

Production of Bio-oil from Palm Oil Shell

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ABSTRAK

Biojisim dalam bentuk kulit kelapa sawit, suatu bahan buangan pepejal agro-industri yang banyak terdapat di Malaysia, pertama kali dipirolisis diikuti dengan pemecahan bermangkin di dalam sebuah sistem pirolisis pantas bermangkin sepadu. Proses pirolisis dijalankan di dalam satu sistem lapisan terbendalir manakala rawatan bermangkin dilakukan di dalam suatu sistem lapisan tetap. Di dalam lapisan terbendalir pasir silika digunakan sebagai bahan lapisan manakla di dalam lapisan tetap H-ZSM-5 dan H-USY zeolit digunakan sebagai mangkin. Gas nitrogen digunakan sebagai gas pembawa. Pirolisis pantas dilakukan dengan menyuap bahan mentah zarahhan langsung ke dalam lapisan terbendalir panas pada suhu 400 to 600°C. Hasil minyak maksimum 58% diperolehi pada suhu optimum 500°C dengan masa mastautin ketara wap 1.48 saat. Produk yang diperolehi ialah biominyak cecair, arang pejal, gas dan kok. Perubahan hasil produk dan komposisi produk dengan suhu lapisan mangkin untuk mangkin H-ZSM-5 dan H-USY dipertimbangkan dalam kajian ini. Hasil cecair didapati menurun dengan peningkatan suhu lapisan mangkin manakla hasil gas dan kok bertambah dengan peningkatan suhu lapisan mangkin. Sebatian kimia yang diperolehi ialah asid organik, fenol, hidrokarbon, alkohol, ester dan keton. Fenol merupakan bahan kimia penting dengan penggunaan yang luas seperti sebagai agen penuangan untuk komponen automotif, alat rumah, komponen elektrik, resin perekat untuk pelapisan papan lapis dan bahan penebat. Sebaliknya kandungan hidrokarbon yang tinggi menunjukkan ia boleh digunakan sebagai bahan api mentah di dalam enjin automotif. Semua bahan kimia ini bernilai tinggi dari segi nilai dan harganya.

ABSTRACT

Biomass in the form oil palm shell, an agro-industrial solid waste abundantly available in Malaysia was first pyrolysed followed by catalytic cracking in an integrated catalytic fast pyrolysis system. The pyrolysis process was carried out in a fluidized-bed system while the catalytic treatment in a fixed-bed system. In the fluidized-bed silica sand was used as bed material while in the fixed-bed zeolites H-ZSM-5 and H-USY were used as catalysts. Nitrogen gas was used as the carrier gas. The fast pyrolysis was performed by feeding granulated raw materials directly into the hot fluid-bed at temperature ranging from 400 to 600°C. The maximum oil yield of 58 wt% was obtained at optimum temperature of 500°C with an apparent vapor residence time of 1.48 sec. The products obtained were liquid bio-oil, solid char, gases and coke. The variation of product yields and product compositions with catalytic bed temperature for catalysts H-ZSM-5 and H-USY were considered in the study. The liquid yield was found to be

decreasing with the increase of catalytic reactor bed temperature while the gas and coke yields were increasing with catalytic bed temperature. The chemical compounds obtained were organic acids, phenols, hydrocarbons, alcohol, esters and ketones. Phenol is an important chemical with divergent application. For example, it can be used moulding products for automotive parts, household appliances, electrical component, adhesive resins for laminating plywood, and insulating materials. On the other hand high hydrocarbon content indicates it can be used as raw fuel in automotive engines. All these are considered to be very high value chemicals from the point of view of value and price.

INTRODUCTION

It is an accepted fact that the demand for energy continues to outstrip supply and necessitates the development of the renewable energy option. Of different types of renewable sources getting increased attention, biomass is one of the most promising ones. The fascination of biomass is its easy availability, high carbon content, low moisture content, low ash content, renewability and keeping environment clean. Maniatis and Ferrero (1994) listed the reasons for the attractiveness of biomass as an energy carrier as given below:

1. Sustainable and renewable resource.
2. Air pollution abatement. Biomass is very low in sulfur, chlorine or heavy metals.
3. Global warming. When biomass is grown on a sustainable basis, it does not contribute to carbon dioxide emissions.
4. Among the renewable sources of energy, biomass appears to have a large potential.
5. Fuel supply diversity.
6. Biomass can provide economic development and employment opportunities in rural areas. Biomass energy applications appear to be among the few alternatives, which exist for farmers in providing income if food production is uneconomic.
7. Land restoration. Degraded land areas may be restored with energy plantations.

