

Solvolytic Liquefaction of Oil Palm Empty Fruit Bunch (EFB) Fibres: Analysis of Product Fractions Using FTIR and Pyrolysis-GCMS

(Pencecairan Solvolik Serabut Tandan Kosong Kelapa Sawit: Produk Pencirian melalui FTIR dan Pirolisis-GCMS)

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ABSTRACT

Oil palm empty fruit bunch (EFB) fibers were subjected to solvolytic liquefaction to convert into liquid products using ethylene glycol (EG) as a supporting agent. The process was carried out at 250°C for 60 min. The water-insoluble product fraction was exhaustively extracted with acetone (ASL fraction) to separate all less polar. FTIR and comparative analytical pyrolysis GC/MS of the parent EFB fiber and the ASL fraction confirmed the formation of larger amounts of long-chain lipophilic compounds under liquefaction conditions. Furthermore, a considerable amount of less polar thermal lignin degradation products were obtained comprising all of the three main lignin building blocks, i.e. 4-hydroxyphenyl- (P units), 4-hydroxy-3-methoxyphenyl- (G units) and 3,5-dimethoxy-4-hydroxyphenyl (S units) substituted compounds. 4-Prop-2-en-1-yl substituted phenolic compounds contributed mostly to the cumulated peak area of all lignin derived pyrolysis products obtained by analytical Curie point pyrolysis GC/MS at 600°C. The results of both instrumental-analytical methods confirm the formation of phenol and its derivatives, furan derivatives, organic acids, hydrocarbon, ester, benzene groups and alcohols.

Keywords: Ethylene glycol; FTIR; oil palm empty fruit bunch; pyrolysis-GCMS; solvolytic liquefaction

ABSTRAK

Tandan kosong kelapa sawit (EFB) telah ditukar kepada produk cecair dengan menggunakan proses pencecairan solvolitik dengan kehadiran agen penyokong, etilena glikol (EG). Proses telah dijalankan pada 250°C selama 60 min. Hasil pecahan yang tidak larut dalam air diekstrak oleh pelarut aseton (ASL) untuk memisahkan produk kurang kutub. Analisis FTIR dan pirolisis GC/MS ke atas fiber EFB dan hasil pecahan ASL telah mengesahkan pembentukan sebatian lipofilik rantai panjang. Tambahan pula, sejumlah hasil produk daripada degradasi terma lignin terbukti mengandungi ketiga-tiga komponen utama lignin iaitu: 4-hidroksifenil (unit-P), 4-hidroksi-3-metosifenil (unit-G) dan 3,5-dimetosi-4-hydrosifenil (unit-S) sebatian-sebatian serabut. Merujuk kepada keputusan analisis pirolisis GC/MS pada takat Curie 600°C, sebatian fenolik gentian, 4-prop-2-en-1-il merupakan penyumbang utama hasil produk pencecairan solvolitik. Kedua-dua keputusan analisis FTIR dan pirolisis GC/MS mengesahkan bahawa pencecairan solvolitik EFB telah membentuk asid karbosilik dan terbitan, terbitan furan, asid-asid organik, hidrokarbon, kumpulan benzena dan alkohol.

Kata kunci: Etilena glikol; FTIR; pencecairan solvolitik; pirolisis-GCMS; tandan kosong kelapa sawit

INTRODUCTION

Biomass is widely considered as a sustainable source of renewable energy particularly in countries with plentiful of agricultural activities. Over the last two decades, special attention has been paid to conversion of residual biomass and renewable materials into bio-oil or liquid fuels (Khor et al. 2009). Malaysia, being a country that actively promotes agricultural activities has abundant of biomass wastes. Oil palm is the most important agriculture crop in Malaysia, since Malaysia is one of the main palm oil producer and exporting countries in the world. In year 2008, 4.88 million hectares of land in Malaysia is covered by oil palm cultivation which produces 90.4 million tons of fresh fruit bunches (FFB). 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) January 2009). Indiscriminate disposal of these wastes will cause serious environmental problems. On the other hand, lately, it has been proven that biomass sources can become an economical source of renewable energy. Therefore, developing new technologies for converting oil palm biomass to energy sources (liquid or gas) becomes an attractive research area (Mazaheri et al. 2010).

