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In-situ Upgrading of Napier Grass Pyrolysis vapour over Microporous and Hierarchical Mesoporous Zeolites

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Abstract

This study presents in-situ upgrading of pyrolysis vapour derived from Napier grass over microporous and mesoporous ZSM-5 catalysts. It evaluates effect of process variables such catalyst-biomass ratio and catalyst type in a vertical fixed bed pyrolysis system at 600 °C, 50 °C/min under 5 L/min nitrogen flow. Increasing catalyst-biomass ratio during the catalytic process with microporous structure reduced production of organic phase bio-oil by approximately 7.0 wt%. Using mesoporous catalyst promoted nearly 4.0 wt% higher organic yield relative to microporous catalyst, which translate to only about 3.0 wt% reduction in organic phase compared to the yield of organic phase from non-catalytic process. GC-MS analysis of bio-oil organic phase revealed maximum degree of deoxygenation of about 36.9 % with microporous catalyst compared to the mesoporous catalysts, which had between 39 and 43 %. Mesoporous catalysts promoted production olefins and alkanes, normal phenol, monoaromatic hydrocarbons while microporous catalyst favoured the production of alkenes and polyaromatic hydrocarbons. There was no significant increase in the production of normal phenols over microporous catalyst due to its inability to transform the methoxyphenols and methoxy aromatics. This study demonstrated that upgrading of Napier grass pyrolysis vapour over mesoporous ZSM-5 produced bio-oil with improved physicochemical properties.

Keywords: Napier grass; characterization; in-situ deoxygenation; Microporous ZSM-5; Mesoporous ZSM-5; hydrocarbons

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1. Introduction

Production of alternative fuels from renewable sources continue to gain attention in recent times due to the fear of energy insecurity in the near future and environmental impact associated with the use of petroleum-based fuels together with socio-political issues [1-4]. Lignocellulosic biomass (non-food materials) is being considered as an alternative feedstock for the production of renewable biofuel due to the presence of carbon in their building blocks, which can be processed into liquid fuel. Pyrolysis remains an attractive route for the thermochemical conversion of biomass as it comprises fewer steps and capable of high liquid yield (known as pyrolysis oil or bio-oil) through a careful control of process variables such pyrolysis temperature, heating rate, vapour residence time in the reactor, and rapid cooling of the volatile in the condenser [4, 5]. Pyrolysis oil from biomass is a complex mixture consisting predominantly of oxygenated organic compounds, phenolics, light hydrocarbons and traces of nitrogenous and sulphur containing compounds depending on nature of the source biomass. The high level of the oxygenated compound in the oil is responsible for the poor physicochemical characteristics such as low pH, low chemical stability, low energy content [4-6] and therefore rendered the oil unsuitable for direct application as fuel or refinery-ready feedstock for quality fuel production and other consumer products.

Upgrading of pyrolysis vapour is one of the methods being employed to improve pyrolysis oil quality. This process is performed in a vapour phase with the aid of catalyst through a series of chemical reactions such as decarboxylation, dehydration, and decarbonylation where oxygen is removed in the form of CO₂, H₂O and CO prior to condensation of volatiles [7]. Upgrading of pyrolysis vapour can be carried out in-situ or ex-situ. In the former, the catalyst is physically mixed with the biomass followed by pyrolysis while in the latter, catalyst is arranged in a separate parked bed reactor after

the pyrolysis reactor. Volatiles from the pyrolysing biomass passes through the catalyst bed where the deoxygenation reactions take place. Process variables governing the yield and quality of bio-oil produced via the in-situ upgrading of pyrolysis vapour include pyrolysis temperature, heating rate and catalyst-biomass ratio (CBR) [8, 9]. Effect of pyrolysis temperature was investigated by Liu et al. [9] during upgrading of pyrolysis vapour from duckweed over HZSM-5. The authors reported that high temperature promoted production of monoaromatic hydrocarbons, which was attributed to exothermic nature of the oligomerization reactions. The work of Park et al. [10] on catalytic fast pyrolysis of waste pepper stems over HZSM-5 at 550 °C pyrolysis temperature showed that increasing CBR up to 3 promoted production of monoaromatic compounds while other oxygenates such as acids and phenolics were significantly reduced. Similarly, investigation by Gamliel et al. [11] in situ catalytic pyrolysis of miscanthus × giganteus using a PyGC-MS microsystem revealed that high production of aromatic hydrocarbon was accompanied by the increasing CBR. On the contrary, report by Ojha and Vinu [12] on resource recovery from polystyrene via fast catalytic pyrolysis using a zeolite-based catalyst indicated that increasing CBR promoted production of benzene among the monoaromatic hydrocarbons while the yield of polyaromatic hydrocarbons increased with CBR. Similar observation was also reported by Luo and Resende [13] during in-situ upgrading of pyrolysis vapours from beetle-killed trees. The authors stated that higher CBR increase mass and heat transfer resistances and limit aromatic production, which in turn favoured more carbonaceous residues. These dissimilarities could be attributed to differences in the catalyst characteristics used.