There are several technologies available for biomass conversion for energy recovery. These are liquefaction, gasification, combustion and pyrolysis. Each gives a different range of products and employs different equipment configurations operating in different modes. These are summarised in Table 1. Liquefaction is a high pressure expensive process for obtaining liquid products. Gasification is designed to produce non-condensable gases, usually with the addition of a small amount of oxygen or air (sub-stoichiometric), directly to the reactor to provide the process heat for the gasification reactions. Pyrolysis is a precursor to the gasification process. Combustion implies the addition of air or oxygen directly to the reactor in sufficient quantity to completely/stoichiometrically oxidise the biomass, usually with an excess of oxygen to ensure burn-out. During combustion of biomass, it is first pyrolysed to gases and organic vapours, which are then

TABLE 1. Thermochemical conversion technologies, products and applications (Bridgwater 1992)

Technology	Primary Product	Example of Application
Pyrolysis	Gas	fuel gas
	Liquid	liquid fuel and chemicals
	solid char	solid fuel or slurry fuel
Liquefaction	liquid	liquid fuel substitution
Gasification	gas	fuel gas
Combustion	heat	heating

burned in flaming combustion. The char burns in glowing combustion after the pyrolysis step. The combustion of biomass as received has been and is yet the simplest energy conversion process, but unfortunately it exhibits technological limit and low efficiencies, that have induced researchers to find out more efficient systems (Trebi et al. 1997). According to Maggi and Elliott (1997) direct combustion remains the most energy efficient use of biomass but liquids, rather than solids or gases, are preferred. Pyrolysis is attractive because biomass and its solid waste, which are difficult and costly to manage, can be readily converted to liquid products. Liquids are particularly interesting as energetic vector because they have, in comparison to gas and solid, a high energy density and offer advantages in transport, storage, combustion, retrofitting, and flexibility in production and marketing (Bridgwater 1992). According to Conti et al. (1997), a wider commercial exploitation on a sustainable basis of biomass and solid waste resource awaits the development of modern technology to enable this resource to compete with conventional energy carriers and that pyrolysis seems one of the most suitable way to reach this aim because of its high yields of crude bio-oils production from biomass pyrolysis. Thus, pyrolysis is considered to be an emerging, new and potential method to recover high value energy, fuel and chemicals from biomass (Bridgwater and Bridge 1991). This technique has been applied for different types of biomass (Besler et al. 1992; Islam and Ani 1998; Ani and Islam 1998).

According to Diebold and Bridgwater, 1997, as biomass and waste are heated, a sequence of physical and chemical changes takes place. Pyrolysis occurs with heating in the absence of oxygen or air to produce a mixture of solid char, condensable liquids, and gases. In some cases a small amount of air is added to the recycled char or to the recycled pyrolysis gases to provide process heat by partial combustion but do so in such a manner that the condensable organic yields are not compromised. The most recent and accepted theory is that primary vapours are first produced, the characteristics of which are influenced by heating rate. These primary vapours then further degrade to secondary tars and gases if held at a high temperature for long enough for secondary reactions to occur. The proportions and characteristics of these secondary materials are a function of temperature and time (Elliott 1988). Rapid quenching causes the liquid intermediate products to condense, before further reaction breaks down higher molecular weight species into gaseous product (Bridgwater 1992). A possible reaction pathway of biomass solid pyrolysis process is shown in Figure 1.

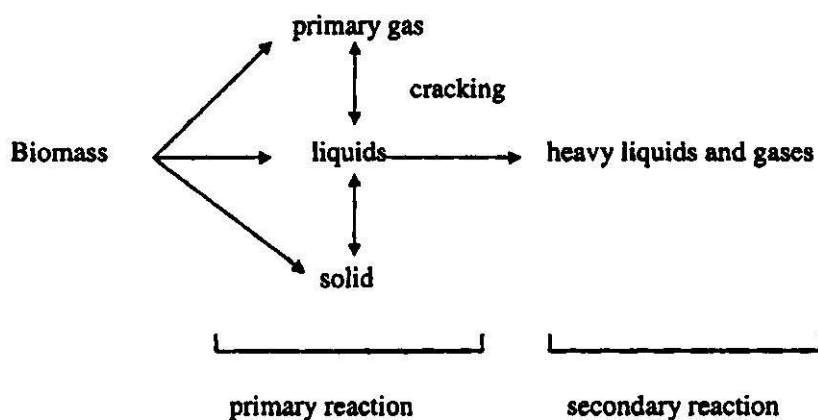


FIGURE 1(a). A possible reaction pathway of pyrolysis of biomass solid waste.

