Abstract. Biomass is a promising alternative energy resource due to its sustainability and environmental friendliness. In addition, it is also a potential candidate for chemical feedstock since many chemicals can be extracted or synthesized from biomass. Oil palm empty fruit bunch (EFB) is a biomass waste coming from the oil extraction process in a palm oil mill. In this study, potential recovery of chemicals from such biomass waste will be explored by hydrothermal treatment. Slurry of 300 mL of water and 30 g of material was treated in a 500 mL batch autoclave in temperature range of 200-350°C and initial pressure of 2.0 MPa. The slurry was heated up gradually to designed temperature, and then was kept for 30 min residence time. After filtrated, the liquid product was obtained. The liquid products were analyzed by TOC meter and HPLC. The analysis result showed that the liquid product contained several valuable chemicals from the decomposition of sugar compounds such as glucose, xylose, furfural, 5-hydroxymethylfurfural (5-HMF), formic acid and acetic acid. Yield of each compound varies at different temperatures. At elevated temperature, yield of sugar-derivative compounds tends to decrease.
Despite its benefit, oil palm plantation generates a huge amount of biomass waste which is considered as potential environment pollutant. Oil palm empty fruit bunch (EFB) is a biomass waste coming from oil extraction activity in palm oil mill to produce CPO. Ying et al [2] reported approximately 15.8 million ton per year of EFB was generated in Malaysia. According to our previous report [3], oil palm EFB contains a significant amount of polysaccharides e.g. cellulose (35.8 %) and hemicellulose (21.9 %), which can be decomposed into numerous sugar-derivative compounds through hydrolysis reaction. Considering its abundant availability with various organic substances can be derived from, EFB is obviously potential chemical feedstock.

Currently, most of the oil palm industries just conventionally use such EFB in land application as mulch [4]. However, unpleasant smell coupled with a slow release of CO$_2$ and CH$_4$ gas coming from their decomposition, which could last for up to 1 year, is the most common problem [5]. Therefore, a better method in managing such wastes is highly required.

Hydrothermal treatment is a common method used for converting wet biomass. Usually, this method is used to upgrade the calorific value of raw biomass. EFB is a solid waste from palm oil mill which has high moisture content. In the present work, potential recovery of valuable chemicals from liquefaction of EFB by hydrothermal treatment was studied.

2. Materials and methods

2.1. Materials

Oil palm EFB was obtained from a palm oil mill in Indonesia. The EFB was air dried and grinded to be powder with a particle size less than 1.0 mm. The composition of raw EFB (on dry basis) was as follows: 35.8% cellulose, 21.9% hemicellulose, 17.9% kland lignin, 4.0% wax, 3.0% ash, and 17.4% others. The compositions (e.g. cellulose, hemicellulose, lignin, etc.) of raw EFB and residual solid were determined according to a procedure developed by the US National Renewable Energy Laboratory [6].

2.2. Hydrothermal treatment

Experiments were carried out using the same apparatus and the same procedure that were described elsewhere [5]. Briefly, slurry of 300 mL of water and 30 g of EFB was treated in a 500 mL batch autoclave in temperature range of 200–350°C and initial pressure of 2.0 MPa. The slurry was heated up gradually to the target temperature, and then was kept for 30 min residence time. The autoclave was then cooled to ambient temperature by forced-convection air-cooling using a blower. After cooling, the liquid product was separated from the residual solid by vacuum filtration.

2.3. Liquid product characterization

After filtrated, the liquid product was obtained and its volume was measured. Total organic carbon (TOC) was measured on a Shimadzu TOC-5000A instrument. In addition, HPLC instrument (Column of Shodex KC-811 with RI detector of Jasco RI-2031 plus) was used to determine the concentration of chemical compounds. Analysis parameters for the HPLC were as follows: oven temperature of 50°C, carrier fluid (HClO$_4$ solution) of 2 mmol/L, and flow rate of 0.7 mL/min. The yield of a compound in the liquid product was evaluated according to the following equation:

$$\text{Yield} = \frac{\text{liquid volume (mL)} \times \text{concentration (mg/mL)}}{\text{feed material, dry basis (mg)}} \times 100\%$$  \hspace{1cm} (1)

3. Results and discussion

3.1. Liquid product characteristics
Hydrothermal treatment led to thermal degradation of the feed material. Physical and chemical bonds in the feed material were broken, so that large long-chain compounds such as cellulose, hemicellulose and lignin were broken down into smaller and simpler molecules. Furthermore, some of the molecules were dissolved into liquid part and some others were further degraded to gases. The remainder of feed material was recovered as a solid residue.

