

Production of Pyrolytic Oil for Enhanced Oil Recovery

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Abstract

In enhanced oil recovery (EOR), the objective of chemical flooding is to recover additional oil after a waterflood. However, chemical flooding is not widely applied in the oil fields due to the high cost of chemicals. The goal of this study is produce pyrolytic oil from oil palm shell as enhanced oil recovery additive. Oil palm shell as a solid waste from the palm oil industrs was converted into liquid oil by a fast bed pyrolytic process. The pyrolysis oil was collected in ice-cooled collector. The chemical compositions of the pyrolysis oil were then analyzed by Gas Chromatography – Mass Spectrometry (GC – MS). The chemical composition of pyrolysis oil was complex, comprising of mainly phenolic compounds, carboxylic acids and aldehydes. The physical properties of pyrolysis oil were also carried out. The phenolic compounds were further separated from the pyrolysis oil by liquid-liquid extraction using alkali and organic solvent. The extracted phenol fractions were analyzed by the Fourier Transform Infra-red (F.T.I.R) spectroscopy. Those phenolic compounds can be used as a starting material in the development of chemicals for enhanced oil recovery because they are inexpensive, high recoverability, and the most important thing is, they are not petroleum derivatives.

Keywords: pyrolysis, extraction, enhanced oil recovery, phenol, additive

1.0 Introduction

Enhanced oil recovery is an oil recovery process by the injection of materials not normally present in the reservoir. Chemical flooding of oil reservoirs is one of the most successful to enhance oil recovery from depleted reservoirs at low pressures. However, chemical flooding is not widely applied due to the high cost of chemicals. Malaysia as the world's largest producer of palm oil generates a significant solid wastes annually. More than 7 million tons of empty fruit brunches, 6.0 million tons of fibre and 2.4 million ton of palm shell are estimated to be generated annually [1]. Pyrolysis may be described as the thermal degradation of materials in the complete absence of inadequate presence of oxygen [2]. Three products are usually obtained from pyrolysis process: gas, liquid and char. Both the product yield and chemical composition of pyrolysis oil can be varied according to the pyrolysis methods and process conditions. [3]. Pyrolysis is being considered to be an emerging, new and potential technology to produce value-added products, fuels and chemicals from oil palm waste. Chemicals have been produced from biomass in the past, are being produced at present, and will be produced in the future due the demand for the organic chemicals has increased on a worldwide basis. For example, isolation of

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chemicals at the industrial scale has been performed to recover commodity compounds such as methanol, acetone, acetic acid and mixture of phenols [4]. Isolation of phenols from *Eucalyptus* wood pyrolysis tar was carried out with the objective of recovering valuable pure phenols, such as phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol [5].

The aim of this study is to produce pyrolysis oil from oil palm shell. After obtaining the pyrolysis oil from the pyrolysis process, it was characterized for the chemical and physical properties. The valuable phenols in the pyrolysis oil was then isolated using liquid-liquid extraction for potential use in EOR.

2.0 Materials and Methods

2.1 Material

Oil palm shell was obtained locally at Kulai, Johor (Malaysia). The oil palm shell waste was grinded and sieved to a particle size of 212 – 425 μm . It was then dried in the oven for 24 hours at 100 °C prior to pyrolysis process.

2.2 Experimental

The procedures start from grinding, sieving and oven – drying of the oil palm shells. The oil palm shell particles were then feed into the reactor by a motor driven screw feeder. The experimental system used to produce pyrolysis oil was a fluidized bed pyrolysis unit with silica sand as the bed material. The reactor was constructed of stainless steel with full gas flow and temperature control. The reactor was heated externally. The incoming fluidizing gas was nitrogen and was preheated before entering the reactor.

The silica sand in the fluidized bed has a mean size 256 μm diameter. The biomass wastes fed via a screw feeder and nitrogen gas stream to the fluidized bed at a feed rate of 0.7 kg/hr. The fluidized bed temperature was maintained at 450°C. The products obtained from the process were pyrolysis oil, char and gas. The char was entrained and blown from the fluidized bed while retaining the sand in the bed. The vapors and the gases were passed through a water-cooler condenser to ice-cooled collectors to trap the derived liquid oil. Pyrolysis vapor condensed into liquid and was collected in the liquid collectors. The non- condensed vapors was flared to the atmosphere. The general layout of the pyrolysis process is showed in the Figure 1.