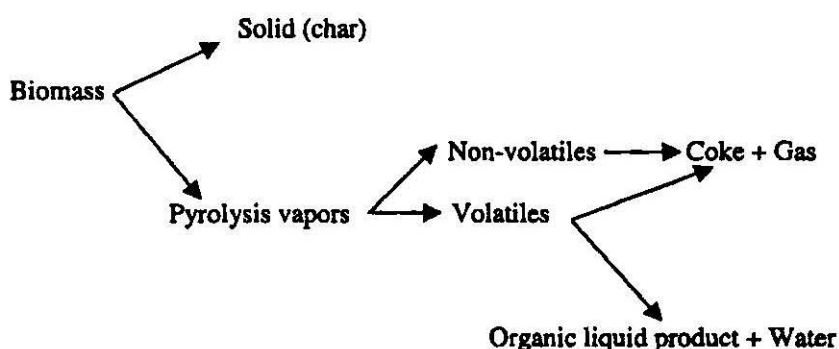


FIGURE 1(b). A possible reaction pathway of catalytic treatment of pyrolysis vapour from biomass solid waste

Malaysia, as being the world's leading producer and exporter of palm oil, has been generating a huge amount of oil palm waste (Yeti 1996). These are fibre, fruit bunch and shell. Considering the availability of oil palm shell in the ASEAN region in a significant amount and its favourable elemental composition and thermo-gravimetric (TG) characteristics pyrolytic liquid was produced from oil palm shell using fluidised bed pyrolysis technique (Zailani 1995). In this study fluidised-bed pyrolysis technique used because it has several effects: good solid mixing behaviour, heat and mass transfer rate is uniform, easier control of temperature, easier scale up, good flexibility with regard to feed rate and composition. According to Soltes (1988), the product yields and product composition are very much dependent on the reaction parameters; especially the pyrolysis temperature. To this regard the effects of pyrolysis reactor bed temperature on the product yields and liquid product composition have been taken into consideration in this study. Like other biomass derived pyrolysis oil, the palm shell pyrolysis oil was found

to be highly oxygenated, complex and acidic in nature (Islam and Ani 1998). Thus, an attempt was taken to upgrade the bio-oil by means of zeolite catalytic cracking combined with fluidised bed pyrolysis at atmospheric pressure. The zeolite catalyst route to upgrading biomass pyrolysis oil is preferred since the process conditions result in a much lower cost than the high-pressure hydro-treatment (Williams and Home 1994). The zeolite ZSM-5 catalysts were selected for this purpose of upgrading because of their strong acidity, high activities and shape selectivities which convert the oxygenated oil to a light hydrocarbon mixture in the C₄-C₁₀ range. In this pyrolysis study biomass was pyrolysed at different fluidised bed reactor temperatures from 400 to 600°C. In the catalytic pyrolysis study the evolved pyrolysis vapours were passed over a fixed bed of zeolite ZSM-5 catalyst placed after the fluidised bed reactor at temperatures 400, 500 and 550°C. The product yields were computed for these process conditions and the liquid products were analysed for their chemical composition.

MATERIAL AND METHOD

BIOMASS

The biomass used was oil palm shell waste obtained from Kulai Palm Oil Mills of Federal Land Development Authority (FELDA), Johore in Malaysia. It was grounded and sieved to the size of 212 - 425 μ m and dried for 24 hours at 105°C prior to pyrolysis.