Application of hierarchical mesoporous ZSM-5 in catalytic deoxygenation of pyrolysis vapour have shown significant selectivity and improvement in the quality of pyrolysis oil [14]. The work of Lee et al. [15] on upgrading of bio-oil derived from biomass constituents over hierarchical unilamellar mesoporous MFI nanosheets revealed that mesoporous catalyst displayed higher cracking and deoxygenation activities, which produced bio-oil with a lower oxygen content. They observed that Levoglucosan,

Ketones, aldehydes, alcohols, phenolics and cyclo-compounds identified in the non-catalytic pyrolysis oil were converted to aromatics with mesoporous catalyst. Increasing CBR was also found to further enhance quality bio-oil production. Gamliel et al. [16] also reported that mesoporous MFI catalysts promoted bio-oil yields from catalytic fast pyrolysis of miscanthus without sacrificing yields to valuable monoaromatic hydrocarbons (benzene, toluene and xylene). They observed that production of aromatic hydrocarbon led to a significant decrease in the solid yield, which was attributed to mesoporous structure of the catalyst.

Napier grass (NG) (*Pennisetum purpureum*) also known as elephant grass, Uganda grass, an underutilized herbaceous plant which can be cultivated up to four times annually. Ratio energy output to energy input has been reported to be in the range of 25:1 with 25-35 oven dry tons/hectare biomass yield. This value corresponds to 100 barrels of oil energy equivalent per hectare [17-19]. Comparing with other energy grasses such as Miscanthus, switchgrass, these materials have only between 10 and 20 oven dry tons biomass yield per hectare per annum and require some nutrient input during cultivation [20-25]. Flores et al. [18] have reported that NG can be grown without any nutrient or fertilizer input. They evaluated the performance of two NG species with and without application of nitrogen fertilizer under the Cerrado climatic condition (semi-humid tropical climate). Their findings revealed that the biomass yield was between 30 to 42 oven dry tons per hectare and showed no response to nitrogen fertilization. Tsai and Tsai [26] have reported recent study on environmental and economic benefit analysis of NG. Their result shows that NG can mitigate CO₂ emissions to the order of 5 million Gg per annum. The energy equivalent was found to be 11 million barrels per 100 000 hectare annually which equals to 110 barrels of oil energy equivalent per hectare. This value strongly agrees with the findings reported by Samson et al. [17]; Flores et al. [18]. Cultivation of NG follows conventional farming practices. It outcompetes weeds and

therefore, requires lower establishment costs. This makes it one of the best potential energy crops for the development of efficient and economic bioenergy systems [17, 18].

Studies on the in-situ catalytic upgrading of bio-oil from Napier grass are very limited. Only recently, Braga et al. [27] reported catalytic upgrading of pyrolysis vapour from NG using WO_3 supported on rice husk ash and RHA-MCM-41 as the catalysts in a micro-reactor. The authors reported that phenols, furans, ketones and acetic acid were converted to monoaromatic hydrocarbons over WO_3/RHA at 600 °C and was attributed to the catalytic activity of WO_3 . High CBR of 15 (wt/wt) was employed, which may not be practicable technically and economically. Mass balance on the pyrolysis product distribution was not accounted. This information is needed in order to evaluate the actual energy carrier resulting from the process. Therefore, there is need for further investigation so as to establish more detailed information on the yield and characteristics of pyrolysis oil from the in-situ catalytic upgrading of NG pyrolysis vapour. The objective of this study was to increase valorisation of Napier grass to high-grade bio-oil via in-situ upgrading of pyrolysis vapour over micro and mesoporous ZSM-5.