The traditional methods such as composting and incineration are not suitable to process these organic solid wastes, whereas the nitrogen content of EFB is too low for composting, incineration and the smoke evolved would

cause serious environmental pollution by volatiles and dust particles. It is supposed that pyrolytic conversion of EFB into char, EFB vinegar and bio oil would be a viable valorization approaches (Khor et al. 2009). Lignocellulosic materials can be converted into liquid fuels by thermochemical methods such as gasification, pyrolysis and liquefaction (Qian et al. 2007). Among these methods, liquefaction has been attracted increasing attention recently. The advantage of this biomass converting technology is that it does not require feedstock drying beforehand, which would require a great deal of heating energy due to the high latent heat of water vaporization. The liquefaction process requires a moderate temperature (200–300°C) and generates therefore liquid organic compounds that still have a comparatively highly oxygen content. The finished products has a potential fuel additives or can be used as sources for producing valuable chemicals (Liu et al. 2006).

Solvolytic liquefaction as a special technology employing high-boiling, chemically largely inert liquids has been intensively studied in the past years. Besides the distinctly lower energy requirements, solvolytic liquefaction has several advantages compared with the other thermomechanical processes: The polymeric constituents of the biomass depolymerize only to a desired extent and react subsequently with a specific organic reagent to various valued-added polymer precursors or chemicals (Lim et al. 2004) and the presence of a solvent keeps the concentration of products low and prevents secondary reactions, cross-linking or re-polymerisation. Solvent has a remarkable effect on the efficiency of liquefaction reaction, for example, the use of supercritical alcohol, rather than water can effect the efficiency (Liu & Zhang 2008).

The purpose of this paper was to develop a characterization approach to determine the major chemical compounds of the liquid product from solvolysis of oil palm empty fruit bunch (EFB) using FTIR and analytical pyrolysis GC/MS. The ultimate goal is to develop a process that is able to produce value added product from waste such as desired bio-oil or liquid fuel from the biomass.

EXPERIMENTAL DETAILS

METHODS

The experiment was carried out in a 200 mL stainless-steel autoclave with a stirrer. In each test, the reactor was charged with 5 g EFB fibre and 20 mL EG. The headspace inside the autoclave was purged with nitrogen for at least 5 min, the reactor was heated to 250°C and stirring was continued for 60 min. Then, the autoclave was allowed to cool down to room temperature before it was depressurized. The volume of gas released was measured and recorded. The remaining liquid (water-soluble fraction, WS) and solid phases were separated by filtration and water was largely removed from the WS fraction by heating up to 120°C to give the water-soluble fraction. The remaining water-insoluble fraction (WIS) was exhaustingly extracted with

acetone (ASL fraction). The combined acetone extracts was removed under vacuum. The acetone-insoluble fraction on the other hand was dried at 105°C to obtain solid residue. Figure 1 shows a flow chart of the overall process. The yield of the oil is defined as weight percentage of the raw biomass. All the weight were based on the mass after oven-dried. The conversion rate and oil yield were calculated using the following formulas:

$$\text{ASL Yield (wt\%)} = (\text{weight of ASL}) / (\text{weight of biomass}) \times 100\% \quad (1)$$

$$\text{Residue (wt\%)} = (\text{weight of solid residue}) / (\text{weight of biomass}) \times 100\% \quad (2)$$

