Characterization of Fe$_2$O$_3$/FeOOH Catalyzed Solvolytic Liquefaction of Oil Palm Empty Fruit Bunch (EFB) Products

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Abstract

The addition of Fe$_2$O$_3$/FeOOH nanoparticles as a catalyst in solvolytic liquefaction of oil palm empty fruit bunch (EFB) could be cheaper and efficient alternative for biomass industry in Malaysia. Fe$_2$O$_3$/FeOOH can be found naturally in limonite ores and it is cheap, but work efficiently in catalyzing liquefaction. The purpose of this study is to understand the effects on the combination of Fe$_2$O$_3$/FeOOH, as the catalyst in solvolytic liquefaction of EFB. Solvolytic liquefaction of EFB fiber, with and without Fe$_2$O$_3$/FeOOH, was carried out in the nitrogen gas atmosphere using an autoclave. This liquefaction mainly yielded solvolytic oil, n-hexane insoluble preasphaltene and asphaltene phase (PA+A), and solid residue. The presence of catalyst has significantly increased the liquefaction yield and solvolytic oil fraction. Chemical elemental analysis has showed that the products with lower oxygen content are obtained when Fe$_2$O$_3$/FeOOH is used. FT-IR spectroscopy proved that the conversion of the higher molecular compound to the lower molecular compounds with larger number of functional groups has occurred. The analytical Pyrolysis-GCMS revealed the existence of lower molecular weight alcohols, ketones, phenolic and aromatic compounds.

Keywords: Biomass; Catalyst, Empty fruit bunch; Solvolytic; Liquefaction

Introduction

Oil palm industries in Malaysia generate about 90 million tons of renewable biomass per year. Oil palm biomasses include oil palm trunks, pruned and felled fronds, shells, palm press fiber and Empty Fruit Bunches (EFB). EFB is a suitable renewable biomass material for the conversion into the valuable products, because it is locally abundant and rich in lingo cellulose components [1].

Biomass can be converted into useful chemicals and liquid fuels via thermo chemical conversion processes, including combustion, gasification, pyrolysis, liquefaction and carbonization. Among them, liquefaction is a promising way to provide either valuable chemicals or liquid fuels [2]. Solvolytic liquefaction has been intensively studied in recent years, as a method that allowed the production of useful polymer precursors or chemicals by chemical treatment of biomass, in the presence of specific organic solvents (media). Depending on both, the type of biomass and the reaction conditions, different products can be obtained [3].

Metallic catalysts are known to be effective additives in direct coal and biomass liquefaction. Previous studies [4-8] showed that the addition of catalysts can greatly improve the conversion rates and yield, and affect the composition of the liquid product. Biomass liquefaction, using Fe$_2$O$_3$ as a catalyst, is a common method to produce liquid fuel and useful chemicals, and also effective in improving the yield of biomass conversion [5,9,10]. FeOOH catalyst was also applied in the coal liquefaction, with high yield of conversion and high catalytic activity observed from previous studies [11,12]. Combination of Fe$_2$O$_3$ and FeOOH catalysts obtained from natural resources of limonite ores for coal liquefaction was studied by Kaneko et al. [13], showed high liquefaction activity and excellent oil yield from the process.

This paper reports on the effects of using Fe$_2$O$_3$/FeOOH nanoparticles on the yield and composition of the solvolytic oil obtained from oil palm Empty Fruit Bunches (EFB), through solvolytic liquefaction. Instead of the commonly used phenol, ethylene glycol (EG) was used as a solvent, because it is less harmful [14]. Nanoparticles size of Fe$_2$O$_3$/FeOOH is used to increase the dispersion and optimize the activity of these catalysts [15].

Materials and Methods

EFB fiber was supplied by Suttech Engineering Sdn. Bhd. The average fiber size is about 0.8 mm in dimension. The properties of EFB fiber are shown in Table 1. Ferric chloride (FeCl$_3$) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich and used as received.

