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OIL PALM SHELL AS A SOURCE OF PHENOL

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Oil palm shell was pyrolysed in an externally heated 5 cm diameter, 30 cm high fluidized-bed fast pyrolysis reactor with nitrogen as the fluidization gas and silica sand as the bed material. The products obtained were liquid oil, solid char and gas. The pyrolysis reactor bed temperature was maintained at 500°C with a fluidization gas flow rate of 1.26 m^3 hr^{-1} because this was found to be the optimum condition for maximum liquidproduct yield. The maximum liquid product was found to be 58 wt% of dry oil palm shell feed. The liquid was a single-phase product. The liquid was characterized by FT-IR, GCIFID and GC-MS for its detailed chemical composition. From the analyses, the liquid was found to contain a very high concentration of phenol and its derivatives, viz., cresol, catechol, guaiacols, syringol, eugenol; 43.3 wt% of total liquid oil. All these are considered to be very high-value chemicals from the point of view of value and price. Thus, an appropriate separation and extraction method is required to find out how to obtain these chemicals, especially phenol, from the pyrolysis oil.

INTRODUCTION

Malaysia as the largest producer of palm oil in the world, generates a significant amount of oil palm wastes. This is true in the cases of some other Asean countries as well. According to a study by Yatim (1996), Malaysia generates 7.7 million tonnes of empty fruit bunches (EFB), 6.0 million tonnes of fibre and 2.4 million tonnes of palm shell every year as wastes. EFB are not considered for fuel because of its high moisture content (65%). The fibre wastes are used to generate energy to run the palm oil mill by incinerating the waste for power and fertilizer purposes. According to Ngan and Ang (1996), it must be emphasized that palm oil mills generally have excess fibre and shell which are not used and have to be disposed off separately. There are more than 270 palm oil mills operating in Malaysia that utilize mainly fibre and partly shell in their boilers as fuel to generate power and steam required by the industry. The fibre is fully required in the mill for this purpose. However, only about 30% of shell is utilized for this purpose (Abd Halim, 1985). Thus, the mills have generally excess shell which is not used and which needs to be disposed of separately. Besides, the present utilization of this palm waste as boiler fuel is creating a serious emission problem in the industry. From a recent study conducted by Ramli and Rozaine (1997), it appears that more than 80% of the boilers emit particles exceeding 0.4 g Nm^{-3}; the permissible limit set by the Department of Environment. The study showed that the range of emission varied from 0.25 to 3.73 g Nm^{-3}. From another study by Yusof and Rozainee (1993), it was found that the boilers, using palm waste as fuel at palm oil mills, are producing very much higher levels of dust emission of up to 11.6 g Nm^{-3} compared to the allowable limit of 0.4 g Nm^{-3} causing a serious environmental problem. Thus, it is important to find some ways and means to use these wastes in a manner that does not pollute the environment and at the same time, provide improved materials and energy. It is currently widely acknowledged that the most ecologically sound way to treat a worn-out/waste product is pyrolysis.

Pyrolysis is considered to be an emerging, new and potential technology to produce value-added products, fuel and chemicals from oil palm waste. Pyrolysis may be described as the thermal degradation of materials in the complete absence or inadequate presence of oxygen (Bridgewater and Bridge, 1991). More recently, pyrolysis is meant for liquid production although solid char and gas are also obtained as by-products. The term fast pyrolysis is used to describe a process designed to optimize the formation of condensable organic vapors, with a minimum of gas and char. This is considered to be the most advanced pyrolysis process, oriented to high yield production of an organic liquid oil. Considering the availability of oil palm waste in Malaysia and its favourable elemental composition, an attempt was made to produce pyrolysis liquid oil from oil palm shell using a fluidized-bed fast pyrolysis technique. A fluidized-bed reactor has several advantages as chemical reactor over other types of reactor: higher heat and mass transfer rates between the gas and solid particles, easier control of temperature, easier to scale up and flexible with regard to its feed rate and composition (Islam, 1998). The products obtained were liquid oil, solid char and gas. The maximum liquid product obtained was 58 wt% of the dry solid feed at a fluidized-bed temperature of 500°C. The liquid was characterized by FT-IR, GC/FID and GC-MS techniques for its detailed chemical composition.

Phenol is considered as an important chemical with divergent applications. For example, it can be used to manufacture moulding products for automotive parts, household appliances, electrical components; in bonding and adhesive resins for laminating, plywood, protective coating, insulation materials, abrasive coating; in foundry industries for sand moulds and cores, Phenol has been commercially synthesized from petroleum resources; however, the production of petroleum-based phenol is quite expensive. Hence, phenols derived from oil palm shell have been looked at as a potential substitute for petroleum-based phenol. To this regard, an appropriate separation and extraction method for phenols is intended.