Figure 1 shows the volume of liquid product obtained after treatment. Approximately 78–93% of the total amount of water in the feed slurry was recovered as liquid product, while some amount was evaporated and carried over by gas product, and the rest was retained in the filtration cake. The amount of liquid product obtained from different temperature treatments did not vary significantly.

![Figure 1. Volume of liquid product obtained from different temperature treatments.](image)

Organic compounds degraded during the hydrothermal treatment were dissolved into liquid part, as indicated by relatively high total organic carbon (TOC) of the liquid. The liquid product from treatment of EFB had TOC of 15,520–18,660 ppm. Figure 2 illustrates that the TOC of liquid tended to increase within 200–270°C ranges. However, a slight decrease in TOC was observed from 200 to 240°C. Meanwhile, TOC decreased progressively at temperature above 270°C. This decrease was caused by increased polymerization reaction of water-soluble compounds to form aromatic compounds which subsequently precipitated during cooling period. This was confirmed by an increase of ligneous solid content of the residue (Fig. 4).

High-TOC of the liquid reflected many organic compounds were contained in the product. Various organic compounds (such as HMF, furfural, acetic acid, phenol, etc.) were detected in liquid product. Both cellulose and hemicellulose are long-chain polymers of sugar units. Under hydrothermal treatment, cellulose and hemicellulose were subjected to be hydrolyzed by water molecules. Hence, chemical bonds of cellulose and hemicellulose were cleaved, and several sugar monomers were leached and dissolved into liquid. The water-soluble sugar monomers were then underwent fast secondary decomposition to form acids or aldehydes.
Figure 3 shows the yields of glucose, xylose, 5-hydroxymethyl furfural (HMF), furfural, formic acid, and acetic acid. All of these compounds belong to sugar-derivatives compounds. HMF was derived from dehydration of glucose; a sugar monomer resulted from hydrolysis of cellulose [7]. The dehydration reaction of glucose to produce HMF was simply written in equation (2).

\[
C_6H_{12}O_6 \rightarrow C_6H_{10}O_3 + 3 \text{ H}_2\text{O}
\]  

Glucose \quad \text{HMF} \tag{2}

It can be seen from Figure 3 that the highest amount of HMF was obtained at 240°C. Furthermore, there was no HMF detected anymore at temperature above 270°C suggesting complete degradation of cellulose.

Different from HMF, furfural was produced from a fast multiple water cleavage reaction of a xylose, a sugar unit resulted from decomposition of hemicellulose [8,9]. Hence, a xylose molecule was dehydrated and lost 3 molecules of water to produce a furfural, based on the equation (3):

\[
C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3 \text{ H}_2\text{O}
\]  

xylose \quad \text{furfural} \tag{3}

Figure 3 indicates that the maximum of furfural was obtained at 200°C. Since it was the lowest temperature applied in the experiments, it can be suggested that fragmentation of hemicellulose has
begun at temperature below 200°C. At higher temperature, furfural amount continued decrease and finally disappeared in temperature over 270°C.

As shown in Figure 3, acetic acid was present in all temperature range. Srokol et al [7] reported that acetic acid could be formed from aldol cleavage of glucose with the following pathway:

\[
\text{glucose} \rightarrow \text{glyceraldehyde} \rightarrow \text{pyruvaldehyde} \rightarrow \text{acetic acid.}
\]

Figure 3 shows xylose was detected at 200–240°C, while formic acid was obtained at 200–300°C. The yield of xylose and formic acid tends to decrease at elevated temperature.