The loading of the Fe$_2$O$_3$/FeOOH catalyst onto the EFB fibers was accomplished by the in-situ synthesis, as reported earlier [16]. Distilled water (100 ml) were filled into a round bottom flask, heated to 90°C and purged with nitrogen gas. EFB fiber (5 g) was then added into the flask and agitated using mechanical stirrer at 600 rpm. FeCl$_3$ (0.305 g) were added to the suspension, and agitation was continued for another 5 minutes for Fe$^{3+}$ ions to disperse thoroughly in the suspension. Subsequently, 5.75 ml of an aqueous NaOH solution (0.023 mol) were added to the fiber suspension to form the Fe$_2$O$_3$/FeOOH. After washed with acetone and distilled water, the fiber suspension was filtered and dried at 105°C for 24 hours. EFB and EG (mass ratio of 4:1) were placed into a 200 ml autoclave equipped with stirring and heating systems. After purging with nitrogen gas, the autoclave was then heated to 250°C, followed by a reaction time of 60 minutes. After the

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reaction completed, the autoclave was allowed to cool down to room temperature. Both liquid and solid products were collected for further analyses. The liquid product was separated into two fractions: Those soluble in THF, but insoluble in n-hexane, are referred to preasphaltene and asphaltene (PA+A), while oil is referred to those which are soluble in both solvents. Oil is later known as solvolytic oil fraction. Figure 1 shows the flowchart of solvolytic liquefaction process carried out in this study. The residue fraction is referred to those which do not dissolve in the solvents.

The total conversion and the yield of solvolytic oil, PA+A and residue fractions obtained in the solvolytic liquefaction reaction were calculated according to following equations:

\[ X\% = (1 - \frac{W_s}{W_0}) \times 100\% \]  
\[ PA+A\% = \frac{W_a}{W_0} \times 100\% \]  
\[ O+G\% = [X - (PA+A)] \times 100\% \]  

where \( X \) is total conversion of EFB, \( O+G \) is the total yield of solvolytic oil and gas fractions, \( W_s \) is the dry weight of residue, \( W_a \) is the dry weight of PA+A, and \( W_0 \) is the dry weight of EFB.

C, H, N and S contents of oil products were determined using Thermo Finnigan Eager-300 CHNS analyzer. Oxygen content was estimated based on the difference of C, H, N and S contents of the samples. The HHV of the oil products was then calculated using the Dulong formula developed by Demirbas [17], as followed:

\[ \text{HHV (MJ/kg)} = \{33.5[C] + 142.3[H] - 15.4[O] - 14.5[N]\} \times 10^{-2} \]  

The samples for FT-IR were prepared with equal sample weight mix with KBr, to form pellets. The samples were recorded using a Perkin-Elmer FTIR2000 spectrophotometer in the near IR region (4000-370 cm⁻¹).

Curie point pyrolysis GC/MS was performed using a Pyromat (GSG Ltd.), coupled with a GC 6890 and MSD 5973 (Agilent Technologies). About 200 µg of the sample had undergone pyrolysis at 600°C (Fecralloy™) for 10 seconds. The pyrolysate was carried by helium into the inlet (250°C, split 1: 20) of the gas chromatograph. Separation was achieved using a fused silica column (DB-5 ms, 30 m, 0.25 mm, 25 µm), a column flow of 0.9 ml min⁻¹, an oven programmed starting with 50°C (5 min), then 5°C min⁻¹ to 280°C (2 min), and an auxiliary temperature of 250°C. The mass spectrometer was operated in El mode at 70 eV, 230°C, and 1.5×10⁻³ Torr.

**Results and Discussion**

Figure 2 shows the total conversion and yield of the solvolytic liquefaction of EFB, with and without Fe₂O₃/FeOOH. As shown in Figure 2, the total conversion of EFB liquefaction increase from 44.26% to 65.58%, when Fe₂O₃/FeOOH presence in fiber. The same trend can be observed for the yield of O+G. In the presence of catalysts, the yield of O+G obtain is 51.40%. If compared to the sample without catalysts, the yield of O+G is lowered by 15.36%. The yield of PA+A has also increased from 8.22% to 14.18%, in the presence of Fe₂O₃/FeOOH. From the results, we can conclude that the presence of Fe₂O₃/FeOOH as catalyst in the solvolytic liquefaction of EFB has significantly enhanced the bond cleavage, cracking and thermal degradation of the fiber.

**Table 1: Proximate and ultimate properties of EFB (wt %).**

| Component/Property       | Measured Value | Method          |
|--------------------------|----------------|-----------------|
| Proximate analysis       |                |                 |
| Moisture                 | 10.40          | ASTM E871       |
| Ash                      | 3.60           | ASTM D 1102-84  |
| Volatile matters         | 77.50          | ASTM E872       |
| Fixed carbon             | 18.90          | By difference   |
| Chemical Properties      |                |                 |
| Elemental analysis       |                |                 |
| Carbon                   | 45.01          | CHNS Analyzer   |
| Hydrogen                 | 6.35           |                 |
| Nitrogen                 | 0.09           |                 |
| Sulphur                  | 0.00           |                 |
| Oxygen                   | 46.55          | By difference   |
| Chemical composition     |                |                 |
| Holocellulose            | 76.54          | ASTM D 1104-56  |
| Alphacellulose           | 49.30          | ASTM D 1103-60  |
| KIason lignin            | 16.23          | ASTM D 1106-56  |
| Extravites (Alcohol-toluene soluble) | 3.29 | ASTM D 1107-56  |
| Extravites (Hot water soluble) | 5.82 | ASTM 1110-56    |

