

Preparation of Biopolyol by Solvolysis Liquefaction of Oil Palm Mesocarp Fibre using Polyhydric Alcohol

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Abstract. Liquefied oil palm mesocarp fibre (LOPMF) is a promising natural material that can be used as biopolyol of polyurethane foam. The aim of this study was to utilizing solvolysis liquefaction conversion technology of oil palm mesocarp fibre (OPMF) for polyurethane (PU) foam. LOPMF was obtained with liquefaction of fibre in polyhydric alcohol (PA) such as ethylene glycol (EG), polyethylene glycol (PEG) and glycerol (GLY) as liquefaction solvent and sulphuric acid (H₂SO₄) in three different OPMF/PA ratio (1/2, 1/3 and 1/4) in conventional glass reactor. During the liquefaction, cellulose, semi-cellulose and lignin are decomposed, which results in changes of acid value and hydroxyl value. Liquefied OPMF and residues were characterized by Fourier transform infrared (FT-IR) spectroscopy. The results revealed that almost 50% of the OPMF converted into biopolyol product within 2 hours with OPMF/PA ratio of 1/4. Biopolyol produced under different condition showed viscosities from 210 to 450 Pa.s. The hydroxyl and acid values of the liquefied OPMF varied with the liquefied conditions. It was observed that with an increase in the liquefaction solvent (PA) amount in the mixture resulted in a high acid value and hydroxyl value for the OPMF. High reaction temperature combining with low OPMF material to solvent ratio resulted low hydroxyl number of LOPMF. The result in this study showed that biopolyol was suitable monomer for polyurethane synthesis.

1. Introduction

Nowadays, some products made from fossil fuels are an emergent problem, as consequence of their nature and lower biodegradability. There has been increased desire for more effective utilization of lignocellulosic biomass waste due to their potential to replace the petroleum based product and aid economic development. One of the great and most important agricultural industrial in Malaysia is palm oil processing and its cultivated in large areas. The amount of oil palm biomass produced by these oil palm plantations in year 2008 is estimated to be about 37.0 million tons, consisting of 22% empty fruit bunch (EFB), 13.5% fruit press fiber (FPF) and 5.5% shell (Malaysia Palm Oil Council (MPOC), 2004 and Malaysia Palm oil Board (MPOB) [1]. The aim of this research is utilizing liquefaction conversion technology to liquefied oil palm mesocarp fibre. In the fields of bioenergy and materials, various solvents have been used for liquefaction to produce biomass-based chemicals such as water, acetone, ethanol [2], phenol, ethylene glycol (EG), ethylene carbonate (EC), polyethylene glycol (PEG) [3], glycerol, and diethylene glycol (DEG) [4,5]. The liquefied products, polyol, can be



used for the production of polyurethane or polyester [6]. The catalytic conversion of oil palm waste biomass to produce biopolyol has received sustained attention because of its potential for lower energy consumption, better efficiency, and milder reaction conditions compared with other thermochemical conversions such as pyrolysis [7] or gasification [8]. liquefaction techniques and their ensuing final products (biopolyol) has been carried out in the different types of biomass in order to break up the chemical backbone of the biomass and functionalize the related fragments, a correctly selected solvent system under acid conditions can be chosen to produce polyols which has wide useful application. The effects of the solvent and liquefaction temperature were analyzed and the liquefaction conditions were optimized. Thus, the potential of biomass liquefaction of OPMF utilizes the rich biomass resource and reduces the dependence of the chemical on the oil resource. It can be forecasted the huge economical and social benefits will achieved if efforts are put into the study on liquefaction of agricultural biomass waste.

2. Experimental

2.1 Material

Oil palm mesocarp fibre was obtained from Sindora Palm oil mill, Johor, Malaysia dried in an oven at 105°C for one night and kept in a desiccator at room temperature before using. Ethylene glycol, polyethylene glycol 400 and glycerol were used as liquefaction solvents. 98% sulfuric acid was used as the catalyst. Phthalation reagent, phthalic anhydride, imidazol, sodium hydroxide and dioxane were used for analyzing the biopolyol properties. All chemical was purchased from Sigma-Aldrich.