$$\text{Conversion rate} = 100\% - \text{weight of residue (wt\%)} \quad (3)$$

EFB fibres were analyzed using a Perkin-Elmer FTIR spectrophotometer 2000. Each sample was scanned at 4 cm⁻¹ resolution and a scan interval of 1 cm⁻¹. KBr pellets were used to obtain the FTIR spectra. The chemical composition for EFB fibers and ASL products were determined by pyrolysis-GC/MS. Curie-point pyrolysis GC/MS on the parent EFB fibres and the ASL extracts were performed using a CPP-40 pyrolyser (GSG) coupled with a GC 6890 and MSD 5973 (AGILENT TECHNOLOGIES). Two hundred and sixty µg of the sample was pyrolysed at 600°C (FECRALLOY™) for 10 s. 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 HP-5ms column (30 m, 0.25 mm, 25 µm) and a column flow of 1.0 mL min⁻¹. Oven program: 50°C (5 min), 5°C min⁻¹ to 180°C, then 10°C min⁻¹ to 280°C (9 min). Auxiliary temperature: 250°C (18 min), 10°C min⁻¹ to 280°C (14 min). Mass spectrometer: EI mode (70 eV); ion source 230°C; quadrupole 150°C, 7.6·10⁻⁶ torr.

RESULTS AND DISCUSSION

BIOMASS CONVERSION RATE

As shown in Table 1, the yield of ASL from solvolysis liquefaction of EFB fibers is 82.84% and the gas yield at about 500 cm³. The obtained ASL is oil in black colour after extraction.

ELEMENTAL COMPOSITIONS

Table 2 shows the results of elemental analysis and the higher heating values (HHV) of the raw EFB fibers and the oily ASL fraction obtained from the former by solvolytic liquefaction using ethylene glycol as a high-boiling solvent. The data reveal that the lipophilic liquid fraction has a significantly higher oxygen content of 61.95 w% compared with the parent EFB fibers (48.44 wt%). The ASL fraction

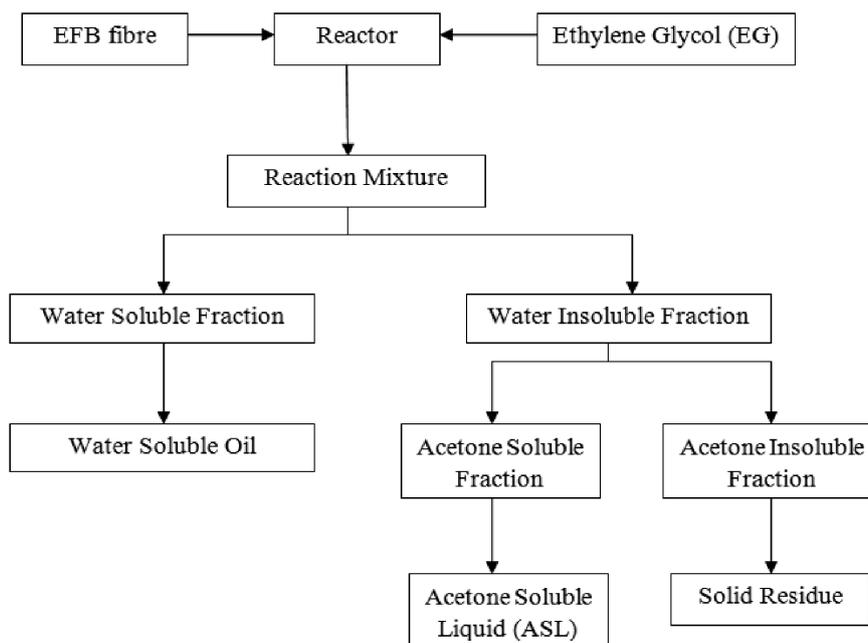


FIGURE 1. A brief scheme of the solvolysis liquefaction process and product separation

TABLE 1. Yield of oil and gas for EFB

Sample	EFB
Yield of ASL (%)	82.84
Yield of Gas (cm ³)	500

TABLE 2. Elemental compositions of EFB fibers and the oils produced by solvolytic liquefaction process at 250°C for 60 min without catalyst