2.3 Physical properties and chemical compositions

Physical properties of the pyrolysis oil were determined using standard methods. Viscosity was determined at 50°C using glass capillaries according to ASTM D445. Density was measured at ambient temperature by ASTM D 5004, and heating value according to ASTM D240. Flash point was measured according to ASTM D93 and pour point according to ASTM D97.

Fourier Transform Infra-Red (FTIR) spectrophotometer was used to characterize the pyrolysis oil from oil palm shell. The functional groups presence in the pyrolysis oil can be determined

from the infra-red spectrum. GC-MS technique was used to identify the individual compounds in the pyrolysis oil. The GC-MS system was an HP 5989x Hewlett Packard unit with J & W Scientific DB 1701 capillary column. Methanol is used as the standard solution. The following conditions are used for the DB 1701 column.

Column dimensions : 60 m x 0.25 mm

Film thickness : 0.25 μm

GC condition : Inlet system: split injector, He, 250°C, oven temperature: 40°C isotherm for 4 min, 3°C min⁻¹ to 280°C. Detection: FID/MS, 280°C.

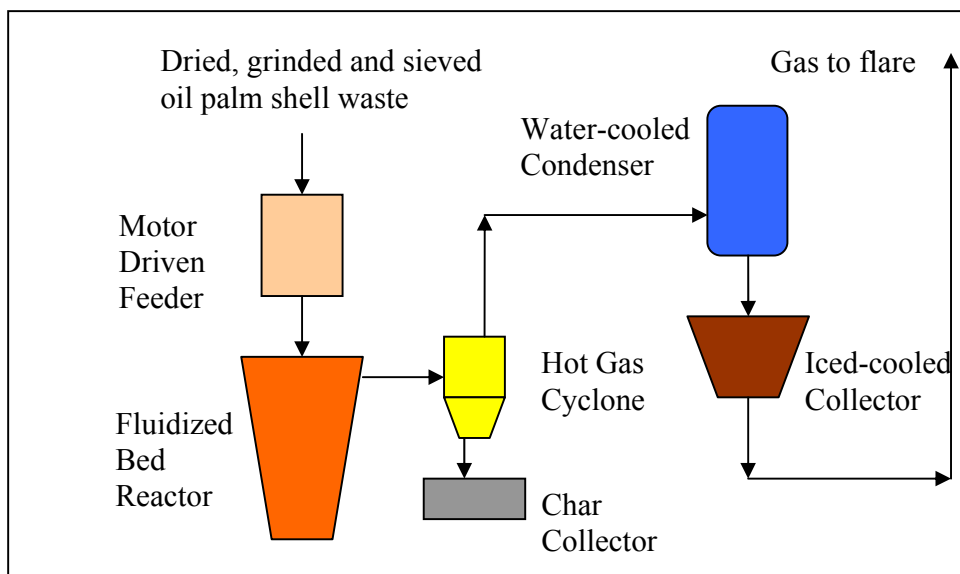


Figure 1 Pyrolysis Process – General Layout

2.4 Liquid-liquid extraction of phenols from pyrolysis oil

The procedure consisted of five main steps:

(a) the pyrolysis oil containing the desired phenols was dissolved in standard solvent; (b) an aqueous sodium bicarbonate solution was added to extract strong organic acids and highly polar compounds; (c) an aqueous sodium hydroxide solution was added to extract phenols by converting them into water-soluble phenolate ions; (d) phenols were regenerated by acidification of the aqueous layer with sulfuric acid; and (e) a phenolic-rich fraction was recovered by solvent extraction of the acidic aqueous layer. The experiment was performed at room temperature.

3.0 Results and Discussion

3.1 Physical Properties Analysis

Table 1 shows the physical properties of the pyrolysis oil in this study. These were compared to M.N.Islam et al.'s study (1999). In this study, the energy content in terms of higher heating value of the pyrolysis oil was low, 9.9 MJ/kg, due to the presence of high percentage of moisture and oxygenated components. The density of pyrolysis oil was 1.1083 g/cm³, it was relatively low. The kinematic viscosity of pyrolysis oil at 50°C was 2.06 cSt. The pyrolysis oil produced can be

estimated have higher water contents. The pH of pyrolysis liquids is low (pH 2.42). The pH was affected mainly by high amounts of volatile acids, mainly acetic and formic acids. The pour point was lower for the present study than M.N.Islam et.al's study. For the pyrolysis liquids analyzed the low viscosity was an indication of a low pour point. The flash point was 50°C. This is due to a high amount of low boiling volatile compounds in pyrolysis oil.