2. Materials and method

2.1 Materials and characterization

Chemical reagents, zeolite catalyst used in this study were analytical grades purchased from Fisher Scientific Sdn. Bhd. Selangor, Malaysia, Sigma-Aldrich Sdn. Bhd. Selangor, Malaysia or Evergreen Engineering and Resources Sdn. Bhd. Selangor, Malaysia. Locally grown NG at the crops for the future (CFF) field research centre (2°56'07.6"N 101°52'42.8"E) Semenyih, Malaysia was used as biomass feedstock. Fresh Napier grass stem (NGS) samples (around 3cm) were collected and assessed as received. The material was dried at 105 °C in an electrical oven to a constant weight in accordance to British standard, BS EN 14774-1. Subsequently, the dried samples were shredded in a Retsch® rotor beater mill (SM100, Retsch GmbH, Germany) to particle sizes between 0.2 mm and 2.5 mm and stored in air tight plastic bags for further analysis.

Proximate and ultimate analyses on dry basis were carried out according to the relevant standard procedures. Volatile matter and ash content were determined following BS EN 15148 and BS EN 14775 respectively. Fixed carbon was computed from the remaining bone dry sample mass. Major inorganic elements in the ash were determined according to BS EN 15290. About 500 mg (0.2 mm), homogenized sample was placed in a digestion tube (42 x 300mm Fovorit, PLT Scientific Sdn. Bhd. Selangor, Malaysia). Hydrogen peroxide (H₂O₂: 30 %, 3.0 mL), nitric acid (HNO₃: 65 %, 8.0 mL) and hydrofluoric acid (HF: 40 %, 1.0 mL) was added and the vessel was closed after a reaction time of 5-10 min to avoid pressure build-up. Another tube was treated in the same manner but without the biomass sample (blank). The tubes were arranged with the aid of retort stands in a metallic container filled with silicon oil mounted on a hotplate. The level of silicon oil was adjusted so that it covers the entire section of the tubes containing the samples. The system was gradually heated to 220 °C over 60 min and held for another 60 min. The system was cooled to room temperature and subsequently, boric acid (H₃BO₃: 4 %, 10.0 mL) to neutralize the HF. The mixture was reheated rapidly to 180 °C and held for 15 min. after cooling to room temperature, the mixture (digest) was transferred to 250 mL plastic bottles. The digestion tubes were carefully rinsed with deionized water (Milli-Q[®] type 1 ultrapure water) such that the total volume of the digest in the plastic bottles was 200 mL. Standard solution of each analyte was prepared at various concentration for calibration graph and the corresponding response (absorbance) was determined using atomic absorption spectrometer (AAS) (Analyst 400, Perkin Elmer Sdn Bhd, Selangor, Malaysia). Absorbance of the analytes in blank and digest were also determined and the corresponding concentration calculated using equation 1

$$w_i = \frac{(C_{is} - C_{ib}) \times V}{m} \quad (1)$$

Where w_i is the concentration of element in the sample (mg/kg), C_{is} and C_{ib} is the concentration element in the diluted digest (mg/L) and blank sample respectively. V is

the total volume of the diluted digest (200 mL) and m is the mass of biomass sample used (0.5 g)

Biomass higher heating value (HHV) was determined using an oxygen bomb calorimeter (Parr 6100, Parr Instruments, Molin, USA). Elemental compositions such as carbon, hydrogen, nitrogen, sulphur and oxygen (CHNSO) were determined using CHNS/O analyser (2400 Series II CHNS/O analyser, Perkin Elmer Sdn Bhd, Selangor, Malaysia). Structural analysis of the biomass was performed using High-performance liquid chromatography (HPLC-1260 infinity, Agilent Technologies Sdn Bhd, Selangor, Malaysia) according to the Analytical Procedure outlined by National Renewable Laboratory NREL/TP-510-42618.