Sample	Element				Higher heating value, HHV ^c (MJkg ⁻¹)
	C	H	N	O ^b	
EFB	44.75	6.39	0.42	48.44	18.69
ASL EFB	29.29	8.75	0.01	61.95	15.92

^b By difference and assuming that the sulfur content is negligible

^c Higher heating value; calculated by the formula, i.e. $HHV \text{ (MJ kg}^{-1}\text{)} = -1.3675 + 0.3137C + 0.7009H + 0.0318O$

is supposed to consist mainly of less polar compounds due to the preceded separation of the water-soluble fraction. Therefore, the increased oxygen content of the ASL fraction is supposed to be mainly due to the presence of EG oligomers as well as EG etherification and esterification products formed in secondary reactions. The wider C/H ratio of the oil evidences that the aromaticity of the ASL fraction is distinctly lower than in the EFB fibres. This, in turn, confirms the enrichment of long-chain aliphatic compounds in this fraction in disfavor of aromatic, most likely lignin-derived compounds.

The ASL fraction was furthermore found to virtually lack any nitrogen. This indicated that most of the EFB's nitrogen might be bound in lower molecular compounds, preferably as ammonia salts of organic acids or as amides

or polymers which would remain in other fraction such as residue. However, considering the fact that the C/N ratio of EFB has been reported previously (Hamdan et al. 1998) to drop from 60 to 16 upon composting for 52 days only – which is closely to the C/N ratio of humid substances – it is assumed that nitrogen can easily be bounded to mineralizable ammonia or amide groups.

The obtained higher heating values of 15.92 MJ kg⁻¹ were somewhat lower than the typical gross caloric values reported in the literature for bio-oil (~17 MJ kg⁻¹) (Mohan et al. 2006). The lower heating value is highly likely due to the: comparatively high oxygen content; residual amounts of water and lower density of the ASL fraction compared with bio-oil which might be due to the presence of EG derivatives. Thorough washing of the

remnant after separating the water-soluble phase, drying of the acetone-soluble fraction prior to evaporating the solvent and the use of a suitable catalyst are factors that would highly likely further increase the bio-oil quality with regard to its caloric value.

FT-IR ANALYSIS

Figure 2 shows the FT-IR spectra of EFB fibres and the acetone-soluble fraction obtained by solvolytic liquefaction of EFB. In Table 3, various bands in the spectra was identified as corresponding to OH (3410.83 cm^{-1}), methoxy (2928.87 cm^{-1}) and aromatic rings ($\sim 898 - 829\text{ cm}^{-1}$). According to previous study (Qian et al. 2007), the C-H stretching bands at range $2800\text{--}3000\text{ cm}^{-1}$ (partially also caused by O-H stretching) and the bands in the region of $\sim 1000\text{--}1400\text{ cm}^{-1}$, caused by combination and overlapping of C-O stretching bands and by several deformations. The width and intensity of the bands between $1000\text{--}1100\text{ cm}^{-1}$ is dependent on the presence of sugars in the samples, while the bands for the hydroxyl group above 3000 cm^{-1} are due to alcoholic or phenolic components.

PYROLYSIS-GCMS

The comparative analytical pyrolysis GC/MS of EFB fibres and the ASL fraction was carried out to get more information about individual compounds that were formed in the course of solvolytic liquefaction. The EFB and ASL products were characterized by pyrolysis GC/MS for identification of their chemical components. Tables 4 and 5 give the identified compounds in the EFB and ASL from the solvolytic liquefaction of EFB in ethylene glycol under high pressure and 250°C for 60 min without catalyst. All the identified compounds are shown in the table. It is clearly seen that phenolic compounds are the major compounds identified in the EFB fibers such as phenol, 2,6-dimethoxy, phenol,2,6-dimethoxy-4[2-propenyl], phenol,2-methoxy-4-methyl and others phenolic compounds. The furan derivatives, organic acids, long-chain alkanes, ester and alcohols existed in the ASL. Some of the fatty acids were detected in the ASL EFB, such as hexadecanoic acid which might have already existed in EFB before the solvolytic liquefaction process. It is believed that the furan derivatives and the organic acids were formed from the cellulose and hemi-cellulose