2.2. Preparation of liquefied OPMF.

Ethylene glycol (EG), polyethylene glycol 400 (PEG400) and glycerol was used as the main liquefaction solvent. In addition, sulfuric acid was added as the catalyst. First, oven dried oil palm fruit waste (20g) and liquefaction reagent were mixed at 1/2, 1/3 and 1/4 weight ratio with 5% sulfuric acid as a catalyst. Then the mixture was placed into a 250 mL three-branch flask equipped with thermometer and magnetic stirrer. Liquefaction temperature and time was 150°C and 120 min (2 hours), respectively. The liquefaction was carried out in an oil bath. After that, cooled down to stop the reaction. The liquefied oil palm wastes were dissolved in 100 mL of methanol for 4 h. The liquefied solutions were then vacuum-filtered through filter paper. The filtrated liquid was evaporated at 70°C using rotary evaporator to remove methanol, the obtained black liquid was designated crude biopolyols [9][10].

2.3. Determination of percentage of unliquefied OPMF residue.

In order to determine the percent of unliquefied oil palm wastes residue, methanol-insoluble residue (R) was calculated by using following equation:

$$\text{Residue content, } R (\%) = (W_r / W_o) \times 100\% \quad (1)$$

$$\text{Liquefaction yield } (\%) = 100 - R (\%) \quad (2)$$

where R is the percentage of residue content; W_o is the initial oven-dried oil palm waste (g); W_r is the oven-dried weight of the solid residue (g) after filtration of the liquefied mixture.

2.4. Determination of acid value and hydroxyl number of liquefied OPMF.

Acid value must be known in order to determine the hydroxyl value of liquefied oil palm waste. A mixture of 8 g LOPFW, 80 ml 100% 1,4-dioxane and 20 ml water was titrated with 1 M sodium hydroxide (NaOH) solution to the equivalence point. The acid value in mg KOH/g of sample was calculated by the following equation:

$$\text{Acid value (mg KOH/g)} = \frac{(C - B)N \times 56.1}{W} \quad (3)$$

where C is the titration volume (mL) of the sodium hydroxide solution at the equivalence point (mL); B is the volume of the blank solution (mL); N is the equivalent concentration of KOH solution used, and W is the weight of LOPFW (g).

Hydroxyl number was determined as follows: a mixture of 1 g LOPFW sample and 25 mL of a phthalation reagent was heated at 110°C for 20 min. After that, 50 mL of 100% 1,4-dioxane and 25 mL of distilled water were added and the mixture titrated with 1 M sodium hydroxide solution to the equivalence point using pH meter. The phthalation reagent consisted of a mixture of 150 g phthalic anhydride, 24.2 g imidazol and 1000 g dioxane. The hydroxyl number in mg KOH/g of sample was calculated by the following equation:

$$\text{Hydroxyl value (mg KOH/g)} = \frac{(B - A)N \times 56.1}{W + \text{Acidvalue}} \quad (4)$$

where B is the volume of the blank solution; A is the volume (mL) of the NaOH solution after the phthalation liquefied of reaction sample; N is the normality of the NaOH solution; W is the weight of LOPFW (g).

2.5 Determination of liquefied OPMF viscosity.

The viscosity of biopolyols was determined according to ASTM D 4878-08 using a Brookfield DV I Prime viscometer, equipped with a small sample adapter, temperature probe, and temperature control unit. Viscosity was determined at $25 \pm 0.5^\circ\text{C}$ using rotational speeds recommended in the standard.

2.6 Fourier transforms infrared spectroscopy (FT-IR).

The Fourier transform infrared spectroscopy system that was employed in this work was Perkin Elmer spectrometer (Spectrum 100) Universal ATR Sampling Accessory. Liquefied oil palm wastes samples were drop into small cube (10 x 10x 10 mm) and place it at FTIR sample holder. FTIR spectra were recorded in the range of 400 to 4000 cm^{-1} collecting 35 scans with 4 cm^{-1} resolution, in the transmittance mode.