Table 1 Physical properties of pyrolysis oil and its comparisons

Physical properties	Pyrolytic Oil (present study)	M.N Islam et al's study, 1999
Calorific value (MJ/kg) ASTM D240	9.9	22.1
Density (kg/m ³) ASTM D 5004	1.1083	1.2
Viscosity (at 50°C) (cSt) ASTM D 445	2.06	14.63
pH	2.42	2.7
Flash Point (°C) ASTM D 93	50	54
Pour point (°C) ASTM D 97	-22	-10
Distillation (°C) ASTM D 86		
IBP (initial boiling point)	99	94
10%	100	100
30%	100	120
50%	101	155
70%	170	182
75%	-	190
80%	238	-
90%	-	-
Decomposed at	238	190

3.2 Compositional Analysis

The pyrolysis oil produced from oil palm shell was characterized by using FTIR. The spectrum recorded after scanning on the FTIR is shown Figure 2. Table 2 represents the functional group compositional analysis for the pyrolysis oil. The presence of water impurities and other

polymeric O–H in the pyrolysis oil was indicated by the absorbance peak of O–H stretching vibration between $3650 - 3100 \text{ cm}^{-1}$. The alkynes group was indicated by the absorbance peak of $\text{C}\equiv\text{C}$ stretching in between $2200 - 1950 \text{ cm}^{-1}$. The absorbance peaks between $1780 - 1640 \text{ cm}^{-1}$ represented the $\text{C}=\text{O}$ stretching vibration indicated the presence of ketones and aldehydes. The frequency range of $1680 - 1580 \text{ cm}^{-1}$ presented alkenes of $\text{C}=\text{C}$ stretching. The peaks in

