Degradation of Oil Palm Empty Fruit Bunch (OPEFB) in Super-Critical Organic Solvents Affecting the Chemicals Distribution of Bio-Oil

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ARTICLE INFO

Article history:

Received date : 23 May 2017

Revised date : 29 May 2017

Accepted date: 13 June 2017

Available online at :

<http://inajac.lipi.go.id>

Keywords:

EFB, liquefaction, bio-oil composition

Abstract

Hydrothermal liquefaction (HTL) of oil palm empty fruit bunch (OPEFB) in different organic solvents (methanol, ethanol, acetone, toluene and hexane) to produce bio-oil were comparatively investigated. Experiments were carried out in an autoclave at different temperature of 300, 350 and 400 °C with a fixed solid/liquid ratio of 4 gram in 50 mL solvent, without catalysts and reaction time of 5 hours. The liquid products were analyzed using GCMS to determine the chemical composition. Result showed that the chemical compositions were greatly affected by the solvent types. Each solvent has a major component in bio-oil products. The major compounds resulted from methanol and ethanol solvent were ketones/others. The major compounds resulted from toluene and hexane solvents were organic acid, which favoured high temperature. Meanwhile, esters and organic acid were the major products from acetone solvents. Temperature operation resulted more variations in the chemical composition and the percentages of the bio-oil.

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1. INTRODUCTION

Biomass can be converted into smaller molecules in fuel grade level using thermo-chemical processes. Cellulose molecules are bound to each other by inter- and intra-molecular hydrogen linkages through their hydroxyl groups, and crystalline cellulose is difficult to decompose. Direct liquefaction of biomass in sub- and super-critical solvents (water, alcohols, and phenol) has proven to be an effective approach to convert lignocelluloses materials into low molecular weight chemicals [1].

The knowledge about thermal characteristics and decomposition mechanism of biomass is considerably important for optimization of the conversion process and efficient utilization of the liquid products [2,3]. Currently, liquefaction is used by many researchers for biomass utilization because of its advantages, such as (1) the presence of solvent could dilute the concentration of the

products, decrease the opportunity for cross-linked reactions and reverse reactions, and (2) the relatively low temperature in comparison to pyrolysis [4,5].

Solvents have a remarkable effect on the liquefaction reaction. Some articles have reported that the liquefaction of biomass in the presence of organic solvents were effectively lowers the viscosity of heavy oil derived from biomass liquefaction [6]. Although solvents have shown obvious reactive activity in many works, it is still unclear how solvents affect the biomass liquefaction process. Liquefaction of biomass with proper solvents is a benign process that can prospectively be integrated with optimized conditions to produce fuel and valuable chemicals [7].

The role of the solvent is usually to fragment the biomass and stabilize the fragmented products to ensure maximum production of bio-oil. The better solvent stabilizing the fragments, the higher the oil

yield and the lower the solid biochar fraction [8]. Correspondingly, solvents tend to increase the fragmentation of the biomass and disrupts the stability of the reaction mixture which further increase the yield of solid bio-char. The characteristic of organic solvents as shown in Table 1.

Tabel 1. The characteristic of organic solvents

Organic solvent	P critical (atm) ^a	T critical, °K ^a	°C	Dielectric constant ^b
Methanol	78.5	513		32.7
		240		(25 °C)
Ethanol	63	516		24.55
		243		(25 °C)
Acetone	46.6	509		20.7
		236		(25 °C)
Toluene	41.6	594		2.38
		321		(25 °C)
n-Hexane	29.9	508		1.88
		235		(20 °C)
Water	228	647		80.1
		374		(20 °C)

^a Smith⁽⁹⁾

^b Anon1⁽¹⁰⁾

It is expected that low dielectric constant of the solvent would increase and dissolve the biomass fragmented products which further increase the liquefaction process. Solvent polarities can be classified into three categories: polar protic, dipolar aprotic and non-polar solvents. Polar protic solvents such as water and alcohols refer to compounds with a hydrogen atom attached to an electronegative atom like oxygen. Dipolar protic solvents such as acetone and 1,4-dioxane describe a molecule that does not contain an O-H bond. All solvents in this class contain a bond with a large bond dipole, which is a multiple bond between carbon and either oxygen or nitrogen. Non-polar solvents are compounds that have low dielectric constants and are not miscible with water such as benzene and diethyl ether [11].