3. Result and discussion

3.1 Effect of liquefaction solvent on OPMF biopolyol synthesis

Liquefaction of oil palm mesocarp fibre with three different liquefaction solvent or polyhydric alcohols (ethylene glycol, polyethylene glycol 400 and glycerol) was studied. Figure 1a shows the effect of OPMF/PA ratio on residue content and viscosity. The residue content for OPMF/EG decreased slightly from 79% to 69% when the ratio decreased from 1/2 to 1/4. The residue content of OPMF/PEG reached 73% to 65% from 1/2 to 1/4 ratios. OPMF/PEG and OPMF/GLY ratio shows decreasing on residues content from 1/2 to 1/4 ratios. OPMF/EG a ratio was the most effective solvent for oil palm mesocarp fiber (OPMF) liquefaction. The decreasing residue content obtained from 1/2 to

1/4 ratio could be attributed to recondensation reactions of the liquefied components due to the high raw material concentration and this would break the liquefaction process [11]. The relatively lower residue content obtained in this study might be explained by the use of a different liquefaction solvent and different lignocellulosic biomass [12][13]. Thus, it could be concluded that the effect of different liquefaction solvent on the liquefaction rate of Liquefied oil palm fruit waste is greatly dependent on the oil palm fruit waste/PA ratio.

Figure 1a also presents effect of liquefaction solvent on OPMF/PA ratio on viscosity. It was observed that with an increase in the liquefaction solvent (PA) amount in the mixture, the viscosity value of the polyols gradually increased. Figure 3a shows that liquefied OPMF/PEG increased from 400 to 450 Pa.s when the liquefaction ratio decreased from 0.5 to 0.25. Previous studies have suggested that an increase in the biomass conversion/liquefaction ratio usually results in a increase in biopolyol viscosity due to the liquefaction of biomass [11]. At the beginning of the liquefaction, oil palm fruit waste is insoluble in the solvent and the viscosity of the reaction system is high. Along with the progress, more and more macro-molecules are dissolved by the solvent, resulting the decrease of the viscosity [12][13][14]. The viscosity of biopolyols continued to increase with further increases in the amount of liquefaction solvent. This might be caused by the fact that the liquefaction process occurred over a short reaction time and additional side reactions (e.g., recondensation of the liquefied components) occurred after liquefaction.

