



# Catalytic pyrolysis of oil palm mesocarp fibre on a zeolite derived from low-cost oil palm ash



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## ABSTRACT

Oil palm mesocarp fibre (OPMF) was pyrolysed on zeolite synthesised from oil palm ash (OPAZ) by using a slow heating fixed-bed reactor at 400 °C–600 °C. The maximum bio-oil yield of OPAZ-catalysed pyrolysis at 550 °C was 37.98 wt%, which was higher than that of non-catalytic pyrolysis (31.95 wt%) at the same temperature. GC–MS revealed the extensive variety of oxygenated organic compounds in the bio-oils derived from the non-catalytic and catalytic pyrolysis. Catalytic pyrolysis increased the amount of light phenol relative to that of heavy phenols and remarkably reduced the amount of acids, alcohols, hydrocarbons and hydrocyclic compounds. The oxygen content of the bio-oil decreased, resulting in enhanced fuel potential of the bio-oil and other valuable chemicals. The morphology and textural characteristics of OPAZ sustained the propensity of the catalyst-driven pyrolysis by upgrading the OPMF pyrolysis oil into a fuel-grade bio-oil.

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## 1. Introduction

Global supply of fossil fuels, mainly crude oil, dwindles because of political instability in resource-laden areas, fuel cost and the possible extinction of this resource resulting from overexploitation. Contemporary energy scenario supports the diversification of energy sources derived from biomass due to its critical carbon neutral characteristics [1,2]. A typical energy scenario involves the conversion of residual biomass into energy using thermochemical treatments, such as combustion, hydrothermal liquefaction and pyrolysis. Direct combustion of residual biomass serves as feedstock for renewable heat that is useful in numerous industrial processes [3]. Hydrothermal carbonization and pyrolysis of biomass under an inert atmosphere generally produce bio-oil (liquid) and biochar (solid) [4]. Optimal operating conditions are required to achieve substantial yields of bio-oils relative to the yields of other pyrolysis products. Parameters that tailor pyrolysis reactions in reactors include heating rates, transfer of heat to biomass, precise reactor temperature, residence times of pyrolysis vapours and quenching of pyrolysis vapours [1].

A pyrolysis oil has widely distributed fractions of oxygenated organic compounds, primarily heavy phenolic and alkylated (poly-) phenols with relatively small amounts of phenol, eugenol, cresols and xylenols [5–7]. Moreover, a substantial amount of

water co-exists with organic compounds, which suppress the fuel characteristics of bio-oil. Bio-oils become extremely unstable and tend to repolymerise during storage as a response to aging, causing drawbacks in the fuel properties of bio-oil [8].

Catalyst-driven pyrolysis principally improves product yields and distribution, as well as enhances the stability and quality of bio-oils [9]. A catalyst significantly influences product selectivity and distribution of bio-oil components [10]. Varying pyrolysis conditions, such as catalyst loading, also influence the yields and composition of bio-oils. Operating parameters are tempered to direct the pyrolysis reaction and ultimately achieve the desired quality and quantity of bio-oils. The typical operating parameters for biomass pyrolysis studies include catalyst loading pattern, biomass particle size, N<sub>2</sub> flow rate, temperature and time [11,12]. The design of efficient and economical catalysts faces the challenges of the industrial-scale application of biomass pyrolysis [13]. Cheap and reliable catalysts demonstrating phobia toward coke formation can limit the economic and technical difficulties in the industrial application of pyrolysis. Additionally, catalyst/biomass ratio must be optimised to guarantee efficient contact between pyrolysis vapours and the active sites on the catalyst and ultimately achieve precise industrial application of pyrolysis.

A catalyst in biomass pyrolysis increases the light organic fractions in bio-oils, exceeding the light organic fractions in thermally produced bio-oils. Catalysts promote reactions that invoke cracking of side chain structures and methoxy groups of aromatics in pyrolysis vapours. A catalyst is used to enhance the presence of

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light organic compounds, which modify and improve bio-oil as precursor for fuel and viable chemicals, such as phenols [14,15].

To improve the quality of bio-oils derived from biomass pyrolysis, Gong et al. [16] and Hussain et al. [17] respectively proposed the use of zeolite and cement as catalysts. Zeolite catalysts, such as ZSM-5, HZSM-5 and FCC, influences the stability of the chemical compositions of bio-oils and the characteristics of fuels during biomass pyrolysis [18–20]. The acidity of zeolite rendered by Si/Al is responsible for oxygen reduction in bio-oil. The acidic sites in zeolite catalysts play a crucial role in deoxygenating a bio-oil to improve its energy density [21]. Catalysts aromatise and deoxygenate pyrolysis vapours into bio-oils that display low H/C and O/C ratios; in some cases, catalysts increase or decrease bio-oil yield [22].

Malaysian oil palm mills generate huge quantities of residual oil palm mesocarp fibre (OPMF) that ends up in dump sites. Moreover, ashes produced from burning of residual OPMF in boilers for energy remains unattended for any typical use. These residual renewable materials both threaten the environment; for instance, OPMF ash leaches through the soil and contaminates the aquifer. Scholars [23–25] have reported on the use of fly ash to synthesise zeolite for catalytic and adsorption activities under moderate atmosphere. Zeolites outsourced from fly ash exhibit reliable surface morphology and chemistry for adsorption and catalytic reactions. These approaches help in the promotion of oil palm ash as renewable precursor in synthesis of zeolite, which can be used in catalytic activities during biomass pyrolysis. For this reason, this study aimed to synthesise oil palm ash zeolite (OPAZ) for catalytic pyrolysis of OPMF. This study compared non-catalysed and OPAZ-catalysed pyrolysis to reveal the effect of zeolite on product distributions and yields and on the chemical compositions of bio-oil.