**Table 2: Conversion and yield of liquefaction of EFB with and without FeOOH/Fe₂O₃ loading. Condition: 250°C, 60 min and N₂ gas.**

![Diagram of solvolytic liquefaction process.](image-url)

![Conversion and yield of liquefaction of EFB with and without FeOOH/Fe₂O₃ loading. Condition: 250°C, 60 min and N₂ gas.](image-url)
Table 2 shows the results of elemental analysis and the Higher Heating Values (HHV) of different product fractions from both catalytic and non-catalytic liquefaction process. In the absence of catalyst, preasphaltene/asphaltene fraction (PA+A) is found to have the highest carbon and the lowest oxygen content from all product fractions that resulting in the highest HHV value. Meanwhile, solvolytic oil fraction contains the least carbon and highest oxygen. Hence, its HHV value is slightly higher than the residue. This is probably due to the higher content of hydrogen. However, the HHV of these two fractions (solvolytic oil and residue) are very low, because of the unfavorable C/O ratio. The presence of the Fe$_2$O$_3$/FeOOH catalyst during solvolytic liquefaction only resulted to slightly increases of carbon contents and HHV values of these fractions, but has a comparatively strong effect on the PA+A fraction.

Figure 3 compares the IR spectra of EFB fiber (a) and the solvolytic oil fraction (b) obtained from catalytic liquefaction using ethylene glycol, as reacting/heat transferring medium. The vibration band pattern of spectrum 3(a) is similar to that of woody biomass [18], and contains typical signals of cellulose, hemicelluloses and lignin. The presence of cellulose is confirmed by the characteristic bands such as O-H stretching (3428 cm$^{-1}$), C-H$_2$ shearing (1437 cm$^{-1}$), C-H stretching (1376 cm$^{-1}$), O-H in-plane bending (1330 cm$^{-1}$), C-O-C asymmetry stretching (1162 cm$^{-1}$) and C-O stretching (1050 cm$^{-1}$ and 1020 cm$^{-1}$). Typical signals reducing end group for hemicellulose and cellulose can be found at 1734 cm$^{-1}$ (carbonyl C=O stretching), 1376 cm$^{-1}$ (C-H stretching), 1162 cm$^{-1}$ (C-O-C asymmetry stretching), 1050 cm$^{-1}$ (C-O stretching) and 1020 cm$^{-1}$ (C-O stretching). These bands caused by aromatic C=C stretching (1631 cm$^{-1}$ and 1505 cm$^{-1}$), C-H$_2$ bending (1437 cm$^{-1}$), aromatic in-plane C-H deformation (1256 cm$^{-1}$), and C-H in-plane bending (891 cm$^{-1}$) are strongly indicative for the presence of lignin in the EFB fibers. Table 3 and 4 summarized the FTIR bands and functional groups assignment of EFB fiber and solvolytic oil fractions, respectively.

The IR spectrum of the oil fraction is presented in Figure 3b. The broad stretching band of hydroxyl groups (3600-3200 cm$^{-1}$) is assumed to be due to the presence of considerable amounts of non reacted ethylene glycol, EG oligomers and EG derivatives, a distinctly increased number of hydroxyl groups in lower molecular compounds obtained from the EFB fibers by thermal hydrocracking, and residual amounts of water (Table 4). The intensity of C-H stretching (3000 to 2800 cm$^{-1}$) and C-H bending (1465 to 1350 cm$^{-1}$) bands increase as more alkane groups formed from the liquefaction reaction. The formation of carbonyl compounds (carboxylic acids, ketones and aldehydes, e.g.) due to the decomposition of cellulose and hemicellulose is shown by peaks at 1730 to 1650 cm$^{-1}$ (increased intensity of C=O stretching). The bands appearing in the range of 1300 to 950 cm$^{-1}$ can be assigned to C-O stretching and O-H bending, indicating the presence of primary, secondary and tertiary alcohols, phenols, esters and ethers. The sharp
signal at 1080 cm⁻¹ and 1040 cm⁻¹ are most likely due to C-O stretching confirming the presence of alcohols and ethers, as they are also detected in the analytical pyrolysis of GC/MS. Furthermore, the appearance of signals that could be clearly attributed to the presence of aromatic (1460 cm⁻¹, 1240 cm⁻¹, 1120 cm⁻¹ and 870 cm⁻¹), and carbonyl groups (1720 cm⁻¹) indicate that the oil fraction contains a certain percentage of lignin derived decomposition products.