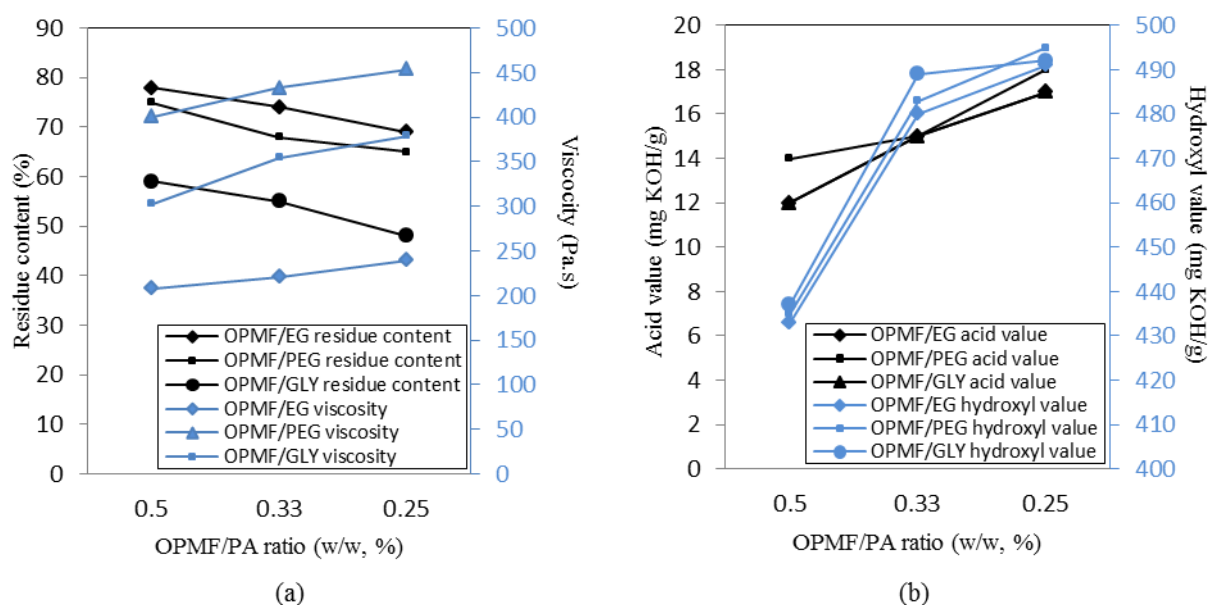


Figure 1. Effect of liquefaction solvent on OPMF/PA ratio on (a) residue content and biopolyol viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm mesocarp fibre/liquefaction solvent ratio, 1/2, 1/3, 1/4; temperature, 150°C; reaction time, 120 min; biomass loading, 20g; acid loading, 5%.

Figure 1b shows the acid value and OH number was significantly increase from 0.5 to 0.25 of OPMF containing different liquefaction solvent (PA) at 150°C. The acid value of the OPMF/EG ratio (13-16.2 mg KOH.g⁻¹), OPMF/PEG (14-17.2 mg KOH.g⁻¹) and OPMF/GLY (12-16 mg KOH.g⁻¹). Moreover, OPMF/PEG (445-495 mg KOH.g⁻¹) ratio contributed to higher hydroxyl values than OPMF/EG (432-490 mg KOH.g⁻¹) and OPMF/GLY (435-492 mg KOH.g⁻¹) ratios. It was observed

that with an increase in the liquefaction solvent (PA) amount in the mixture, the acid value and hydroxyl value of the polyols gradually increased. The increase in acid number can be attributed either to the increase of acidic substances or to the oxidation of the carbohydrates and lignin during the liquefaction. Besides, the increase in hydroxyl number can be probably attributed to the cleavage of ester or ether linkages between the lignin units [15][16]. Moreover, high content of liquefaction solvent contributed to higher acid number and hydroxyl values. This indicates that although the liquefaction solvent in the mixture can provide the hydroxyl group of the polyols, a loss of hydroxyl groups occurred during the liquefaction reaction which could be largely attributed to the alcoholysis reaction of oil palm fruit waste in liquefaction solvent and to the formation of ethers. The increase of acid value could be attributed to the increase of the liquefaction solvent with 5% H_2SO_4 , and also to the increase of acidic substances produced with the decomposition of oil palm components and the oxidation of alcohols as the liquefaction proceeded [17]. This result reveals that the reaction of the hydroxyl groups of the solvents with the oil palm waste components occurred during the liquefaction.

3.2 Effect of liquefaction temperature on OPMF biopolyol synthesis

Figure 2a shows the changes of the residue content and biopolyol viscosity as a function of the OPMF/PEG ratio at different two reaction temperatures. As expected, the residue content decreased as the OPMF/PEG ratio decreased, and the efficiency liquefaction process was enhanced with an increase of liquefaction temperature. However, liquefaction temperature interacted with OPMF/PEG ratio to impact the residue content. At a high OPMF/PEG ratio (i.e., 1/2), the temperature had little effect on residue content as OPMF/PEG ratio decreased to 1/3, the residue content decreased significantly for both liquefaction temperatures. The decrease in residue content leveled off with a decrease in the OPMF/PEG ratio at 120°C; while the residue content gradually decreased to the lowest residue content at 150°C. It is evident that higher temperature resulted in less residue content for all BF/PA ratios. As the amount of liquefaction solvent (i.e., PEG) in the mixture increased, the difference between the residue content in the same OPMF/PEG ratio under the two temperatures became gradually notable. Thus, it could be concluded that the effect of temperature on the liquefaction rate of LOPMF is greatly dependent on the OPF/PEG ratio.