The recovery of pure chemicals from pyrolysis oils by modern thermal processes has received little attention over the last decades while the demand for these chemicals has increased on a worldwide basis. In the past, isolation of chemicals at the industrial scale has been performed to recover commodity compounds such as methanol, acetone, acetic acid and mixtures of phenols (Soltes and Elder, 1983). Chum and Black (1990) fractionated phenolic/neutral fraction from pine sawdust-derived pyrolysis oil using liquid-liquid extraction. Suzuki et al. (1992) prepared a wood tar-based phenol adhesive by isolating the phenolic content of the tar at 1.3 kPa using reduced-pressure distillation. Guha et al. (1987) fractionated rice husk pyrolysis oil by applying a low pressure distillation. It was shown that the germicidal activity increased as the composition of volatile phenols increased in the fraction. Carazza et *al.* (1994) distilled a wood tar under reduced pressure in two steps to isolate guaiacylic and syringylic compounds which had potential market value in the pharmaceutical industry and for the synthesis of new compounds. Isolation of phenols from an Eucalyptus wood tar obtained by carbonization has been carried out with the objective to recover pure phenolic compounds such as syringol and guaiacol (Amen-Chen, 1995).

EXPERIMENTAL

Materials

Oil palm shell waste was obtained from Kulai Palm Oil Mills of Federal Land Development Authority (FELDA), Johor in Peninsular Malaysia. It was then grounded and sieved to a size of 212.425 μm and dried for 24 hr at 105°C prior to pyrolysis. The elemental composition, proximate analysis and gross calorific value of solid oil palm shell waste are presented in *Table 1.*

TABLE 1. ELEMENTAL COMPOSITION, PROXIMATE ANALYSIS AND GROSS CALORIFIC VALUE OF SOLID OIL PALM SHELL WASTE

Elemental composition (wt%)		Proximate analysis (air dry wt%)		Gross calorific value (MJ kg^{-1})
Carbon	55.35	Volatile matter	68.90	19.10
Hydrogen	6.43	Fixed carbon	20.40	
Nitrogen	0.37	Moisture content	8.40	
oxygen	37.85	Ash content	2.30	
Sulphur	-			

Method

The fluidized-bed pyrolysis system consisted of a gas preheater, screw feeder, pyrolysis reactor, cyclone, char collector, condenser and liquid collectors. The pyrolysis reactor was a 30 cm high and 5 cm diameter fluidized-bed system. The volume of the reactor was 520 cm^3. The feed was milled into the required particle sizes, sieved and oven-dried to less than 2% moisture. The system was fabricated from stainless steel. Nitrogen gas was used as the fluidization medium and silica sand of 256 pm average particle size the fluidized-bed material. The products obtained from the process were pyrolysis liquid oil, char and gas. The liquid was collected in a series of ice-cooled liquid collectors after being condensed through a water-cooled condenser. The char was separated in a cyclone and collected in a char pot. Separation of the char was done by a method known as 'blow-through' in which the char was entrained and blown from the bed while retaining the sand in the bed (Scott and Piskorz, 1984). This was done by careful selection ofthe sand size, feed particle size and fluidizing gas flow rate. A fume cupboard and piping system was used for the gases to flare to the atmosphere by means of a motor driven exhaust blower. The entire experimental set-up was enclosed by a transparent perspex sheet so that the pyrolysis product gases could not be spreaded in the laboratory atmosphere. The temperature of the reactor was measured and controlled by thermocouples and a PID temperature controller. The pyrolysis reactor bed temperature was maintained at 500°C with a fluidization gas flow rate of 1.26 m^3 hr^{-1}. In order to feed the particles into the reactor, a motor driven screw feeder was used. Two electric tube heaters, each of 1 kW power, supplied the heat to the pyrolysis reactor and the gas preheat chamber. The system was maintained at a pressure slightly above atmospheric. The fluidization gas flow rate was measured and controlled by gas flow meters. The flow sheet of the process is presented in Figure *1.*

Pyrolysis Oil Analysis

Functionalgroup composition. The functional group composition of pyrolysis oil was analysed by Fourier Transform Infra-red spectroscopy (FT-IR). The FT-IR instrument was a Perkin Elmer 1650 model-Series 1600 with an on-line pen plotter available at the Department of Polymer Engineering of the Faculty of Chemical Engineering of Universiti