Non-polar solvents have low dielectric constants (<5) and are not good solvents for charged species such as anions. Dipolar aprotic solvents also have dielectric constant in the range of 5 to 20. Moreover, they have intermediate polarity and they are also good solvents for a wide range of reactions. Polar protic solvents tend to have high dielectric constant and high dipole moments. All of these

solvents have large dielectric constants (>20). They possess O-H or N-H bonds and can also participate in hydrogen bonding [12]. Recently, instead of water, organics solvents such as ethanol, methanol, acetone etc., have been utilized as the reaction medium to enhance the yield of bio-oil with low oxygen content [7, 13-14].

The basic reaction mechanisms of biomass liquefaction can be described as follows: (i) depolymerization of the biomass; (ii) decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination; (iii) recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds [15]. In the first step, cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols [16]. The reaction in an organic medium strongly depends on the interactions between the solvents and the substrates. If the liquefaction solvents is a product derived from the biomass itself, such as phenol, alcohol or polyalcohol, the conversion of biomass can be enhanced [17].

The degradation of biomass cannot be described by detailed chemical reaction pathways with well-defined single reaction steps. The reason is that biomass is a combination of cellulose, hemicelluloses, and lignin, and these components interact each other, leading to very complex chemistry [18]. The analysis of complex reactions which occur in the liquefaction of biomass, is important to the description of the reactions behavior and to the optimization of the operating conditions.

The main object of this paper is to study the effect of various organic solvents and temperatures in the bio-oil chemical compositions.

2. EXPERIMENTAL SECTION

2.1. Materials and chemicals

Oil palm empty fruit bunch (OPEFB) was provided from the oil palm industry. The OPEFB was dried and grinded into smaller particle of 80 mesh. The OPEFB contained

cellulose 44.21%, hemi-cellulose 16.68%, and lignin 35.51% [19]. All chemicals are analytical reagent grade provided by Merck.

2.2. Methods

2.2.1. Experimental procedures

Liquefaction experiments were carried out in a 60 mL stainless steel reactor for several hours. Around 4 gram of EFB with 80 mesh particle size was added into the reactor and latter organic solvent of 50 mL was also added. The reactor was sealed properly and make sure that there is no leakage. The reactor was mounted into the furnace and the temperature can be set in certain point as desired. After the reaction time was reached, the reactor was pulled out. The reactor was poured with tap water to decrease the temperature to ambient. After that, the reactor valve was opened to release the gas out, and then the reactor was opened properly to pull out the products. The solid and liquid products are separated by filtering. The solid was rinsed with same solvent and dried at 105 °C until the weight remained unchanged. The filtrate (liquid) was analyzed by GC-MS. The liquid was evaporated in vacuum evaporator to measure the soluble products.

2.2.2. Separation procedure

After the reaction time was reached, the reactor was pulled out. The reactor was poured with tap water to decrease the temperature to ambient. The gas inside was vented out. The liquid and solid was filtered, the solid was washed with the same solvent, until the liquid was cleared. The solid was dried at 105 °C overnight, and then quantified until the weight is unchanged (carbon fraction). The liquids were evaporated under vacuum evaporator overnight until the weight is unchanged (bio-oil).

$$\text{Yield of bio-oil} = \frac{\text{Mass of bio-oil}}{\text{mass of EFB}} \times 100\% \quad \dots\dots\dots (1)$$

$$\text{Yield of carbon} = \frac{\text{Mass of carbon}}{\text{mass of EFB}} \times 100\% \quad \dots\dots\dots (2)$$

$$\text{Conversion rate} = 100 \text{ wt\%} - \text{yield of carbon} \quad \dots\dots\dots (3)$$

2.2.3. Products analysis

The gas produced was not analyzed. The soluble liquid products were analyzed using GC-MS, Agilent technologies 7890B, with DB5 Column (30 m x 0.32 mm x 0.25 µm, detector MSD 5977A, Helium (He) was used for mobile phase or carrier gas with flow rate 1 ml/min. Injector temperature was 250 °C. The temperature of ion source and MS Quadruple were 230 °C and 150 °C, respectively.