Zeolite catalyst was converted to protonic form by calcining at 550 °C in air at 5 °C/min for 5 hours and the resulting solid was designated as ZSM-5. Hierarchical mesoporous ZSM-5 was obtained from desilication of ZSM-5 using NaOH solution. Known amount of ZSM-5 was mixed with different aqueous solution (0.2 and 0.3 M of NaOH) for 2 hrs at 70 °C. The solid was filtered using vacuum filtration with the aid of a polyamide filter and thereafter oven dried at 100 °C. The dried samples were transformed into H-form with 0.2 M ammonium nitrate (NH_4NO_3) solution at 80 °C for 24 hrs, followed by overnight drying at 100 °C and calcination at 550 °C for 5 hrs. The final alkaline treated solids were designated as 0.2HZSM-5 and 0.3HZSM-5. All the catalysts were characterized according to standard procedures. XRD was used to examine the nature of the crystalline system at 2θ angles between 10° and 60°, 25 mA, 45 kV, step size of 0.025°, and 1.0 s scan rate. SEM was used to evaluate the surface and structural characteristics. Specific surface area and pore properties were determined. Acidity of the catalyst was determined via ammonia-temperature programmed desorption (TPD) using a pulse chemisorption system (ChemiSorb 2720, Micrometrics, Norcross, USA).

2.2 In-situ upgrading of pyrolysis vapour and Products characterization

In-situ catalytic upgrading was carried out in a vapor phase prior to condensation of volatiles. The catalyst was mixed with the biomass (2.5 mm bone dry) and the mixture was charged into vertical pyrolysis system. The vertical pyrolysis system consists of a fixed bed reactor made of stainless steel (115 cm long, 6 cm inner diameter), a distribution plate with 1.5mm hole diameter which sit at 25 cm from the bottom of the tube, two nitrogen preheating sections (top and bottom of the reactor) and, a cyclone, oil collector, gas scrubbers and water chiller operating at 3 °C attached to a coil condenser as shown in Figure 1. 200 g feedstock (biomass and catalyst) depending on the biomass-catalyst ratio was placed on a gas distribution plate inside the reactor tube. The setup was heated in a vertical furnace at 50 °C/min to a pyrolysis temperature of 600 °C under 5 L/min nitrogen, which flows upward across the distribution plate from the bottom of the reactor. The pyrolysis reaction temperature was monitored with a thermocouple (K-type, NTT Heating, Sdn Bhd, Selangor, Malaysia). The reaction time was kept at 60 min after the temperature attained the set-value. Pyrolysis vapor was condensed by passing through a condenser attached to the water chiller and condensate (bio-oil) was collected in a container. Bio-oil, bio-char and non-condensable gas yields were calculated using Equation (2), (3) and (4). The experiment was repeated in triplicates and standard deviations were computed.

$$\text{Yield (wt\%)}_{\text{bio-oil}} = \left[\frac{\text{weight of the bio-oil collected}}{\text{weight of biomass feed}} \times 100 \right] \quad (2)$$

$$\text{Yield (wt\%)}_{\text{bio-char}} = \left[\frac{\text{weight of the bio-char collected}}{\text{weight of biomass feed}} \times 100 \right] \quad (3)$$

$$\text{Yield (wt\%)}_{\text{non-condensable gas}} = 100 - (\text{Eq(2)} + \text{Eq(3)}) \quad (4)$$

Characterization of bio-oil and non-condensable gas were carried out accordingly using analytical instruments. Physicochemical properties of bio-oil such as pH, water content, density and viscosity were analysed with a WalkLAB microcomputer pH meter (TI9000, Trans Instruments, Singapore), CHNSO and heating value analyses of bio-oil were carried out using the analytical instruments described in the feedstock characterization. Detail of the chemical composition of the bio-oil was determined using a gas chromatograph-mass spectrometer (GC-MS) (PerkinElmer Clarus[®] SQ 8, Akron, USA) with a quadruple detector and column (30m x 0.25mm x 0.25 μ m) (PerkinElmer-Elite[™]-5ms, Akron, USA). The oven was programmed at an initial temperature of 40 °C, ramp at 5 °C /min to 280 °C and held there for 20 min. The injection temperature, volume, and split ratio were 250 °C, 1 μ l, and 50:1 respectively. Helium was used as carrier gas at a flow rate of 1 mL/min. The peaks of the chromatogram were identified by comparing with standard spectra of compounds in the National Institute of Standards and Technology library (NIST, Gaithersburg, USA). The composition of non-condensable pyrolysis product was monitored offline. The gas sample was collected in a gas sample bag (Tedlar, SKC Inc., USA) and its composition analysed using a gas chromatography equipped with stainless steel column (Porapak R 80/100) and thermal conductivity detector (TCD). Helium was used as a carrier gas and the GC was programmed at 60 °C, 80 °C and 200 °C for oven, injector and TCD temperature respectively.