3.2. Residual solid characteristics

The data of sugar-derivative compounds suggested that decomposition of cellulose and hemicellulose has completed at 270°C. To confirm this, components analysis of solid residue was performed. Figure 4 illustrates the composition of solid residues resulted from 200–300°C treatment in comparison with raw feed.

Due to hydrothermally degraded, the composition of solid residue has dramatically changed. Figure 4 describes that hemicellulose and cellulose components of the feed were relatively easier to decompose than lignin. Decomposition of hemicellulose and cellulose occurred at lower temperature. No hemicellulose was left on the residual solid after being treated at 200°C. It confirmed that decomposition of hemicellulose possibly started at temperature lower than 200°C. On the other hand, cellulose was gradually degraded at elevated temperature and all cellulose was degraded at 270°C. Furthermore, the treatment has significantly degraded both the hemicellulose and the cellulose to produce a more ligneous solid. This behaviour is in agreement with other earlier reports [10,11].

![Figure 4. Residual solid composition of EFB](image)

4. Conclusions

Liquid produced by hydrothermal liquefaction of oil palm EFB contained various chemicals such as glucose, xylose, 5-hydroxymethyl furfural (HMF), furfural, formic acid, and acetic acid. All of these compounds derived from decomposition of carbohydrate polymer of EFB. Glucose and xylose were the primary decomposition product of cellulose and hemicellulose. Acetic acid and HMF were obtained from secondary or tertiary decomposition of cellulose, while furfural was derived from that of hemicellulose. The yield of compounds varied along with temperature. HMF and furfural was only obtained at low temperature treatment (200–270°C), while acetic acid was found in all temperature range. The yield of sugar-derivative compounds tend to decrease at elevated temperature. In cumulative, the yield was approximately 15% in 200°C, and gradually decreased to 8% in 350°C.
Acknowledgements
This study was supported by Japanese Ministry of Education, Culture, Sports, Science and Technology (Mombukagakusho).

References

[1] Oil World 2016 in RSPO Sustainable palm oil: the journey so far - 2015 (a report of GreenPalm, accessed from https://greenpalm.org on July 30, 2019)
[2] Ying T Y, Teong L K, Wan Abdullah W N and Peng L C 2014 The effect of various pretreatment methods on oil palm empty fruit bunch (EFB) and kenaf core fibers for sugar production Procedia Environ. Sci. 20 328–335
[3] Yuliansyah A T, Kumagai S, Hirajima T and Sasaki K 2019 Hydrothermal Treatment of Oil Palm Biomass in Batch and Semi-Flow Reactors Energy Procedia 158 675–680
[4] Zaharah A R and Lim K C 2000 Oil palm empty fruit bunch as a source of nutrients and soil ameliorant in oil palm plantations Malaysian Journal of Soil Science 4 51–66
[5] Yuliansyah A T, Kumagai S, Hirajima T and Sasaki K 2010 Production of solid biofuel from agricultural wastes of the palm oil industry by hydrothermal treatment Waste Biomass Valori. 1 395–405
[6] Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D and Crocker D 2005 Determination of Structural Carbohydrates and Lignin in Biomass The US National Renewable Energy Laboratory
[7] Srokol Z, Bouche A G, van Estrik A, Strik R C J, Maschmeyer T and Peters J A 2004 Hydrothermal Upgrading of biomass to biofuel; studies on some monosaccharide model compounds Carbohyd. Res. 339 1717–1726
[8] Antal M J, Leesomboon T, Mok W S and Richards G N 1991 Mechanism of formation of 2-furaldehyde from D-xylose Carbohyd. Res. 217 71–85
[9] Kruse A and Dinjus E 2007 Hot compressed water as reaction medium and reactant: 2. degradation reactions J. Supercrit. Fluid 41 368–369
[10] Ando H, Sakaki T, Kokusho T, Shibata M, Uemura Y and Hatate Y 2000 Decomposition behavior of plant biomass in hot-compressed water Ind. Eng. Chem. Res. 39 3688–3693
[11] Ehara K and Saka S 2005 Decomposition behavior of cellulose in supercritical water, subcritical water, and their combined treatments J. Wood Sci. 51 148–153