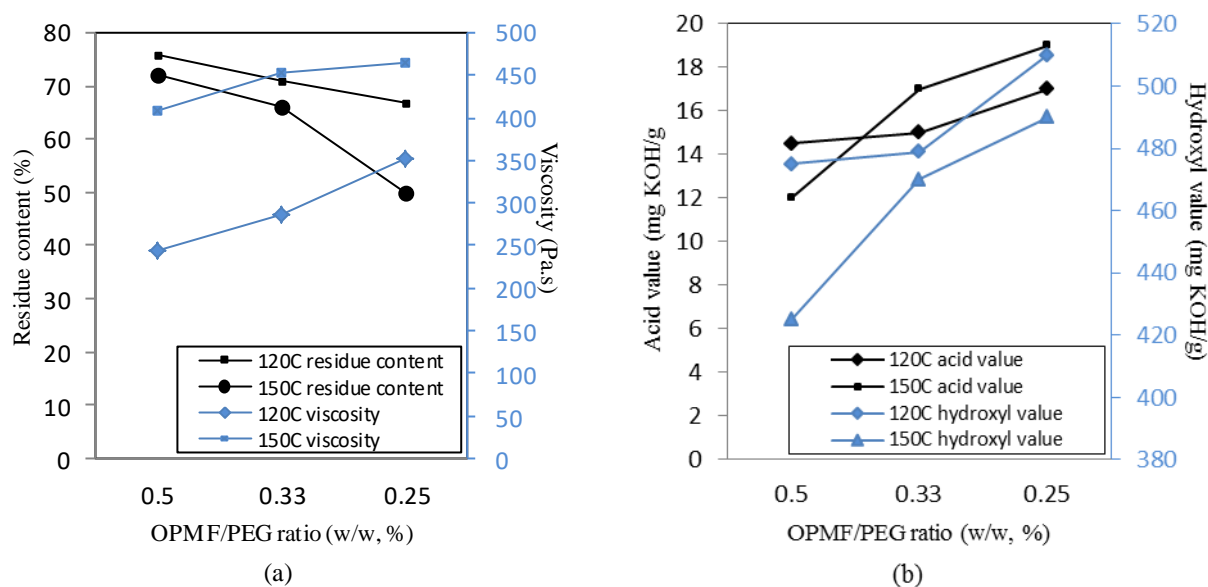


Figure 2. Effect of liquefaction temperature on OPMF/PEG ratio on (a) residue content and biopolyol viscosity (b) acid value and hydroxyl value. Reaction condition: Oil palm mesocarp fibre/liquefaction

solvent ratio, 1/2, 1/3, 1/4; temperature, 120°C, 150°C; reaction time, 120 min; biomass loading, 20g; acid loading, 5%.

The viscosity of the liquefied OPMF/PEG ratio at both temperatures increased drastically from 1/2 to 1/4. At the beginning of liquefaction, OPMF is insoluble in the solvent and the viscosity of the reaction system is low. The liquefaction temperature in this reaction is below 200°C because thermal decomposition of biomass weight occurred above 200°C based on TGA data in the previous studies. With respect to the biopolyol viscosity, it increased with increasing temperature. Generally, increases in the reaction temperature enhanced recondensation reactions between the liquefied components during the liquefaction process, resulting in formation of biopolyols with higher viscosity.

The effect of OPMF/PEG ratio on acid value and hydroxyl value of the liquefied products (polyols) from 120°C and 150°C are shown in Figure 2b. It was showed that with an increasing amount of PEG solvent in the mixture, the hydroxyl value of the biopolyols will increased. Besides, high temperature contributed to smaller hydroxyl values, value of the polyols prepared at 120°C was higher than that of the biopolyols prepared at 150°C. The oxidation and recondensation reactions among the liquefaction solvents and the decomposed OPMF fibre components could also take place during the liquefaction to consume hydroxyl groups and influence the hydroxyl value. With decreasing OPMF/PEG ratio, the hydroxyl value slightly increased. This result is in accordance with the finding of the work on the liquefaction of soybean straw [18]. The higher hydroxyl value for the polyols from the reaction with high solvent loading may be due to the higher biomass conversion and that extra solvent in the reaction mixture avoided the recondensation reactions. The acid value of the OPMF was in the range of 12.1–19 mg KOH/g. The increase of acid value could be attributed to the increase of the PEG, which contained 5 wt.% H₂SO₄, and also to the increase of acidic substances produced with the decomposition of OPMF components and the oxidation of alcohols as the liquefaction proceeded [19]. This provided further evidence that the OPMF/PEG ratio and temperature can both enhance the liquefaction rate.