3. Results and Discussion

3.1 Feedstock characteristics

Characteristic of NGS used in this study is summarized in Table 1. The proximate analysis result obtained showed significant difference relative to similar properties of Napier grass (NG) reported in the literature. Higher volatile matter and lower ash contents were recorded compared to the values reported by Strezov et al. [26], Lee et al.[28], Braga et al. [29], Sousa et al. [29] and De Conto et al. [31]. Higher heating value (HHV) was 18.05MJ/kg relative to 15.61MJ/kg and 15.77MJ/kg reported by Braga et al. [29] and De Conto et al. [29] respectively. These variations in the proximate

analysis result is attributed to the post-harvest treatment of the NG sample used. The results of ultimate and structural analyses (Table 1) showed good agreement with the literature values. Comparing the structural characteristics of NGS with that of switchgrass and miscanthus, from the work of Imam and Capareda [21] and Rena et al. [23], switchgrass has lower cellulose (32-34 wt%) and lignin (18.8wt%) contents. Similarly, miscanthus has lower lignin content (12-12.58 wt%) but higher cellulose (50.34-52.13 wt%) and hemicellulose (24.83-25.76 wt%) contents as reported by Brosse et al. [32] and Shemfe et al. [24]. Studies on the comprehensive mineral analysis of NG biomass are rarely reported. This information is very important, as biomass mineral composition has been reported to have great influence on both pyrolysis product yield and bio-oil composition [33]. Most literature reported values determined by x-ray fluorescence (XRF) and energy dispersive x-ray (EDX), which are point analysis. In this study, the major elements recorded in the feedstock using atomic absorption spectrometer (AAS) showed mineralogical composition (Na, K, Ca, Al, Fe and Si) similar to that reported by Strezov et al. [27].

3.2 Characteristics of catalysts

Diffractiongram of the catalysts is shown in Figure 2. Both the parent ZSM-5 and mesoporous ZSM-5 samples (0.2HZSM-5 and 0.3HZSM-5) exhibited main peaks between 20° and 25°, which are typical characteristic peaks for ZSM-5. Although the intensity of the modified ZSM-5 decreased with increased NaOH concentration. This observation shows a loss of crystallinity due to desilication, which could also be linked to the formation of mesoporous structures in the material [34, 35]. Physisorption analysis (Figure 3) of ZSM-5 displayed a type I isotherm according to the IUPAC classification. The isotherm showed a very strong adsorption in the initial region and a plateau at high relative pressure (>0.9). This pattern indicates that ZSM-5 is a microporous material [36]. Both 0.2HZSM-5 and 0.3HZSM-5 displayed a combination of type I and IV isotherms with a low slope region at the middle which shows the presence of few multilayers and a hysteresis loop at relative pressures above 0.4, which could be linked to capillary condensation in a mesoporous

material [37, 38]. With increasing NaOH concentration, the hysteresis loop became more pronounced and could also be related to the level of mesoporous structure formed in the sample after the desilication. Other characteristics of catalysts from the physisorption analysis are summarized in Table 2. Comparing ZSM-5 and modified ZSM-5, as expected, the Si/Al ratio decreased between 34-40 % after desilication. Similarly, reduction in Brunauer Emmet Teller (BET) specific surface area (S_{BET}), S_{micro} and V_{micro} were also observed in the modified ZSM-5. This observation shows that some of the micropores in the parent ZSM-5 have been converted to mesoporous structures after the desilication, which have contributed to the resulting mesoporosity in the modified ZSM-5 [37]. Increasing NaOH concentration for desilication from 0.2 M to 0.3 M produced a more mesopore with 17 % increase in surface (S_{meso}) and 37 % increase in total pore volume while the acidity remained within 1% difference. The significant increase in the pore volume can be responsible for the enlarged hysteresis loop observed in sample treated with 0.3 M NaOH. Ammonia-temperature programmed desorption (NH_3 -TPD) analysis (Figure 4) displayed two peaks in the parent ZSM-5 at temperatures around 219 and 435 °C while single peaks around 206 and 258 °C were observed 0.2HZSM-5 and 0.3HZSM-5 respectively. The high temperature peak represents desorption of NH_3 from strong acid sites while those observed at temperatures between 206 and 258 °C is ascribed to the desorption of NH_3 from weak acid sites [37, 38]. Disappearance of the strong acid sites in the modified ZSM-5 is attributed to decreased silica content in the respective samples [37, 38]. Total surface acidity obtained from the area under each peak was found to be 3.8085, 3.0036 and 2.9635 mmol/g for ZSM-5, 0.2HZSM-5 and 0.3HZSM-5 respectively. The SEM-EDX (Figure 5) revealed that ZSM-5 is highly crystalline, with hexagonal prismatic morphology and different particle size of less than 500 nm. Both 0.2HZSM-5 and 0.3HZSM-5 had morphological characteristic similar to the parent ZSM-5 indicating that the morphological integrity of the catalyst was not affected by desilication.