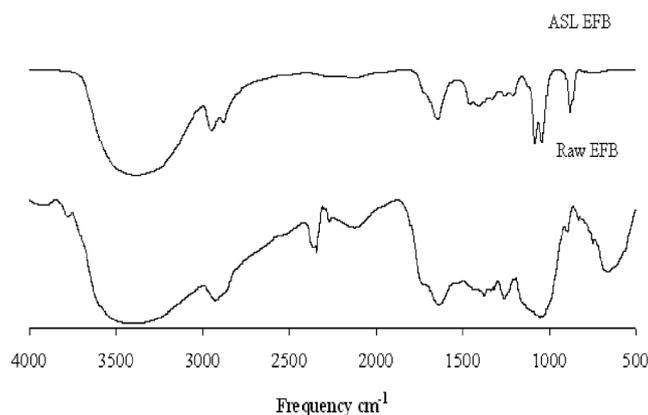


FIGURE 2. FTIR spectra for raw EFB

TABLE 3. FTIR band assignments for EFB fibers and the bio-oil (ASL) fraction obtained by EG solvolytic liquefaction

Functional group	Frequency (cm^{-1})	
	Raw EFB	ASL EFB
O - H, Alcohol, water (broad)	3410.83	3389.22
C - H, stretching (alkanes; CH, CH ₂ , CH ₃)	2928.97	2949.06; 2883.36
C \equiv C, Alkynes	2130.71	2125.27
C = C stretching (alkenes stretching, lignin e.g.)	1638.77	1646.15
C - H bending, Alkanes bending (cellulose, hemi-cellulose; lignin)	1375.73	1456.95; 1411.71
C-O, Alcohol stretching (cellulose and hemi-cellulose; lignin)	1259.69; 1052.95	1256.78; 1211.62; 1084.64; 1043.64
C - H Aromatic rings (out-of-plane bending) (lignin)	898.75; 829.57	882.92
C - X, Alkyl halide	749.14	

TABLE 4. Composition of ASL (acetone soluble liquid) EFB

Peak	Retention time (min)	Compound
1	2.681	1,2-ethanediol
2	5.506	furfural
3	7.524	styrene
4	8.67	2-hydroxy-cyclopent-2-en-1-one,
5	10.397	ethanol,2,2'-oxybis-
6	10.902	Phenol
7	12.285	3-methyl-cyclopentene-1,2-dione,
8	12.279	2-hydroxy-3methyl-cyclopent-2-en-1-one,
9	18.439	1,4:3,6-dianhydro-alpha-D-glucopyranose
10	18.843	triethylene glycol
11	22.214	2,6-dimethoxyphenol (syringol),
12	22.665	ethanol,2,-[4-ethylphenoxy]-
13	23.016	4-morpholineethanol
14	23.597	2-[4-methoxyphenoxy]ethanol
15	24.149	n-propyl benzoate
16	24.695	1,2,3-trimethoxybenzene
17	24.867	Eugenol
18	26.434	ethanol,2-[2-phenoxyethoxy]
19	26.636	benzene,1,2,3-trimethoxy-5-methyl
20	27.675	decanoic acid
21	28.452	phenol,2,6-dimethoxy-4[2-propenyl]-
22	28.708	3-Buten-2-one,4-[2,6,6-trimethyl-1-cyclohexen-1-yl]
23	28.886	2,3,3,4,7-pentamethyl-2,3-dihydro-benzofuran
24	30.785	2-propenoic acid,3-[4-hydroxy-3-methoxyphenyl]
25	31.99	2-isopropenyl-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene
26	32.055	tetradecanoic acid
27	34.322	2-heptadecanone
28	34.032	1-hexadecene
29	32.643	hexadecanoic acid,methyl ester
30	34.032	1-hexadecene
31	34.322	2-heptadecanone
32	34.643	hexadecanoic acid,methyl ester
33	35.1	n-hexadecanoic acid
34	35.504	hexadecanoic acid,ethyl ester
35	36.732	11-octadecanoic acid,methyl ester
36	37.432	1-octadecanethiol
37	37.753	Eicosane