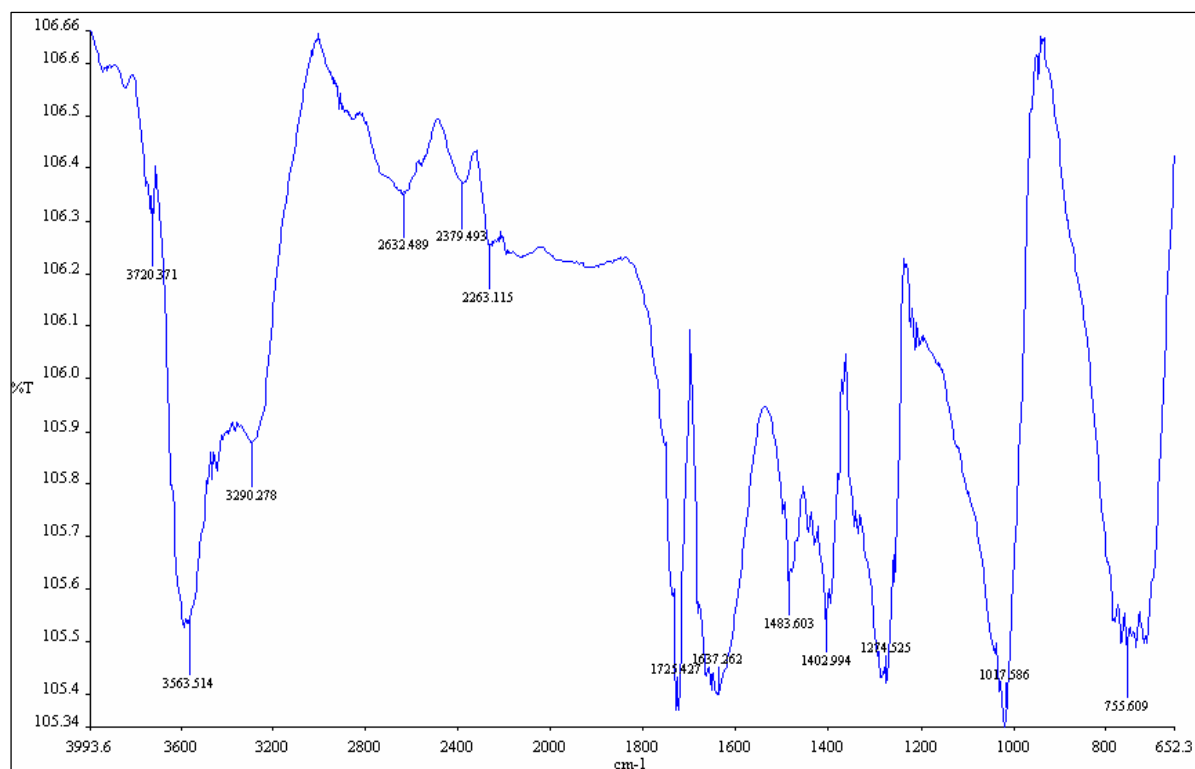


Figure 2. Infra-red spectrum of pyrolysis oil from oil palm shell

between $1300 - 950 \text{ cm}^{-1}$ were indication of the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters due to the $\text{C}-\text{O}$ stretching and $\text{O}-\text{H}$ deformation vibrations. Absorbance peaks between $900 - 650 \text{ cm}^{-1}$ indicated the presence of single, polycyclic and substituted aromatic compounds. Table 3 shows the results of GC/MS analysis of pyrolysis oil from oil palm shell. From the results, it shows that the pyrolysis oil contents high fraction of phenolic compounds, up to 56.042 area %. The other compounds in pyrolysis oil from oil palm shell comprised benzoic acids, ketones (cyclopentenone), aldehydes (benzaldehyde) and benzene.

3.3 Liquid-liquid extraction of phenols.

Liquid-liquid extraction of phenols was performed on the pyrolysis oil at ambient temperature. This oil was completely soluble in selected standard organic solution and filtration of insoluble materials was not necessary. The extraction was started with an aqueous sodium bicarbonate solution at a pH value of 8.7. The aqueous bicarbonate layer extracted the strong organic acids and highly polar compounds. The extraction was then continued at a pH of about 14 in order to extract the phenolic compounds by an aqueous sodium hydroxide solution at a higher pH. The

phenols were regenerated by acidifying the solution with a solution of sulfuric acid 50% by weight to a pH near 6. Additional F.T.I.R analysis of the aqueous layers after standard organic solvent extraction confirmed the present of phenols. The standard organic solvent was evaporated using. The major peaks in the extracted pyrolysis oil from the extraction experiment

Table 2. F.T.I.R functional group compositions of pyrolysis oil

Frequency range (cm-1)	Bond type	Family
3650 - 3100	O-H stretching	Polymeric O-H, water impurities
2200 -1950	C≡C stretching	Alkynes
1780 - 1640	C=O stretching	Ketones, aldehydes, carboxylic acids
1680 - 1580	C=C stretching	Alkenes
1550 - 1490	- NO ₂ stretching	Nitrogenous compounds
1465 - 1350	C-H bending	Alkanes
1300 - 950	C-O stretching	Primary, secondary and tertiary alcohols, Phenols, esters, ethers
900 - 650	O-H bending	Aromatic compounds

Table 3. Identification of chemical compounds in pyrolytic oil by GC/MS

Chemical compounds	Area percent, %
Phenol	36.186
2 methoxy phenol	4.58
2,6-dimethoxy phenol	4.565
2-methoxy -4 methyl phenol	2.399
4-ethyl -2 methoxy phenol	2.211
3-[(trimethylsilyl)oxy]-phenol	1.964
2-methoxy -4(1-propenyl) phenol	1.484
2,6-dimethoxy-4-(2-propenyl) phenol	1.39
2 - methyl phenol (o-cresol)	0.518
4- methyl phenol (p-cresol)	0.485
2- methoxy -4-propyl phenol	0.26
<i>(total of phenol and its derivatives)</i>	56.042
Triphenylphosphine oxide	12.971
4-hydroxy benzoic acid	6.106
4 -hydroxy -methyl ester benzoic acid	2.039
3-hydroxy-4 methoxy benzoic acid	1.906
2-methyl -ethyl ester propenoic acid	0.436
2 hydroxy-3-methyl-2 cyclopentenone	1.361
3-ethyl-2-hydroxy-2-cyclopentenone	0.256
4-hydroxy -3-methoxy benzaldehyde	0.963
4-hydroxy-3,5-dimethoxy benzaldehyde	0.427
1,4-dimethoxy -2,6-dimethyl benzene	0.418
Others	17.075

revealed that the compounds were almost all phenolics. Figure 3 shows the infra-red spectrum of extracted pyrolytic oil from oil palm shell. Liquid-liquid extraction yielded a fraction composed essentially of phenolic compounds. In general, two strong bands can be directly associated with the phenolic grouping. These are the ν (C – O) and a deformation of the COH. From the Figure 3, these two bands near 1243 cm^{-1} and 1165 cm^{-1} . A third band near 1375 cm^{-1} was primary a ν (C =C) of the aromatic ring. It can be therefore used as a characteristic band for phenols. The bands found in the $1400 - 1100\text{ cm}^{-1}$ region of phenols can be correlated with the substitution of the phenolic ring. The specific group frequencies which should be utilized for detecting the presences of a phenolic group are as follows:

ν (O – H)	$3250 - 3000\text{ cm}^{-1}$ for the bonded state
	$3620 - 3400\text{ cm}^{-1}$ for the free state
δ' (OH) and ν (O – H)	$1260 - 1220$ and $1200 - 1160\text{ cm}^{-1}$
ν (C =C) and δ' (OH)	$1370 - 1320\text{ cm}^{-1}$

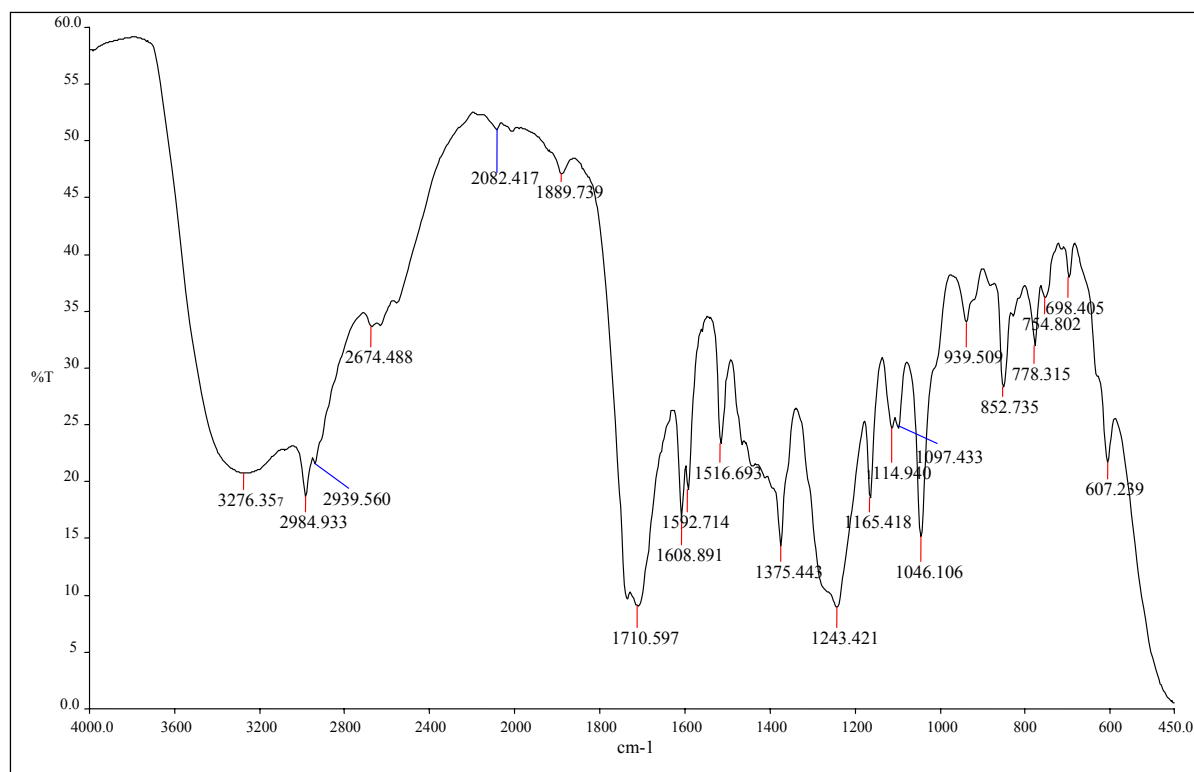


Figure 3. Infra- red spectrum of extracted phenols.

4.0 Conclusion

1. The physical properties analysis showed that the pyrolysis oil from oil palm shell was acidic with low heating value, and had higher water contents.
2. F.T.I.R. and GC/MS analysis showed that the pyrolysis oil from oil palm shell was rich in phenolic compounds that were potential used as a starting material for development of enhanced oil recovery additive. The overall yield of phenolic compounds was founded to be 56.042 area %.

3. Complete recovery of phenols was achieved at a pH of 13-14 by using a concentrated alkaline solution.

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