3.3 Pyrolysis product distribution

Pyrolysis was conducted at 600 °C, 5 L/min N₂ flow and 50 °C/min heating rate. The effect of ZMS-5/biomass ratio (CBR) on pyrolysis product distribution relative to non-catalytic pyrolysis (NCP) (catalyst/biomass ratio: 0.0 wt %) is shown in Figure 6. Total bio-oil (organic and aqueous phase) collected under NCP was 49.20 wt%, which decreased to 47.04, 45.24, 38.08 and 37.13 wt% at CBR of 0.5, 1.0 2.0 and 3.0 wt%. The organic phase collected was 15.69, 13.99, 13.18, 11.70 and 9.11 wt% at CBR of 0.0-3.0 wt%. Increasing CBR between 0.5-1.0 wt% showed no significant decrease in the organic phase yield, which could be attributed to the generation of less reactive pyrolysis vapour via simultaneous dehydration, decarboxylation, and decarbonylation reactions. Under this condition, the aqueous phase yield decreased from 33.05-32.06 wt% compared to 28.02-26.38 wt% recorded at CBR of 2.0-3.0 wt%. Non-condensable gas yield recorded at CBR of 0.5-1.0 wt% was 30.86-32.57 wt% relative to 36.14-36.67 wt% at 2.0-3.0 wt% CBR. This indicates that dehydration reaction was more prevalent at CBR of 0.5-1.0 wt% compared to CBR of 2.0-3.0 wt% where the decarboxylation and decarbonylation reaction appeared to be dominant due to high gas generation. Solid yield was approximately 22.0 wt% at 0.0-1.0 wt% CBR compared to 25.78-26.20 wt% recorded at 2.0-3.0 wt% CBR, which be linked to formation of coke or coke precursors. This observation is in good agreement with the literature [7, 40] Comparing with the existing literature, most researchers employed CBR which generally lead to less liquid yield and more gas production [40-43]. Studies involving catalyst loadings similar to the ones used in this study, particularly between 0.5 and 1.0 wt %, are seldom carried out. Research conducted by Park et al. [44] on catalytic pyrolysis of Miscanthus with ZSM-5 using a catalyst to biomass ratio of 0.1 and a reaction temperature of 450 °C in a fixed bed reactor resulted in a high yield of organic phase (21.5 wt %). Similarly, the work of Elordi et al. [45] on catalytic pyrolysis of polyethylene with ZSM-5 using a catalyst/biomass ratio of 0.03 at 500 °C in a spouted bed reactor generated about 25 wt % organic product. Degree of deoxygenation (DOD) of 20.51 % was recoded in organic

phase with 0.5 wt% CBR. This value increased by 8, 13 and 16 % with CBR of 1.0, 2.0 and 3.0. Similarly, a continuous increase in the higher heating value (HHV) was recorded with increasing CBR, which is attributed to the DOD achieved.