components of the biomass feedstock (EFB fibre). Besides, the phenolic compounds, such as phenol,2,6-dimethoxy-4[2-propenyl] and others which has detected by the GC/MS is originated from the degradation of the lignin component in the feedstock.

According to the previous reports (Huber et al. 2006; Karagoz et al. 2005), the multicomponent mixture are derived primarily from depolymerization and fragmentation reaction of the three key building blocks of lignocellulose: cellulose, hemicellulose and lignin. The syringols (phenol-2,6-dimethoxy) are formed from the lignin fraction. The basic unit of lignin is the phenyl propane (substituted), which is a rich source of phenolic compounds in the liquid hydrocarbons.

The miscellaneous oxygenates, sugars and furans chemical compounds might formed from the cellulose and hemicellulose of the biomass. The formation of esters, acids, alcohols, ketones and aldehydes may probably resulted from decomposition of the miscellaneous

oxygenate, sugars and furans. The presence of the aromatic and oxygenated compounds is attributable to its nature biopolymer on earth such as cellulose and hemicellulose. In future research work, the highly oxygenated organic components would need to be first separated from the aqueous phase and then upgraded using hydrotreating-hydrocracking process in order to further raise their heating values and reduce the corrosiveness when they were used as a potential fuel (Tsai et al. 2006). The upgraded oil has the potential to be bio-fuel and also to produce phenolic resin.

CONCLUSION

In this paper, the identification on the chemical compounds of the solvolytic wood oils by using CHNS, FTIR and pyrolysis GCMS were reported. The FTIR results showed that the ASL for EFB contain different chemical functional groups, such as alkanes, alkenes, alcohols, phenol, esters,

TABLE 5. Composition of raw EFB

Peak	Retention time (min)	Compound
1	2,384	acetic acid
2	3,803	toluene
3	3,844	toluene
4	5,672	furfural
5	6,011	furfural
6	8,468	ethanone, 1-2(furanyl)-
7	10,337	2-furancarboxaldehyd, 5-methyl
8	11,424	phenol
9	11,839	phenol
10	13,175	1,2-cyclopentanedione, 3-methyl
11	13,881	phenol, 2-methyl
12	14,629	phenol, 2-methoxy
13	15,389	2-cyclopentene-1-one, 3-ethyl-2-hydroxy
14	18,504	1,2-benzenediol
15	18,878	benzofuran, 2,3-dihydro
16	19,169	2-isopropoxyphenol
17	20,006	1,2-benzenediol, 3-methoxy-
18	20,297	phenol, 4-ethyl-2-methoxy
19	20,505	1H-inden-1-one, 2,3-dihydro
20	20,876	naphtalene, 2-methyl
21	21,419	2-methoxy-4-vinylphenol
22	22,422	phenol, 2,6-dimethoxy
23	23,003	p-methoxybenzamide
24	24,754	benzoic acid, 4-hydroxy-3-methoxy
25	24,921	phenol, 2-methoxy-4-(1-propenyl)-, €
26	28,458	phenol, 2,6-dimethoxy-4-(2-propenyl)-

ethers and aromatic compounds. Meanwhile, the pyrolysis GC-MS analysis suggested that the ASL from solvolysis of biomass was a multicomponent mixture. It contains a high concentration of phenolics and its derivatives compounds were confirmed with the IR analysis.

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