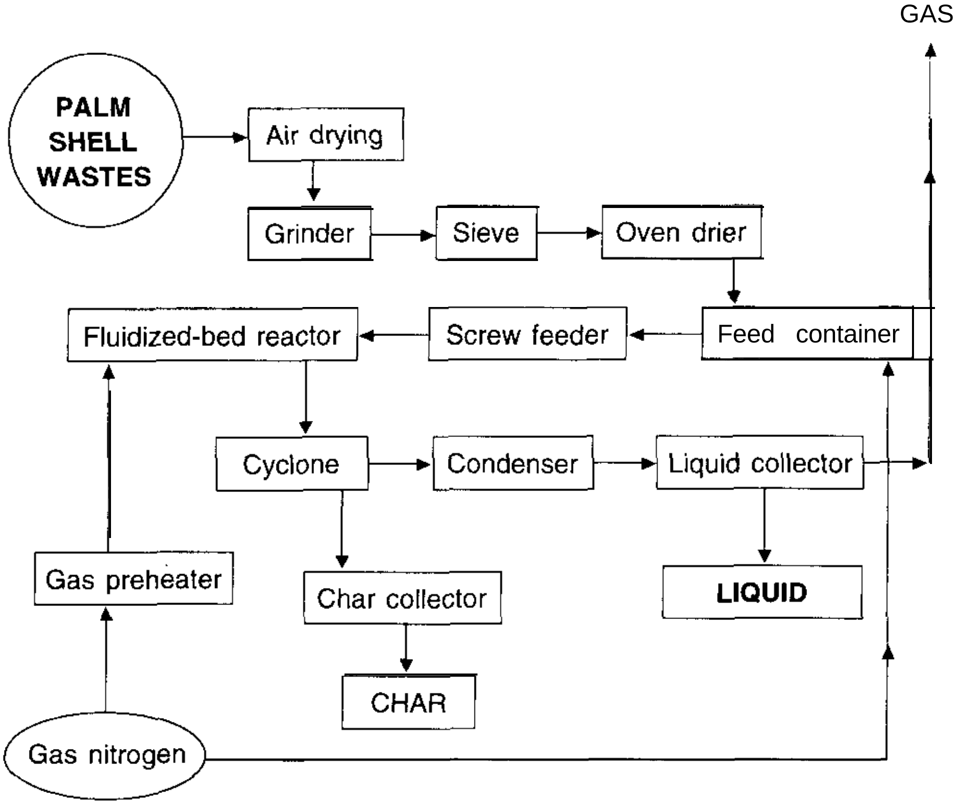

Figure 1. Flow sheet of fluidized-bed solid oil palm waste fast pyrolysis process.

Teknologi Malaysia, Skudai to produce the IR-spectra of the derived liquids. A thin uniform layer of the liquid was placed between two salt cells and exposed to an infrared beam. The absorption frequency spectra were recorded and plotted. It provided the absorption spectrum in percentage incident intensity, along the wave numbers 4400 to 370 cm^{-1}. The standard IR-spectra of hydrocarbons were used to identify the functional group of the components of the derived liquids.

GC-MS analysis. In order to identify the individual compounds in the pyrolysis oil, it was analysed by gas chromatograph-mass spectrometry (GC-MS) technique. The GC-MS system was an HP5989x Hewlett Packard unit with J & W Scientific DB-1701 capillary column. Methanol was used as the standard solution. The following conditions were used for the DB-1701 column:

Column
dimensions: 60 m x 0.25 mm,
film thickness: 0.25 pm,

GC condition: Inlet system: split-injector, He, 250°C,
Oven temperature: 40°C isotherm for 4 min, 5” K min^{-1} to 280°C,
Detection: FID/MS, *280°C.*

The chemical compounds identified in the oil palm waste pyrolysis oil by GC-MS analysis at different fluidized-bed temperatures are presented in *Table* 2 and phenol and their derivatives in the pyrolysis oil at the optimum temperature of 500°C are presented in *Table 3.*

Extraction of Phenol from Oil Palm Shell Pyrolysis Oil

In this study, a standard solvent was used for the purpose of extraction of phenols from the pyrolysis oil obtained from oil palm shell. Selection of the solvent was based on the following criteria: availability, low price, low

TABLE 2. CHEMICAL COMPOUNDS IN FLUIDIZED-BED PYROLYSIS OIL FROM OIL PALM SHELL IN WT% AT DIFFERENT FLUIDIZED-BED TEMPERATURE BY GC-MS ANALYSIS