Fifteen bio-oil samples obtained in different liquefaction solvents (methanol, ethanol, acetone, toluene, and hexane) at the temperature of 300 °C, 350 °C and 400 °C were analyzed, respectively. Extracted bio-oil from solvent of methanol, ethanol, acetone were diluted with acetone until the volume was 4 mL aliquot. Extracted bio-oil from solvent of toluene and hexane were diluted with hexane until the volume was 4 mL aliquot, respectively.

3. RESULTS AND DISCUSSION

The results of experiment were shown in Table 2 to 7. The effects of organic solvents and temperatures were examined. Biomass was firstly decomposed and depolymerized into smaller fragments or lighter molecules during the liquefaction process. Those unstable fragments rearranged through condensation, cyclization and polymerization to form new compounds [15]. In general, the higher the reaction temperature, the easier to defragment of the polymers into a liquid oil-rich phase. A further increase in reaction temperature leads to enhanced decomposition of these fragments into gaseous.

The effect of organic solvents resulted different rate of conversion, carbon residue and soluble liquid and the variation of the fragment chemical compositions [20]. In general, the higher reaction temperatures are, the higher the final pressures of the liquefaction process. The elevating pressure

will further result in the increase of the density of liquefaction solvents [11].

3.1. Chemical composition of bio-oil

The bio-oil products from liquefaction of OPEFB were characterized by GC-MS to identify their chemical composition. Typical compositions of bio-oil were shown in Table 2 to 6. There are a great results that any solvent type has a major component in bio-oil product.

The decomposition of OPEFB biomass using methanol solvent resulted the highest percentages of products, including 2-pentanone, 4-hydroxy-4-methyl with molecule carbon of 6 that is the lowest molecule in bio-oil (Tabel 2). By increasing the temperature, the percentage of 2-pentanone, 4-hydroxy-4-methyl resulted were also different. At temperature reaction of 300 °C the percentage of 2-pentanone, 4-hydroxy-4-methyl was 57.43%. At temperature of 350 °C the percentage of 2-pentanone, 4-hydroxy-4-methyl was 69.19%, which was the highest percentages obtained. At temperature of 400 °C the percentage of 2-pentanone, 4-hydroxy-4-methyl was 61.33%, which was slightly lower compared with the result for 350 °C.

The second highest component was hexadecanoic acid, methyl ester. The increase

in the temperature also increase the percentage of hexadecanoic acid, methyl ester. At temperature 300 °C the percentage of hexadecanoic acid, methyl ester was 10.18%. At temperature 350 °C the percentage of hexadecanoic acid, methyl ester was 13.17% and at temperature 400 °C the percentage of hexadecanoic acid, methyl ester was 19.52%.

The third highest component was octadecanoic acid, methyl ester. The increase in the temperature was also increased the percentage of octadecanoic acid, methyl ester. At temperature 300 °C the octadecanoic acid, methyl ester percentage was 5.43%. At temperature 350 °C octadecanoic acid, methyl ester percentage was 6.89% and at temperature 400 °C the octadecanoic acid, methyl ester percentage was 9.83%.

Another amazing phenomena was hexadecanoic acid, ethyl ester, at temperature 300 °C the percentage of hexadecanoic acid, ethyl ester was 8.78%, by increasing the temperature the percentage of hexadecanoic acid, ethyl ester decreased drastically. At temperature 350 °C the percentages of hexadecanoic acid, ethyl ester was 0.99%, and at 400 °C was 1.54%.

Table 2. Chemical composition of bio-oil obtained in methanol solvent at different temperature.