Figure 4 and 5 show the gas chromatograms of the solvolytic oil fractions obtain through the liquefaction process, with and without...
Fe$_2$O$_3$/FeOOH nanoparticles, respectively. The pattern and the intensity of the peaks clearly reveal that the composition of both solvolytic oil samples differ significantly. The presence of larger number of compounds is detected in the solvolytic oil fraction that is obtained by catalytic liquefaction. The results show that the presence of catalyst has enhanced the molecular bonds cleavage, and the cracking of EFB fiber into compounds with low molecular weight. The solvolytic oil fraction from non-catalytic liquefaction shows significantly larger amounts of ethylene glycol. In the presence of the Fe$_2$O$_3$/FeOOH nanoparticles, the peaks of EG oligomers (di-, tri-, and tetraethyleneglycol) and EG condensation products with alcohols, phenols and organic acids are detected. Furthermore, in the presence of catalyst, higher amounts of lignin-derived degradation products, namely 4-methyl-, 4-ethyl-, 4-vinyl-, 4-propyl-, 4-(prop-1-enyl)-derivatives of guaiacyl and syringyl formed. Partially, the phenolic lignin combustion products are found, which correspond to the ethylene glycol ethers (phenol, benzoic acid, guaiacol). A similar trend is observed for the polysaccharide degradation products. Higher yield of polysaccharide degradation products is obtained for that solvolytic oil fraction in the presence of catalyst. The identification of these compounds in the solvolytic oil fractions were determined by GC/MS is listed in Table 5.

The percentage of peak area for each identified oil fraction compounds were quantified and distributed based on chemical functional groups, are summarized in Figure 6. Alcohols are the dominant chemical groups in both non-catalytic and catalytic oil fractions, as the total area (%) were 70.17% and 72.48%, respectively. As can be seen in Figure 4 and 5, majority of alcohols group in non-catalytic oil fraction are from ethylene glycol (Peak 3), and small amount of EG derivatives such as di-, tri- and tetra ethylene glycol. Whereas, huge amount of diethylene glycol (Peak 12) was detected in catalytic oil fraction, together with other alcohols group such as ethylene glycol, tri ethylene glycol, tetra ethylene glycol and EG derivatives, and also 3-pentanol and 2-methyl-3-hexanol from holocellulose decomposition. The increase of diethylene glycol compound in catalytic oil fraction showed that the presence of Fe$_2$O$_3$/FeOOH enhanced the reaction between EG molecules through dehydrolysis, releasing free radicals of H$^+$ and OH$^-$ for the cracking reaction of polysaccharide materials, as shown in Figure 7. Hence, this has increased the amount of furans group from 1.50% to 7.15%. Small amount of acids, hydrocarbons, ketones and aldehydes are detected in both non-catalytic and catalytic oil fraction.

**Conclusion**

The presence of Fe$_2$O$_3$/FeOOH nanoparticles as catalyst in EG-based solvolytic liquefaction of empty fruit bunches significantly increased the yield of both polysaccharide and lignin degradation products in the solvolytic oil fraction at comparatively low temperature (250°C). As the HHV for catalytic liquefaction products were only slightly higher compared to non-catalytic process, further purification and separation of the lower-molecular liquefaction products, such as alcohols, ketones, carboxylic acids, and aromatic compounds (phenol, guaiacyl and syringyl derivatives) would be a good step towards further valorization of the oil fraction.