CATALYST

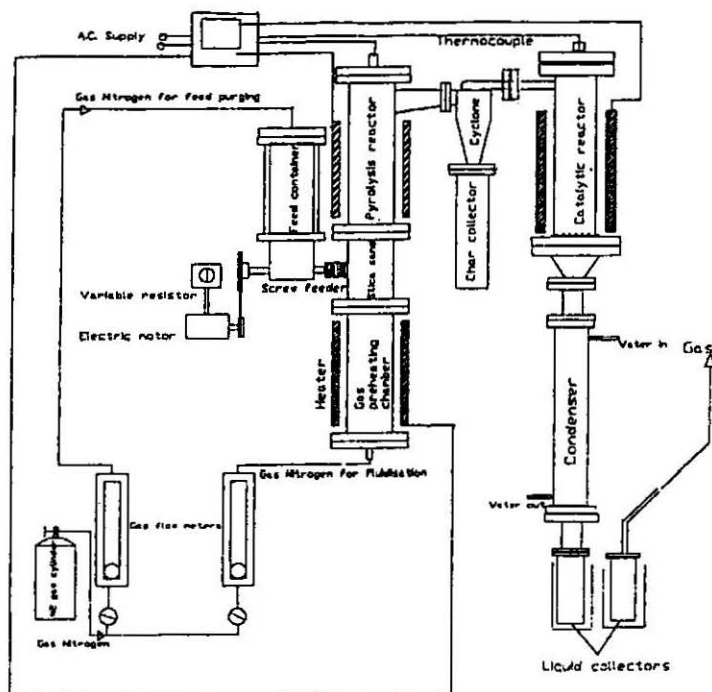
The catalysts used were zeolites H-ZSM-5 and H-USY type and were obtained commercially from PQ Corporation, USA. The zeolites consisted of 0.16 cm diameter cylindrical extrudates. The physico-chemical properties of the zeolites are presented in Table 2.

METHOD

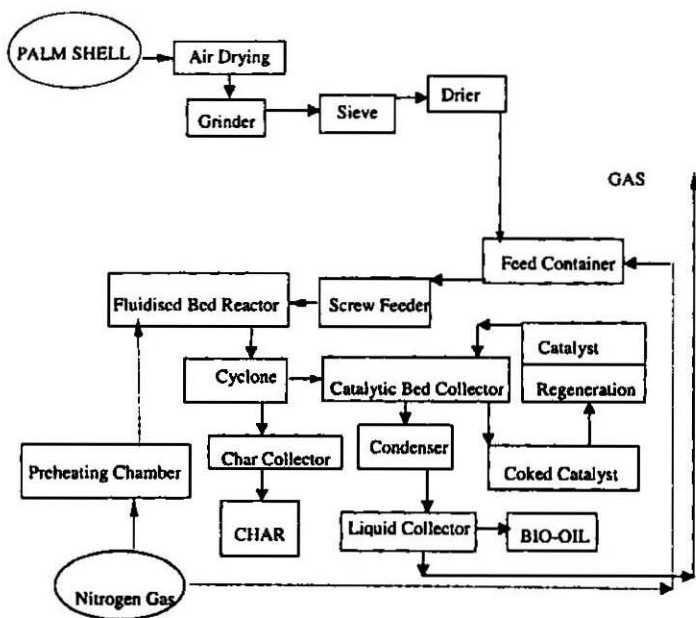
The experimental system consisted of gas preheating chamber, screw feeder, pyrolytic reactor, cyclone, char collector, catalytic reactor, condenser and liquid collector. The schematic diagram of the experimental set-up is shown in Figure 2. Both the fluidised bed and the fixed bed reactors were 5 cm diameter x 30 cm high, constructed of stainless steel with full gas flow and temperature control. The reactors were heated externally and the fluidised bed and the fixed bed could be separately temperature controlled. The flow

TABLE 2. Physico-chemical properties of the catalysts

Properties	H-ZSM-5	H-USY
Si/Al	25	2.6
Pore size (Å)	0.51 x 0.55	7.4
Supercage	No	yes
Amount of total acid sites (moles/kg)	0.7252	1.348



FIGURES 2. Schematic diagram of the experimental set-up of combined fluidised bed pyrolysis system with catalytic treatment