Retention time (RT)	Compounds name (Formula)	Temperature (°C)		
		300	350	400
		% area	% area	% area
4.935	2-pentanone, 4-hydroxy-4-methyl (C ₆ H ₁₂ O ₂)	57.43	69.19	61.33
14.829	Dodecanoic acid, methyl ester (C ₁₃ H ₂₆ O ₂)	-	0.53	0.59
15.106	Dodecanoic acid (C ₁₂ H ₂₄ O ₂)	8.22	6.17	0.07
15.409	Dodecanoic acid, ethyl ester (C ₁₄ H ₂₈ O ₂)	1.79	-	-
16.896	Methyl tetradecanoate (C ₁₅ H ₃₀ O ₂)	0.86	1.32	2.73
17.627	Tetradecanoic acid, ethyl ester (C ₁₆ H ₃₂ O ₂)	0.94	0.5	1.09
18.975	Hexadecanoic acid, methyl ester (C ₁₇ H ₃₄ O ₂)	10.18	13.17	19.52
19.416	Hexadecanoic acid (C ₁₆ H ₃₂ O ₂)	1.77	0.3	-
19.643	Hexadecanoic acid, ethyl ester (C ₁₈ H ₃₆ O ₂)	8.78	0.99	1.54
20.664	Octadecanoic acid, methyl ester (C ₁₉ H ₃₈ O ₂)	5.43	6.89	9.83
21.269	Ethyl oleate (C ₂₀ H ₃₈ O ₂)	2.45	-	-
21.483	Octadecanoic acid, ethyl ester (C ₂₀ H ₄₀ O ₂)	1.45	-	-
21.685	Cis-10-nonadecenoic acid, methyl ester (C ₂₀ H ₃₈ O ₂)	-	-	0.37
22.479	Octadecanoic acid, 10-oxo-, methyl ester (C ₁₉ H ₃₆ O ₃)	-	-	0.83
22.643	Eicosanoic acid, methyl ester (C ₂₁ H ₄₂ O ₂)	0.27	0.38	0.55
Total		99.6	99.44	98.45

It meant that by increasing the temperature hexadecanoic acid, ethyl ester was converted into another fragments. The component of dodecanoic acid is similar to the hexadecanoic acid, ethyl ester. By increasing the temperature, the percentage also decreased drastically. At temperature of 300 °C, the percentage of dodecanoic acid was 8.22 %. At 350 °C the percentage was 6.17%, and at 400 °C the percentage was 0.07%. At 400 °C, the major component of dodecanoic acid was converted into another substances.

The highest component resulted from the degradation of OPEFB with the solvent of ethanol were 2-pentanone, 4-hydroxy-4-methyl. At the temperature reaction of 300 °C, the percentage of 2-pentanone, 4-hydroxy-4-methyl was 42.05 %. At temperature reaction of 350°C the percentage of 2-pentanone, 4-hydroxy-4-methyl was 91.67% and temperature of 400 °C gave the lower component of 2-pentanone, 4-hydroxy-4-methyl, which was 54.75% (Table 3).

The second highest component was hexadecanoic acid, ethyl ester. At temperature of 300 °C the percentage of hexadecanoic acid, ethyl ester was 19.14 %, at 350 °C the percentage of hexadecanoic acid, ethyl ester was 4.05%, and at temperature of 400 °C the percentage of hexadecanoic acid, ethyl ester was 25.36%.

The third highest component was n-hexadecanoic acid. At temperature of 300 °C the percentage of n-hexadecanoic acid was 25.22 %. At 350 °C, the percentage of n-hexadecanoic acid was 0.99%, and at temperature of 400 °C the percentage of n-hexadecanoic acid was 2.51%. By increasing the temperature, a lot of n-hexadecanoic acid was converted into another substances.

The highest component resulted from the degradation of OPEFB with acetone solvent was n-hexadecanoic acid. At the temperature reaction of 300 °C the percentage of n-hexadecanoic acid was 38.08%. At temperature reaction of 300 °C, the percentage of n-hexadecanoic acid was 48.34%, and at temperature of 400 °C the percentage of n-hexadecanoic acid was 31.83 % (Table 4). It meant that the degradation of biomass in ethanol solvent resulted the highest component was n-hexadecanoic acid.