Chemical compounds	**Fluidized-bed temperature (°C)**		
	400	500	550
Phenol	11.02	28.30	25.51
o-Cresol	1.23	0.79	1.06
m-Cresol		4.82	
p-Cresol		2.32	1.66
Catechol	1.55	2.02	1.87
Pyrocatechol	1.69	2.16	1.09
Guaiacol	2.91	2.45	2.08
Syringol	1.10	1.37	0.99
Eugenol	1.25	1.36	1.83
Phenol, 2, 6-dimethoxy	2.83	3.25	3.61
Butanoic acid	2.83		1.23
Acetic acid	23.57	16.90	15.57
1,2-Benzenediol	1.23	3.47	2.39
Benzaldehyde		1.20	1.08
1-Octane	1.16	1.25	
2-Propanone, 1-hydroxy-	1.94	1.66	1.65
Phenol, 4-(1-methylethyl)	0.89		0.49
Pentanoic acid	2.13	1.86	1.34

TABLE 3. PHENOL AND THEIR DERIVATIVES FROM OIL PALM SHELL PYROLYSIS OIL IN WT% AT OPTIMUM FLUIDIZED-BED TEMPERATURE OF 500°C BY GC-MS ANALYSIS

Chemical compounds	**Fluidized-bed temperature (°C)**
	500
Phenol	28.30
o-Cresol	0.79
m-Cresol	4.82
p-Cresol	2.32
Catechol	2.02
Pyrocatechol	2.16
Guaiacol	2.45
Syringol	1.37
Eugenol	1.36
Phenol, 2, 6-dimethoxy	3.25

boiling point, relatively low solubility in water and high oil solubility. It is to note that the requirements for the standard solvent is that it should have at least a moderate solubility parameter, moderate degree of polarity, and good hydrogen bonding capability, capable of extracting phenol and their compositions from fast-pyrolysis oil.

The pyrolysis oil was dissolved in the standard solvent to an oil: solvent ratio of 1: 3 by weight at a pH of 3.1. It was then filtered with Whatman filter paper (1) of specification 12.5 cm 100 circles. The oil-solvent mixture was collected in a separating funnel and the thick residual tarry portion removed. A 5 % aqueous standard solution was mixed with this oil-solvent mixture at a proportion of 1: 2 by weight, The pH value of this standard solution was maintained at 8.9. As a result of mixing, the mixture separated into two phases: (i) a standard solvent soluble portion containing the phenols, and (ii) a standard solvent insoluble portion. This standard solvent soluble layer was then separated and the solvent evaporated by an evaporation technique. In this method, an E-01611-00 Economy Rotary Evaporator was used. The evaporation was carried out under the following conditions:

Temperature	78°C
Pressure	600 mm Hg vacuum
Rotation speed	100 rpm
Vacuum oil pump	1/6 H.P.
Water bath	Type TE 2, 1000 Watt

After evaporating the solvent, the liquid product was collected and stored in laboratory conditions. This was then subjected to GC/FID analysis using DB-1701160 mm x 0.25 mm x 0.25 µm capillary column in order to identify and quantify the phenols in the liquid product. The flow sheet of the experimental procedure is presented in Figure 2. The carrier gas used was helium.