Impact of mesoporous 0.2HZSM-5 on pyrolysis product distribution is shown in Figure 7. Production of organic and aqueous phases decreased from 15.69-13.28 wt% and 33.51-24.83 wt% as the CBR increased from 0.0-3.0 wt%. Significant increase in the yield of non-condensable gas was observed. At 0.0 CBR, the non-condensable gas recorded was 28.74 wt%. This increased to 34.13, 35.51, 36.64 and 38.78 wt% at 0.5, 1.0, 2.0 and 3.0 wt% CBR, which are evidence deoxygenation reaction. The solid yield remained at approximately 23.0 wt%. Comparing with the performance of ZSM-5 (Figure 6), the organic phase recorded with 0.2HZSM-5 was 0.7-4.0 wt% higher, which can be linked to the improved pore characteristics. Similarly, higher non-condensable gas yield in the range of 0.5-3.0 wt% recorded with 0.2HZSM-5 relative to ZSM-5 is an indication of superior catalytic activity. Decrease in aqueous phase bio-oil with 0.2HZSM-5 from 33.51 wt% at 0.0 wt% CBR to 27.77, 27.40, 26.49 and 24.83 wt% at 0.5, 1.0, 2.0 and 3.0 wt% CBR suggest that the reaction proceeds via decarbonylation or decarboxylation reaction, which is also in agreement with the increased non-condensable gas yield recorded with CBR. DOD and HHV increased with increasing CBR. 3.0 wt% 0.2HZSM-5 CBR yielded highest values of DOD (39.42 %) and HHV (37.34 MJ/kg) compared to 36.92 % and 31.51 MJ/kg recorded at 3.0 wt% ZSM-5 CBR.

Pyrolysis product distribution over 0.3HZSM-5 is shown in Figure 8. Organic phase produced over 0.3HZSM-5 decreased from 15.69 wt% to 14.18 wt% at CBR of 0.5 wt% and subsequently to 13.66, 13.08 and 12.58 wt% at 1.0, 2.0 and 3.0 wt% CBR. These values are not significantly different (0.5-0.7 wt%) from the organic phase yield recorded over 0.2HZSM-5 under the same CBR condition but higher than the organic yield collected over ZSM-5 in the range of 0.2-3.5 wt% at CBR of 1.0-3.0 wt%. Substantial decrease in aqueous phase (25.43 to 20.09 wt %) and significant increase in

non-condensable gas (38.18 to 47.20 wt %) recorded with 0.3HZSM-5 as CBR increased from 1.0 to 3.0 wt% is an evidence of high selective deoxygenation through either decarbonylation or decarboxylation reaction. Highest DOD and HHV of the organic phase recorded with 0.3HZSM-5 at 3.0 wt% CBR was 43 % and 38.71 MJ/kg, which is approximately 6 % and 23 % respectively higher than the highest DOD and HHV recorded in the organic phase produced over ZSM-5. Other physicochemical properties of bio-oil are summarized in Table 3.

3.4 GC-MS analysis of organic phase product

Twenty most abundant organic compounds identified in the bio-oil samples consist various hydrocarbons (HCs), phenol (PHOL), aromatic hydrocarbons (ARHCs), methyl esters (MEST) and other value added chemicals (OVAC), which are summarized in Table 4. Increasing ZSM-5 CBR promoted production of HCs, which could be linked to the deoxygenation of holocellulose derived oxygenates such as acids, aldehydes, ketones (AAK) and cracking of long chain organic molecules. Increasing ZSM-5 CBR from 1.0-3.0 wt% decreased the amount of AAK by 50, 90 and 96 % while HCs increased in 3.5, 5.0 and 6.0 folds respectively relative to 0.0 wt% CBR. This suggest that the AAK are small enough to enter the micropore of the ZSM-5, which has sufficient surface area and active sites. Study by Li et al. [46] showed that microporous ZSM-5 can effectively converts small oxygenates. The authors recorded complete conversion of carbohydrate-derived oxygenates during catalytic fast pyrolysis of beech wood, which was attributed to the efficient mass transfer of oxygenates into the micropore due to their small size and followed by subsequent conversion. The HCs detected were mainly olefins. This observation can be attributed to the acidity of the ZSM-5 catalyst which is known for the selective production of olefins through cracking of oxygenated compounds at higher temperatures similar to the temperature (600 °C) used in this study [47, 48]. Similarly, the production of ARHCs increased with increasing CBR relative to 0.0 wt% CBR. The nature of ARHCs detected was with ZSM-5 were mainly poly aromatic hydrocarbons (PAH) (naphthalene) at 1.0 wt% CBR, which is mainly the product of condensed

fragments from the surface active sites of the ZSM-5. While methyl benzene and ethyl benzenes constituted main ARHCs detected at CBR of 2.0 and 3.0 wt% (supplementary Table 1 and 2). These compounds are produced via a series of complex chemical reactions such as cracking, oligomerization, dehydrogenation, and aromatization promoted by the Brønsted acid sites of the ZSM-5 [7]. In this study, production of ARHCs may have originated from conversion of MPHOL to MARHCs and subsequently to ARHCs. Although, only 23-29 % decrease in MPHOL and about 1.2-15.3 increase in MAHCs were recorded while there was no significant changes in the PHOL with increasing CBR. This suggests that PHOL, MPHOL and MARHCs are too bulky to be transferred into the micropores of ZSM-5, as such only pre-cracked species at the external surface small enough diffused into the micropores to form ARHCs.