The second highest component was hexadecanoic acid, ethyl ester. At temperature of 300 °C the percentage of hexadecanoic acid, ethyl ester was 32.46 %. At 350 °C, the percentage of hexadecanoic acid, ethyl ester was 24.39 %, and at temperature of 400 °C the percentage of hexadecanoic acid, ethyl ester was 27.68 %.

Table 3. Chemical composition of bio-oil obtained in ethanol solvent at different temperature.

Retention time (RT)	Compounds name (Formula)		Temperature (°C)		
			300	350	400
			% area	% area	% area
4.759	2-Pentanone,4-hydroxy-4-methyl-	(C ₆ H ₁₂ O ₂)	42.05	91.67	54.75
15.119	Dodecanoic acid	(C ₁₂ H ₂₄ O ₂)	7.70	-	-
15.409	Dodecanoic acid, ethyl ester	(C ₁₄ H ₂₈ O ₂)	1.22	0.69	3.32
17.413	Tetradecanoic acid	(C ₁₄ H ₂₈ O ₂)	1.08	-	-
17.803	Tetradecanoic acid, ethyl ester	(C ₁₆ H ₃₂ O ₂)	0.66	0.57	3.88
18.975	Hexadecanoic acid, methyl ester	(C ₁₈ H ₃₆ O ₂)	1.03	0.46	1.18
19.404	n-Hexadecanoic acid	(C ₁₆ H ₃₂ O ₂)	25.22	0.99	2.51
19.643	Hexadecanoic acid, ethyl ester	(C ₁₈ H ₃₆ O ₂)	19.14	4.05	25.36
21.269	Ethyl Oleate	(C ₂₀ H ₃₈ O ₂)	-	1.06	4.22
21.483	Octadecanoic acid, ethyl ester	(C ₂₀ H ₄₀ O ₂)	0.58	0.51	2.94
Total			98.68	100	98.16

Table 4. Chemical composition of bio-oil obtained in acetone solvent at different temperature.

Retention time (RT)	Compounds name (Formula)	Temperature (°C)		
		300	350	400
		% area	% area	% area
4.847	2-pentanone, 4-hydroxy-4-methyl (C ₆ H ₁₂ O ₂)	11.33	13.10	5.85
15.119	Dodecanoic acid (C ₁₂ H ₂₄ O ₂)	7.92	6.63	5.9
15.409	Dodecanoic acid, ethyl ester (C ₁₄ H ₂₈ O ₂)	2.38	2.01	1.33
17.627	Tetradecanoic acid, ethyl ester (C ₁₆ H ₃₂ O ₂)	0.76	0.17	1.76
18.988	Hexadecanoic acid, methyl ester (C ₁₇ H ₃₄ O ₂)	0.86	0.83	2.74
19.391	n-hexadecanoic acid (C ₁₆ H ₃₂ O ₂)	38.08	48.34	31.83
19.643	Hexadecanoic acid, ethyl ester (C ₁₈ H ₃₆ O ₂)	32.46	24.39	27.68
20.664	9-octadecenoic acid, methyl ester (C ₁₇ H ₃₄ O ₂)	-	-	14.29
20.891	Methyl stearate (C ₁₉ H ₃₈ O ₂)	-	-	3.85
21.269	Ethyl oleate (C ₂₀ H ₃₈ O ₂)	1.61	-	1.33
21.483	Octadecanoic acid, ethyl ester (C ₂₀ H ₄₀ O ₂)	1.29	-	1.37
Total		96.69	95.47	97.93

The third highest component was 2-pentanone, 4-hydroxy-4-methyl. At temperature of 300 °C, the percentage of 2-pentanone,4-hydroxy-4-methyl was 11.33 %, at 350 °C the percentage of 2-pentanone,4-hydroxy-4-methyl was 13.10 %, and at temperature of 400 °C the percentage of 2-pentanone,4-hydroxy-4-methyl was 5.85 %. At the temperature of 400 °C, alot of 2-pentanone,4-hydroxy-4-methyl was converted into another substances.