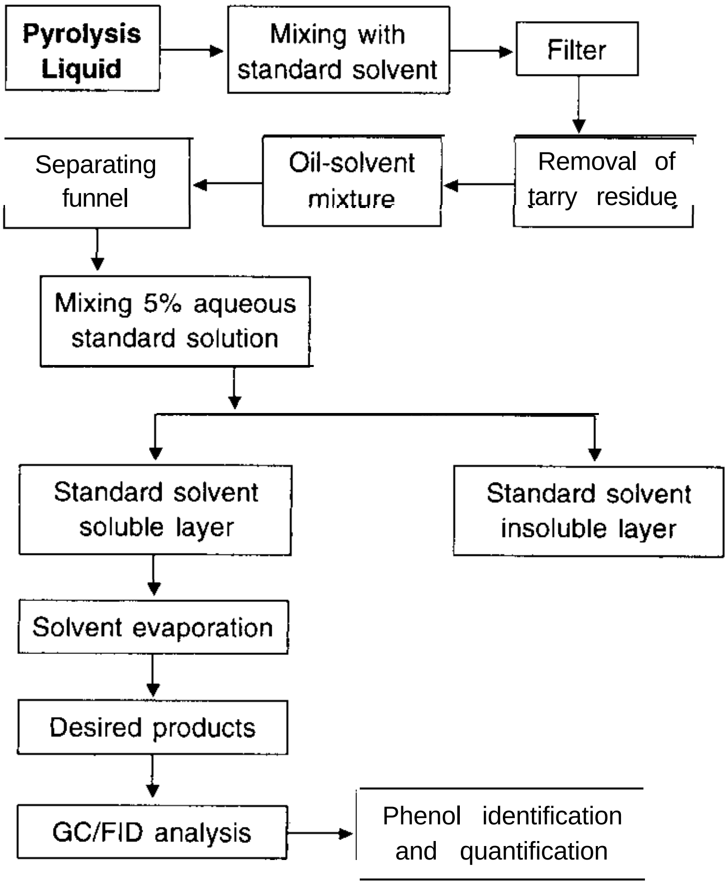

Figure 2. Flow sheet *for extraction of* ***phenol*** *from oil palm waste pyrolysis oil.*

RESULTS AND DISCUSSION

Pyrolysis Product Yield

The single-phase pyrolysis oil obtained in the study was found to be 58 wt% of total feed at the fluidized-bed temperature of 500°C for oil palm shell particle size of 212-425 μm with nitrogen gas as the carrier gas.

Pyrolysis Oil Analysis

Functional group composition. *Table 4* represents the functional group composition of oil palm shell pyrolysis oil. The presence of water impurities and other polymeric G-H in the oil were indicated by the broad absorbance peak of O-H stretching vibration between 3600 and 3200 cm^{-1}. The strong absorbance peaks of C-H vibrations between 3000 and 2800 cm^{-1} and the C-H and deformation vibrations between 1475 and 1350 cm^{-1} indicate the presence of alkanes. The absorbance peaks between 1780 and 1640 cm^{-1} represented the C=O stretching vibration, indicating the presence of ketones and aldehydes. The presence of both O-H and C=O stretching vibrations also indicated the presence of carboxylic acids and their derivatives. The possible presence of alkanes is indicated by the absorbance peaks between 1680 and 1580 cm^{-1}. The absorbance peaks between 1550 and 1490 cm^{-1} represented the -NO, stretching vibration, indicating the presence of nitrogenous compounds. The overlapping peaks between 1300 and 950 cm^{-1} were due to the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters showing the C-O stretching and O-H deformation vibration. Absorbance peaks between 900 and 650 cm^{-1} indicate the possible presence of single, polycyclic and substituted aromatic groups.

GC-MS analysis. From the GC-MS analysis, phenol and its derivatives were found to be more than 43 wt% of the total pyrolysis oil. The pyrolysis oil from oil palm shell was found to be mostly oxygenated. This is the underlying reason for the oil to have a lower heating value. The proportion of phenol and its derivatives was found to be high in the oil palm shell pyrolysis oil indicating the suitability of the oil to be considered for value-added chemicals. It is interesting to note that polycyclic aromatic hydrocarbon (PAH) compounds that are known to be responsible for carcinogenic action were not found in the oil (Lee et al., 1981).

From the experiment for the extraction of phenol, the total amount of extracted soluble liquid oil was found to be 40 wt% of total pyrolysis oil. Prom the GC/FID analysis, the presence of phenol was confirmed comparing the retention time of the liquid product with the standard phenol solution. The quantity of phenol in the extracted liquid was found to be 24.2 wt% of the extracted oil.

TABLE 4. THE FT-IR FUNCTIONAL GROUPS AND THE INDICATED COMPOSITIONS OF OIL PALM SHELL PYROLYSIS OIL

Frequency range (cm^{-1})	Group	Class of compound
3 200-3 600	O-H stretching	Polymeric O-H, water impurities
3 000-Z 800	C-H stretching	Alkanes
1 780-1 640	C=O stretching	Ketones,aldehydes,carboxylic acids
1 680-1 580	C=C stretching	Alkenes
1 550-1 490	-NO, stretching	Nitrogenous compounds
1 475-1 350	C-H bending	Alkanes
950-1 300	C-O stretching	Primary, secondary and tertiary
	O-H bending	Alcohols, phenol, esters, ethers
900-650	O-H bending	Aromatic compounds

CONCLUSION

Fluidized-bed fast pyrolysis technique successfully produced pyrolysis liquid oil from oil palm shell with a maximum liquid product yield of 58 wt% at 500°C. The pyrolysis oil from oil palm shell contained high percentage of phenol and its derivatives of more than 43 wt% of pyrolysis oil. Solvent extraction technique was able to separate the soluble liquid oil from the pyrolysis oil and this was found to be 40 wt% of the pyrolysis oil. The quantity of phenol in the extracted oil was found to be 24.2 wt% of total extracted oil.

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