3.3. Fourier transforms infrared spectroscopy (FT-IR).

Figure 3 shows the FT-IR absorption spectrum for the liquefied OPMF with polyhydric alcohol (PA) at 150°C in the presence of 5% H₂SO₄ as catalyst. FT-IR spectra of oil palm fruits wastes (OPMF) materials are complex due to the various functional groups and the complicated chemical environment that exist in OPFW components. Many peaks in OPFW IR spectra are broad and often overlap with neighboring peaks. FT-IR spectra of the Liquefied OPMF/EG, OPMF/PEG and OPMF/GLY did show some differences between each other. A broad peak around 3000-3400 cm⁻¹ represents the OH groups either from cellulose or from unreacted liquefaction solvent. The peak around 2870 cm⁻¹ represents the C-H symmetric stretching in aliphatic methyl. A shoulder at 1735 cm⁻¹ is primarily due to the carbonyl stretch in unconjugated ketone, ester or carboxylic groups in hemicelluloses [20]. From the growing shoulder of the 1735 cm⁻¹ peak, it can be inferred that hemicellulose is peeled off from adjacent lignin or cellulose into solution [21].

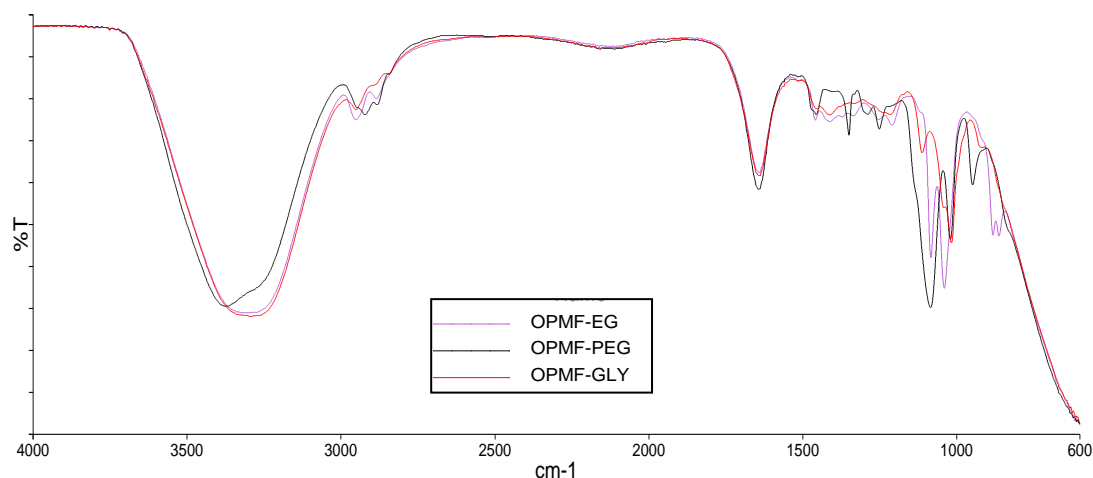


Figure 3. FTIR spectra of liquefied oil palm mesocarp fibre (OPMF) polyol) with polyhydric alcohol (PA). Reaction condition: Oil palm mesocarp fibre/liquefaction solvent ratio, 1/3; temperature, 150°C; reaction time, 120 min; biomass loading, 20g; acid loading, 5%.

Conclusion

In conclusion, that it is possible to convert oil palm mesocarp fibre (OPMF) into biopolyol via solvolytic liquefaction, at atmospheric pressure and moderate temperatures, in the presence of polyhydric alcohol (PA) and sulfuric acid as a catalyst. It was found that the different types of solvent, liquefaction temperature, the biomass/liquefying solvent ratio had great influences on the residue content and viscosity. This liquefied OPMF/PA biopolyol was presented as an environmentally friendly feedstock for polyurethane synthesis due to its suitable OH number and viscosity values. FTIR analyses of the liquefied OPMF showed the characteristic of OPMF differed after undergo the liquefaction process. The result in this study indicated the liquefied OPMF/PA biopolyol have potential for fabrication of polyurethane (PU) foams.

Acknowledgements

The author would like to thanks Sustainable Polymer Engineering, Advanced manufacturing and materials Center (SPEN-AMMC), Universiti Tun Hussein Onn Malaysia (UTHM), Johor and Malaysian Government for supporting this research under GPPS vot U774.

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