V.C. Pandey, K. Singh, J.S. Singh, A. Kumar, B. Singh, R.P. Singh, *Jatropha curcas*: A potential bio-fuel plant for sustainable environmental development, *Renew. Sust. Energ. Rev.* 16 (2012) 2870–2883.
[5] C.J. Ellens, R.C. Brown, Optimization of a free-fall reactor for production of fast pyrolysis bio-oil, *Bioresour. Technol.* 103 (2012) 374–380.
[6] S. Ismadji, Kulit durian sebagai bahan baku pembuatan bio-oil: sumber energi terbarukan, Prosiding Seminar Nasional Teknik Kimia Soebardjo Brotohardjono I, Prodi Teknik Kimia UPN Veteran Jawa Timur 2012, pp. 1–4.
[7] W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor, *J. Anal. Appl. Pyrolysis* 76 (2006) 230–237.
[8] C.E. Wyman, Potential synergies and challenges in refining cellulosic biomass to fuels, *Biotechnol. Prog.* 19 (2) (2010) 254–262.
[9] Direktorat Jenderal Perkebunan, Produksi Buah Kelapa di Indonesia, 2016.
[10] Joardder, Pyrolysis of Coconut Shell for Bio-oil, PhD Thesis, Department of Mechanical Engineering, Rajshahi University of Engineering & Technology, Bangladesh, 2011.
[11] D. Tamado, E. Budi, R. Wirawan, H. Dwi, A. Tyaswuri, E. Sulistiani, E. Asma, Sifat termal karbon aktif berbahan arang tempurung kelapa. Seminar Nasional Fisika Universitas Negeri Jakarta, 2013.
[12] S. Wang, High Efficiency Separation of Bio-Oil, InTech, 2013.
[13] Fitriani Kasim, A.N. Fitrah, E. Hambali, Aplikasi asap cair pada lateks, *J. PASTI* 9 (1) (2012) 28–34.
[14] A. Jazbinšek, G. Viktor, L.F. Žilnik, Isolation of Phenol and Phenolic Compounds from Fast Pyrolysis Bio-oil of Forestry Residue, National Institute of Chemistry, Slovenia, 2008.
[15] S.V. Mantilla, A.M. Manrique, A. Gauthier-Maradei, Methodology for extraction of phenolic compounds of bio-oil from agricultural biomass wastes, *Waste Biomass Valoriz* 6 (2015) 371–383.
[16] Dahlia, Pra rancangan pabrik pembuatan fenol dari tandan kosong kelapa sawit dengan proses pirolisis dengan kapasitas produksi 10.000 ton/tahun, Departemen Teknik Kimia Universitas Sumatera Utara, Medan, 2012.
[17] D.S Fardhyanti, W.B. Sediawan, P. Mulyono, Complex extraction of phenol, o-cresol, and p-cresol from model coal tar using methanol and acetone solutions, *B. J. Appl. Sci. & Technol.* 8 (5) (2015) 427–436.
[18] J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 5th edition Mc Graw Hill International Book Company, New York, 1996.
[19] D.S. Fardhyanti, W.B. Sediawan, P. Mulyono, Predicting the liquid phase equilibrium of multi-components extraction by thermodynamic models, *Int. J. Thermodyn.* 19 (2) (2015) 110–119.