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Table 5: GC/MS analysis results for the oil fractions obtained in solvolytic liquefaction of EFB, without and in the presence of FeOOH/Fe2O3 catalyst.

| Peak No. | RT (min) | MW  | Compound                                      |
|----------|----------|-----|----------------------------------------------|
| 1        | 1.506    | 44  | Carbon dioxide                               |
| 2        | 1.993    | 60  | Acetic acid                                  |
| 3        | 2.640-8.854 | 62 | Ethylene glycol                              |
| 4        | 3.756    | 92  | Toluene                                      |
| 5        | 4.337    | 162 | 1,6-anhydro-beta-glucopyranose (levoglucosan) |
| 6        | 4.931    | 96  | Furfural                                     |
| 7        | 5.500    | 112 | 3-carboxyfurane                              |
| 8        | 6.100    | 104 | Ethylene glycol monooctatate                 |
| 9        | 7.524    | 126 | Styrene+carbohydrate derivatives             |
| 10       | 8.201    | 86  | Butyrofuran                                  |
| 11       | 11.003   | 94  | Phenol                                       |
| 12       | 11.181-13.353 | 106 | Diethylene glycol                            |
| 13       | 11.661   | 114 | 2-methyl-2-propen-1-ol acetate              |
| 14       | 13.460   | 108 | 2-methyl-phenol                              |
| 15       | 14.190   | 116 | 2-methyl-butanolic acid                      |
| 16       | 14.570   | 76  | Propylene glycol                             |
| 17       | 14.718   | 102 | 2-ethyl-1,3-dioxolane                        |
| 18       | 14.843   | 102 | 2-ethyl-1,3-dioxolane                        |
| 19       | 15.080   | 76  | 2-methoxy-ethanol                           |
| 20       | 15.383   | 150 | Triothylene glycol                           |
| 21       | 15.407   | 126 | 3-ethyl-2-hydroxy-2-cyclopenten-1-one        |
| 22       | 15.547   | 150 | 2-methoxy-2-methyl-3-hexanol                |
| 23       | 15.787   | 182 | 2-methoxy-4-propyl-phenol                   |
| 24       | 16.042   | 206 | 2-(2-(2-methoxyethoxy)ethoxy)-acetate ethanol |
| 25       | 16.172   | 132 | Pentanedioic acid                            |
| 26       | 17.247   | 208 | Tetraethyleneglycol monoethyl ether          |
| 27       | 17.427   | 150 | EG derivaties                                |
| 28       | 17.787   | 180 | 4-vinyl-syringol                             |
| 29       | 18.434   | 102 | 2-methyl-3-hexanol                           |
| 30       | 19.080   | 76  | 2-methoxy-ethanol                           |
| 31       | 19.145   | 116 | 3-methyl-2(3H)-benzofuranurone               |
| 32       | 19.438   | 102 | 3-ethyl-2-hydroxy-2-cyclopenten-1-one        |
| 33       | 19.650   | 76  | 2-methoxy-ethanol                           |
| 34       | 19.787   | 150 | Triothylene glycol                           |
| 35       | 19.843   | 102 | 2-ethyl-1,3-dioxolane                        |
| 36       | 19.928   | 116 | 2-methyl-3-hexanol                           |
| 37       | 20.208   | 150 | 4-ethyl-2-methoxy-phenol                     |
| 38       | 20.790   | 132 | 2-methoxy-4-propyl-phenol                   |
| 39       | 21.247   | 132 | 2-methoxy-4-propyl-phenol                   |
| 40       | 21.787   | 150 | Triothylene glycol                           |
| 41       | 22.247   | 182 | 2-methoxy-1,4-benzenedicarboxylic acid, dimethyl ester |
| 42       | 22.316   | 150 | 3-methyl-2(3H)-benzofuranurone               |
| 43       | 22.427   | 150 | Triothylene glycol                           |
| 44       | 22.496   | 132 | 2-methoxy-4-propyl-phenol                   |
| 45       | 22.642   | 126 | 3-ethyl-2-hydroxy-2-cyclopenten-1-one        |
| 46       | 22.687   | 150 | Triethyleneglycol monoethyl ether           |
| 47       | 22.797   | 150 | Triethyleneglycol monoethyl ether           |
| 48       | 23.116   | 150 | Triethyleneglycol monoethyl ether           |
| 49       | 23.710   | 150 | Triethyleneglycol monoethyl ether           |
| 50       | 24.238   | 150 | Triethyleneglycol monoethyl ether           |
| 51       | 24.761   | 150 | Triethyleneglycol monoethyl ether           |
| 52       | 25.376   | 150 | Triethyleneglycol monoethyl ether           |
| 53       | 26.247   | 150 | Triethyleneglycol monoethyl ether           |
| 54       | 26.654   | 150 | Triethyleneglycol monoethyl ether           |

Figure 6: Classification of compound based on chemical functional group in oil fraction obtained from liquefaction of EFB, without and in the presence of FeOOH/Fe2O3 catalyst.

Figure 7: Dehydrolysis of ethylene glycol in the presence of catalyst during solvolytic liquefaction of EFB.

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