The fourth highest component was dodecanoic acid. At temperature of 300 °C, the percentage of dodecanoic acid was 7.92 %, at 350 °C the percentage of dodecanoic acid was 6.63 %, and at temperature of 400 °C the

percentage of dodecanoic acid was 5.90 %. It meant that dodecanoic acid was just slightly decreased by increasing the temperature.

The highest component resulted from the degradation of biomass with solvent of toluene was n-hexadecanoic acid. At the temperature reaction of 300 °C, the percentage of n-hexadecanoic acid was 80.53 %. At temperature reaction of 350 °C, the percentage of n-hexadecanoic acid was 80.53%, and at temperature of 400 °C, the percentage of n-hexadecanoic acid was 79.05 % (Table 5). It meant that the component of n-hexadecanoic was the same eventhough there was in increase in temperature.

Table 5. Chemical composition of bio-oil obtained in toluene solvent at different temperature.

Retention time (RT)	Compounds name (Formula)	Temperature (°C)		
		300	350	400
		% area	% area	% area
14.590	Dodecanoic acid, methyl ester (C ₁₃ H ₂₆ O ₂)	-	0.22	0.14
15.169	Dodecanoic acid (C ₁₂ H ₂₄ O ₂)	11.08	13.74	8.87
16.732	Phenol, 2,6-dimethoxy-4-(2-propenyl)- (C ₁₁ H ₁₄ O ₃)	-	-	0.63
16.883	Tridecanoic acid, 12-methyl-, methyl ester (C ₁₅ H ₃₀ O ₂)	-	0.23	0.17
17.350	Tetradecanoic acid (C ₁₄ H ₂₈ O ₂)	6.06	3.17	2.41
19.139	Hexadecanoic acid, methyl ester (C ₁₇ H ₃₄ O ₂)	-	1.94	2.50
19.505	n-hexadecanoic acid (C ₁₆ H ₃₂ O ₂)	80.39	80.53	79.05
20.664	8-octadecenoic acid, methyl ester, (E)- (C ₁₉ H ₃₆ O ₂)	-	-	1.98
21.458	Octadecanoic acid (C ₁₈ H ₃₆ O ₂)	-	-	2.3
24.458	DEHP (impurities)	0.08	0.16	0.13
Total		98.85	99.99	98.18

Table 6. Chemical composition of bio-oil obtained in hexane solvent at different temperature.

Retention time (RT)	Compounds name (Formula)	Temperature (°C)		
		300	350	400
		% area	% area	% area
14.590	Dodecanoic acid, methyl ester (C ₁₃ H ₂₆ O ₂)	0.12	0.26	0.35
15.157	Dodecanoic acid (C ₁₂ H ₂₄ O ₂)	3.44	8.57	12.33
15.384	Dodecanoic acid, ethyl ester (C ₁₄ H ₂₈ O ₂)	0.45	1.53	-
16.883	Tetradecanoic acid, methyl ester (C ₁₅ H ₃₀ O ₂)	0.48	0.51	1.50
17.375	Tetradecanoic acid (C ₁₄ H ₂₈ O ₂)	1.24	3.05	3.05
17.602	Tetradecanoic acid, ethyl ester (C ₁₆ H ₃₂ O ₂)	1.95	0.93	-
18.181	Pentadecanoic acid, methyl ester (C ₁₆ H ₃₂ O ₂)	2.35	0.18	-
18.610	Pentadecanoic acid, ethyl ester (C ₁₇ H ₃₄ O ₂)	2.04	0.07	-
18.975	Hexadecanoic acid, methyl ester (C ₁₇ H ₃₄ O ₂)	4.69	4.48	11.48
19.492	n-hexadecanoic acid (C ₁₆ H ₃₂ O ₂)	67.67	62.53	47.63
20.664	Octadecanoic acid, methyl ester (C ₁₉ H ₃₈ O ₂)	11.02	10.11	11.31
21.068	Octadecanoic acid (C ₁₈ H ₃₆ O ₂)	2.68	6.31	6.38
22.378	6-octadecenoic acid (C ₁₈ H ₃₄ O ₂)	-	0.2	-
22.479	Octadecanoic acid, 10-oxo-,methyl ester (C ₁₉ H ₃₆ O ₃)	0.7	0.41	1.3
22.643	Eicosanoic acid, methyl ester (C ₂₁ H ₄₂ O ₂)	0.85	0.35	0.64
24.458	DEHP (impurities)	0.13	0.14	0.19
Total		99.81	99.63	96.16