## 2. Materials and methods

### 2.1. Materials

A local oil palm industry in Penang, Malaysia, supplied the OPMF as biomass substrate and the oil palm ash as zeolite precursor. The OPMF was dried overnight in an oven at 100 °C to remove moisture and then divided into portions based on particle size ranging from 63 µm to 500 µm through sieving. NaOH pellets with 99% assay purity were supplied by Sigma-Aldrich. The oil palm ash was used without purification.

### 2.2. Methods

#### 2.2.1. Preparation of OPAZ

For zeolite synthesis, 10 g of oil palm ash was mixed with 2 g of kaolin to produce the required quantity of aluminium oxide for zeolite synthesis, and then 50 mL of 2 M NaOH was added into the mixture. The mixture was magnetically stirred for 3 h at 60 °C and then allowed to age overnight at room temperature. The mixture was subsequently placed in a Teflon-lined autoclave and heated at 100 °C in an oven for 8 h. After hydrothermal treatment, the product was filtered and washed continuously with deionized water to adjust the pH to approximately 7 and then dried overnight at 60 °C in an oven to obtain the requisite OPAZ.

#### 2.2.2. Characterization of OPAZ

For X-ray diffraction (XRD), SIEMENS XRD D5000 equipment was used, and OPAZ was placed in an Al sample holder after sieving through a 0.074 mm sieve. The conditions for operation were as follows: Cu K $\alpha$  radiation at 30 mA/40 kV, scanning rate of 2°/min using a goniometer and 2 $\theta$  range of 5–50°. The surface functional groups of OPAZ were characterized by using Perkin Elmer Spec-

trum GX Infrared Spectrometer at a wavenumber of 4000–400 cm<sup>-1</sup>. FTIR analysis was performed in accordance with the KBr method, in which 0.007 g of OPAZ was mixed with 0.1 g of KBr, grinded, and then pressed to form a transparent pellet.

Nitrogen adsorption by Autosorb I (Quantachrome Corporation, USA) was used to measure the physical property of catalyst surfaces at –196 °C by using the multipoint Brunauer–Emmet–Teller method. External surface area, mesopore volume and mesopore surface area were determined through surface area analysis by using the *t*-plot method. Barrett–Joyner–Halenda method was employed to deduce pore size distribution and average pore width.

The chemical compositions of OPAZ catalyst were determined quantitatively through energy dispersive spectroscopy (EDS) by using a field-emission SEM (LEO SUPRA 35VPFESEM) EDAX-SEM instrument.

NH<sub>3</sub>-temperature programmed desorption (TPD) of OPAZ catalyst was performed on an ASAP 2920 unit (Micromeritics, USA) equipped with a thermal conductivity detector (TCD) to determine the acidic sites present in the catalyst. The sample was pre-treated to remove impurities, if any, by heating the catalyst at 450 °C under N<sub>2</sub> gas flow (100 mL min<sup>-1</sup>). For thermal desorption study, ammonia gas was adsorbed after cooling the sample to 30 °C and then charged into a U-tube reactor heated at 30 °C–600 °C at a rate of 10 °C min<sup>-1</sup> with He as carrier gas (30 mL min<sup>-1</sup>). The concentration of desorbed NH<sub>3</sub> at the exit stream was detected by an online gas chromatograph equipped with TCD. The amount of acid was calculated as the corresponding areas under the peaks obtained from the TCD signals.

#### 2.2.3. Characterization of OPMF

The elemental analyser Perkin Elmer 2400 Series II CHNS/O revealed that the elemental composition of the biomass includes carbon, hydrogen, nitrogen and sulphur. Conversely, the amount of O in the biomass was obtained by difference. The German standard method (DIN 51900-1, 2000) was used to determine the OPMF heating value by using a bomb calorimeter (Model: IKA C 200). A PerkinElmer TGA 7 apparatus was used in proximate analysis of OPMF samples. The procedures described in the well-established American Society for Testing and Materials were used for the proximate analysis of OPMF samples.

The procedures reported in literature [26] were used to ultimately determine the quantity of cellulose, hemicelluloses and lignin in a typical OPMF sample.

Table 1 presents the data for the proximate and ultimate analyses of OPMF samples. Data were consistent with those of other biomasses, such as karanj fruit hulls [3,4], *Jatropha* seed shell [27] and rice husk [28].

#### 2.2.4. Catalytic pyrolysis in slow heating fixed-bed reactor

A stainless fixed-bed reactor with 22.1 mm diameter and 200 mm height facilitated the catalytic upgrading of bio-oil obtained through slow pyrolysis of OPMF. For the catalytic studies, 0.2–1.0 g of OPAZ catalyst and 2 g of OPMF were placed in a two-layer fixed-bed reactor. The reactor was closed tightly, fitted with inert gas flow line, and then NiCr–Ni thermocouple was placed inside the OPMF/catalyst bed. The reactor was enclosed in an electric furnace with heating element and then heated up to the required pyrolysis temperature. The PID controller of the furnace and the reactor were always synchronised to maintain the set temperatures for the reactor and furnace.

Nitrogen (99.99% pure) flowed through the reactor at 200 mL min<sup>-1</sup> for 15 min to create the requisite inert condition for the pyrolysis studies. For each pyrolysis study, the desired input parameters, N<sub>2</sub> flow and reaction time were set to be achieved at a heating rate of 10 °C min<sup>-1</sup>. The N<sub>2</sub> flow of 200 mL min<sup>-1</sup> and the reaction time of 10 min were set for the catalytic pyrolysis. How-

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