FIGURES 3. Flow sheet of biomass pyrolysis process with catalytic treatment

sheet of the process is presented in Figure 3. The incoming fluidising gas was nitrogen and was preheated before reaching the fluidised bed. The bed material was silica sand of mean size 256 μm diameter with a static bed depth of 8 cm. The fluidising velocity was 3 times of the minimum fluidising velocity. The mass of zeolite taken was 90 g. The biomass waste was fed through a screw feeder and nitrogen gas stream to the fluidised bed at a feed rate of 0.18 kg h^{-1} . The weight hourly space velocity (WHSV) representing the weight of reactant per hour/weight of catalyst was 1.16 h^{-1} . However, the WHSV does not include the mass of nitrogen carrier gas. The fluidised bed temperature was maintained at 500°C for all pyrolysis experiments and the fixed bed catalyst temperature was maintained at either 400°, 500° or 550°C. The apparent vapour residence time was 1.48 sec. The outlet from the fixed bed was passed to a series of condensers to trap the derived oils. The char was collected by a method known as blow-through mode (Scott and Piskorz 1984). The gas was flared. The coke formation was estimated from the difference of mass of catalyst before and after each experimental run.

BIO-OIL COMPOSITIONS AT DIFFERENT TEMPERATURES

The bio-oils obtained were characterised using capillary column gas chromatography, coupled to mass spectrometer (GC/MS). This allowed identification and percent distribution of the individual compounds present in the oils. The GC/MS system was a Hewlett Packard 5890 unit with J & W Scientific DB-1701/60m x 0.25 mm x 0.25 μm capillary column of intermediate polarity. The temperature programme was 40°C for 4 min followed by 5°C min^{-1} heating rate to 280°C. Methanol was used as the standard solution.

RESULTS AND DISCUSSION

PRODUCT YIELDS

The determination of product yields with oil palm shell as the feed material of 212-425 (m particle size at a fluidised-bed temperature of 500°C and a WHSV of 1.16 h^{-1} have been presented in Table 3 for different catalytic bed temperature using H-ZSM-5 and H-USY as catalysts and without catalysts. It can be seen that as the catalytic bed temperature was increasing the liquid yield was reducing while the coke and gas yields were increasing. This is because at higher temperature the reaction was faster as a result of the enhancement of the rate of scission of the molecular bonds. Besides at higher temperature the liquid formed by the catalytic treatment subsequently underwent further cracking thus yielding more gas and coke. In the case of H-USY catalyst the coke and gas yield were found to be more and the liquid was less compared to that obtained using H-ZSM-5 as catalyst. The higher coke formation was because of large supercages within their crystallites, the sizes of which are nearly equal to di- or tri-atomic rings. Besides the larger amount of acid sites may be attributed to larger amount of strong acid sites in H-USY zeolite that may accelerate both the cracking and deactivation reactions, yielding higher amount of gas and coke.

Table 3. Effect of reactor bed temperature on product yields for different catalysts and without catalysts (wt% of biomass fed)

Reactor bed temperature (°C)	Without catalysts			Zeolite H-USY				Zeolite H-ZSM-5			
	Liquid	Char	Gases	Liquid	Char	Coke	Gases	Liquid	Char	Coke	Gases
400	42.0	35.0	23.0	24.3	25.7	10.0	40.0	32.0	25.0	6.0	37.0
450	50.0	29.0	21.0	17.5	25.0	11.0	46.5	29.9	25.4	6.0	38.0
500	58.0	26.0	16.0	12.5	25.3	11.8	50.2	27.0	24.5	6.1	42.0
550	53.0	21.0	26.0	10.1	25.5	12.5	52.1	24.0	24.3	6.3	45.0

The higher Si/Al ratio in H-ZSM-5 zeolite means a lower amount of total acid sites than that of H-USY zeolite with a lower Si/Al ratio which was confirmed by the results obtained through ammonia TPD studies. The H-ZSM-5 zeolite is a medium pore size catalyst which has 3-dimensional system of interesting straight channels within its crystallite. On the other hand, the H-USY zeolite has larger size pores. Thus, the larger amount of total acid sites of Y type zeolite along with larger pore structure results in accelerated cracking and deactivation reactions, yielding higher amount of gas and coke. It appears that Y type zeolite has large supercages within their crystallites which may be reason of coke formation. However, H-ZSM-5 zeolite has no supercages in its crystallites, hence coke particles could not be formed that much rendering comparatively less deactivation of zeolite. As in Table 2, the amount of total acid sites in case of H-ZSM-5 is found to be lower than catalyst Y type zeolite. However, the acid site in H-ZSM-5 is reported to lie on the intercrystalline system of the zeolite and are all accessible. Thus, although H-ZSM-5 zeolite has lower amount of total acid sites in comparison to H-USY zeolite, it exhibits a high shape selective properties. The liquid product yield was found to be higher in case of H-ZSM-5 catalyst while coke formation and gas yields were higher for zeolite H-USY. Thus, zeolite H-ZSM-5 appeared to be better so far the liquid product yield was concerned. At lower temperature the liquid yield was more in comparison to that at higher temperature in cases of both the catalysts. However, the char yield was identical indicating the reproducibility of the fluidised bed. The gas yield was lower at lower temperature with a trend of increment in the yield with increasing temperature. The coke formation was found to increase slightly with catalytic bed temperature. A similar trend of product yields were found in the work of Williams and Horne (1994).