Significant conversion of AAK to HCs was also achieved with 0.2HZSM-5 and 0.3HZSM-5. The composition of HCs were mixture of olefins and saturated hydrocarbons (supplementary Table 3 and 4), which is an indication of possible hydrogenation reaction. Maximum ARHCs detected at 3.0 wt% over 0.2HZSM-5 was similar to that recorded with ZSM-5 but differs in composition. Monoaromatic hydrocarbons (MAH) such as alkyl benzenes were the ARHCs detected. ARHCs produced with 0.3HZSM-5 at CBR of 3.0 wt% was approximately 10 % higher the values recorded for 0.2HZSM-5 and ZSM-5 and constituted trimethylbenzene, ethylbenzene, toluene and p-xylene (supplementary Table 3 and 4). PHOL content of oil collected over 0.2HZSM-5 and 0.3HZSM-5 was 26-38 % higher than the PHOL content of the oil produced over ZSM-5, suggesting formation of ARHCs proceeded via conversion of MPHOL to PHOL and MARHCs, and then to ARHCs. Study have shown that cracking of MPHOL proceeds through formation of methyl radical resulting in hydroxyphenoxy radical, which subsequently decarbonylates to cyclopentadienyl radical. Radical-radical reaction between methyl and cyclopentadienyl lead to the formation of phenols [49]. MPHOL were completely eliminated with both 0.2HZSM-5 and 0.3HZSM-5 at CBR of 3.0 wt%. This can be attributed to the improved pore characteristics of the catalysts, which enhanced mass transport of the molecules to

active sites. Higher content of PHOL in the final bio-oil produced over 0.2HZSM-5 and 0.3HZSM-5 relative to ZSM-5 suggests that PHOL molecules are too small and thus flow through the mesopore rather than attaching to the pore for subsequent conversion [46].

3.5 GC-TCD analysis of non-condensable gas

Composition of non-condensable gas collected is at 0.0 and 3.0 wt% CBR is summarized in Table 5. High levels of H₂ in the non-condensable gas at 0.0 wt% CBR is due to thermal cracking, which generally produce small organic molecules during the pyrolysis. Higher composition of CO and CO₂ in the non-condensables from the catalytic process relative the gas product at 0.0 wt% CBR is an indication of catalytic reactions [11]. Gas collected over 0.2HZSM-5 and 0.3HZSM-5 had higher percentages of CO and CO₂ relative to gas produced with ZSM-5, which is an indication of higher degree of decarbonylation and decarboxylation reactions. Reduction in H₂ content in the gas produced with 0.2HZSM-5 and 0.3HZSM-5 is a confirmation that some of the H₂ generated during catalytic reaction are subsequently consumed in the process, which could be responsible for hydrogenation of some olefins to alkanes as observed in the liquid product distribution.

4 Conclusion

In-situ catalytic upgrading of pyrolysis vapour derived from Napier grass was carried out. Increasing catalyst-biomass ratio during the catalytic process with microporous structure reduced production of organic phase bio-oil by approximately 7.0 wt%. Using mesoporous catalyst promoted nearly 4.0 wt% higher organic yield relative to microporous catalyst, which translate to only about 3.0 wt% reduction in organic phase compared to the yield of organic phase from non-catalytic process. Maximum degree of deoxygenation of about 36.9 % was recorded with microporous catalyst compared to the mesoporous catalysts, which had between 39 and 43 %. Mesoporous catalysts promoted production olefins and alkanes, normal phenol, monoaromatic hydrocarbons while microporous catalyst favoured the production of alkenes and polyaromatic hydrocarbons.

There was no significant increase in the production of normal phenols over microporous catalyst due to its inability to transform the methoxyphenols and methoxy aromatics. This study demonstrated that upgrading of Napier grass pyrolysis vapour over mesoporous ZSM-5 produced bio-oil with improved physicochemical properties.

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