The second highest component was dodecanoic acid. At temperature of 300 °C, the percentage of dodecanoic acid was 11.08 %, at 350 °C the percentage of dodecanoic acid was 13.74 %, and at temperature of 400 °C the percentage of dodecanoic acid was 8.87 %. It meant that the component of dodecanoic acid was just slightly decreased by an increase in the temperature.

The third highest component was tetradecanoic acid. At temperature of 300 °C, the percentage of tetradecanoic acid was 6.06 %, at 350 °C, the percentage of tetradecanoic acid was 3.17 %, and at temperature of 400 °C the percentage of tetradecanoic acid was 2.41 %. It meant that the component of tetradecanoic acid was just slightly decreased by an increase in the temperature.

The highest component resulted from the degradation of biomass with solvent of hexane was n-hexadecanoic acid. At the temperature reaction of 300 °C, the percentage of n-hexadecanoic acid was 67.67 %. At temperature reaction of 350 °C, the percentage of n-hexadecanoic acid was 62.53%, and at temperature of 400 °C, the percentage of n-hexadecanoic acid was 47.63 % (Table 6). It meant that the component of n-hexadecanoic was decreased by an increased in the

temperature. Especially at temperature of 400 °C, the component of n-hexadecanoic acid was decreased drastically.

The second highest component was octadecanoic acid, methyl ester. At temperature of 300 °C, the percentage of octadecanoic acid, methyl ester was 11.02 %, at 350 °C the percentage of octadecanoic acid, methyl ester was 10.11 %, and at temperature of 400 °C the percentage of octadecanoic acid, methyl ester was 11.31 %. It meant that the component of octadecanoic acid, methyl ester is just constant by increasing the temperature.

From the tables above (Table 2 – 6), it can be classified that the compounds eliminated by the solvent used. Each solvent has certain selectivity, including esters, organic acids, and ketones/others from the degradation of biomass, as shown in Table 7. Each solvent has a major component in bio-oil product, methanol and ethanol solvents resulted mostly ketones/others as the main components, while toluene and hexane resulted organic acid as the main components, acetone gave the closed amount between ester and organic acid, as shown in Table 7. It meant that the results of biomass degradation is strongly depend on the solvent type.

Table 7. The selectivity of each solvent to the fraction of esters, acids and ketones/others at different temperature.

Compound selectivity	Organic Solvents														
	Methanol			Ethanol			Acetone			Toluene			Hexane		
Temperature (°C)	300	350	400	300	350	400	300	350	400	300	350	400	300	350	400
Ester (%)	28.84	22.46	34.32	22.63	6.28	36.68	37.75	27.4	49.17	0.0	2.39	4.79	24.65	18.83	26.58
Organic acid (%)	9.99	6.47	0.07	34.0	0.99	2.51	46.75	54.0	37.73	97.53	97.44	92.63	75.03	80.66	69.39
Ketones/ Others (%)	60.74	70.51	64.06	42.05	92.73	58.97	12.94	13.97	11.03	0.08	0.16	0.76	0.13	0.14	0.19
Total	99.6	99.44	98.45	98.68	100.0	98.16	96.69	95.47	97.93	98.85	99.99	98.18	99.81	99.63	96.16

The degradation of EFB in many types of organic solvents resulted hydrocarbon from C₆ to C₂₁. It meant that biomass degraded into smaller molecules and then reacted to each others of the reactive molecules into higher molecules.