BIO-OIL COMPOSITION AT DIFFERENT CATALYTIC REACTOR BED TEMPERATURE

After being analyzed chromatographically with GC/MS the liquid products at different catalytic bed temperature, the chemical compounds identified were presented in Table 4 in percent distribution. It revealed from the analysis that the oil still contained oxygenated compounds. This may be attributed to the chemical compositions of the components of biomass, such as cellulose, hemicelluloses and lignin containing a huge quantity of oxygen in their structures. The proportion of acids was higher in case of zeolite H-USY while the proportion of phenols was higher for zeolite H-ZSM-5. The hydrocarbons were found to be higher in case zeolite H-USY. The quality of bio-oil produced from oil palm shell and compared with other fuels together with its economics analysis have already been published elsewhere (Islam et al. 1999).

CONCLUSION

The maximum single phase bio-oil was found of 58 gram at fluidised-bed temperature of 500°C without catalyst, 32 gm at catalytic bed temperature of 400°C using H-ZSM-5 catalyst and 24.3 gm at temperature of 400°C using

TABLE 4. Chemical compounds in catalytically treated pyrolysis liquid in percent distribution using different catalysts at fluidised bed temperature of 500°C and WHSV of 1.16 h⁻¹

Chemical compounds	Catalytic bed temperature					
	400	500	550	400	500	550
	H-ZSM-5			H-USY		
2-Propen-1-ol	—	—	—	—	3.76	—
Acetic acid	10.03	16.41	19.2	5.38	6.07	3.18
Ethenediol, 1, 2-	—	—	—	—	3.78	3.32
Cyclopropyl carbinol	—	—	—	—	12.04	—
Cyclobutanol	—	—	—	—	—	5.85
Phenol	32.11	37.14	59.8	26.3	20.54	17.8
Phenol, 2-methyl-	—	2.09	2.89	—	—	—
Phenols, 3-methyl-	4.22	6.21	7.87	—	—	—
(p-cresol)						
Benzinamine, N,	3.67	—	—	—	—	—
N-dimethy 1-4-						
Benzene	6.61	—	—	—	—	—
Butanal, 3-methyl-	—	—	—	8.95	—	—
Butanoic acid	—	—	—	39.3	21.32	28.9
Thiophene, 2-isobutyl-5-	1.38	—	—	—	—	—
isopentyl-						
Naphthalene, 2-6-bis	—	2.72	—	—	—	3.46
1-Pentene, 3, 3-dimethyl-	—	—	—	—	3.45	2.24
3-Hexene, 2-methyl-	—	—	—	3.67	—	—
Formic acid, 2-propenyl ester	—	—	—	—	—	2.67
Pentalene, Octahydro-	—	—	—	—	2.19	1.86
1, 2-Benzenediol	29.5	24.85	6.94	4.16	5.77	—
2H-Pyran-2-one,	—	—	—	—	2.93	—
tetrahydro-6, 6 dimethyl						
Benzaldehyde, 4-hydroxy-3-	—	—	—	—	—	1.24
methoxy-						
Theobromine	—	—	—	4.03	—	—
1, 2-Benzenedicarboxylic	—	—	—	—	1.79	—
acid, diethyl ester						
Naphtho-furan-4, 9-dione,	—	—	—	8.14	3.46	—
2-isoprop						

H-USY catalyst in 100 gram of oil palm shell fed. The bio-oil from oil palm shell was found to be strongly dependent upon the bed temperatures. The product yield was varying both with fluidised-bed and catalytic bed temperatures. The product compositions were also found to be varying with

the bed temperatures and with type of catalysts. Thus, it can be concluded that the product yield and product composition of bio-oil from oil palm shell can be varied by changing the fluidised-bed and the catalytic bed temperatures.

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