Before chemical reaction acts, the microcrystalline of cellulose reacts in sub- and supercritical solvents require an extra step and time to break down the cellulose crystallite. In subcritical water, the crystallite is hydrolyzed at the surface region without swelling or dissolving. Therefore, the overall conversion rate of microcrystalline cellulose is slow, and there is no cellulose crystal formed in the residue. In contrast, in near-critical and supercritical water, the crystallite can swell or dissolve around the surface region to form amorphous-like cellulose molecules. These molecules are inactive; therefore, they can be easily hydrolyzed to celluloses and celooligosaccharides. Some of the hydrolysate can pass from the polymer phase to the water phase by cleavage of their hydrogen-bond networks [21].

In the first step of reaction hydrolysis, dehydration and hydration were take places, cellulose was converted into glucose and then into carboxylic acid in strong alkalines. In weak alkaline glucose converted into carboxylic acid and 5-hydroxymethyl furfural (5-HMF). In medium alkaline both reaction pathways take places [22]. In acidic pathway 5-HMF further converted into formic acid and levulinic acid by hydration reaction, further dehydration reaction into 1,2,4 benzotriol [23].

In the whole process, the substances of biomass are first hydrolyzed to small molecule

compounds, then further reaction of repolymerization, decomposition and condensation of the intermediates from the different phase may be favored with the increment of reaction temperature and residence time [24]. Carbohydrate is hydrolyzed to produce reduced sugar and non-reduced sugar. Glucose itself reversibly isomerizes into fructose, this is an important reaction since a number studies have confirmed that fructose is more reactive than glucose [24].

Further fragmentation and dehydrations lead to the formation of a variety of low molecular weight compounds such as formic acid, acetic acid, lactic acid, acrylic acid, 1,2,4-benzenetriol. Formation of tar and darkening of the solvent phase was observed, indicating that more heavy products are formed [25]. Under liquefaction conditions, the cellulose degrades to low molecular weight aldehydes and ketones, those aldehydes and ketones then form aromatic compounds by condensation and dehydration. The reactive molecules like organic acids and aldehydes are converted by the reactions with alcohols into higher molecules such as esters and acetals [26]. A completed methods of esterification of bio-oil was reviewed by Hu [27]. They reviewed many methods of esterification bio-oil in many environment mediums.

Esterification of bio-oil under sub-critical conditions is able to convert the carboxylic acids in bio-oil, but the phenolics may not be significantly converted due to the relatively low reaction temperature [28]. Esterification in supercritical alcohols helps to convert the phenolics in bio-oil, Peng [29] found that the super-critical esterification was more effective than the sub-critical esterification. At

temperature condition of 400 °C, for all solvents used there have a higher ester content compared to the other temperature operation (Table 7).

4. CONCLUSIONS

The decomposition of OPEFB in supercritical organic solvents liquefaction in the absence of catalysts has been performed successfully using batch reactor. Different organic solvents resulted different composition of soluble liquid/bio-oil. The bio-oil composition were composed from organic acids, ester and ketones/other. Each solvent type has a major component to each other. The methanol solvent resulted the major component, including 2-pentanone,4-hydroxy-4-methyl-, and hexadecanoic acid, methyl ester. The ethanol solvent resulted the major component was also 2-pentanone,4-hydroxy-4-methyl- and hexadecanoic acid, ethyl ester. The acetone solvent resulted the major component including n-hexadecanoic acid, hexadecanoic acid, ethyl ester and 2-pentanone,4-hydroxy-4-methyl-, respectively. Toluene solvent resulted the major component, including n-hexadecanoic acid and dodecanoic acid. The hexane solvent resulted the major component including n-hexadecanoic acid and octadecanoic acid, methyl ester and dodecanoic acid, respectively. The increasing temperature from 300 to 400 °C was just slightly affecting the change of the major component of bio-oil in percentages.

ACKNOWLEDGEMENT

The research was supported by LIPI/ Indonesian Institute of sciences. Internal project DIPA 2016.

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