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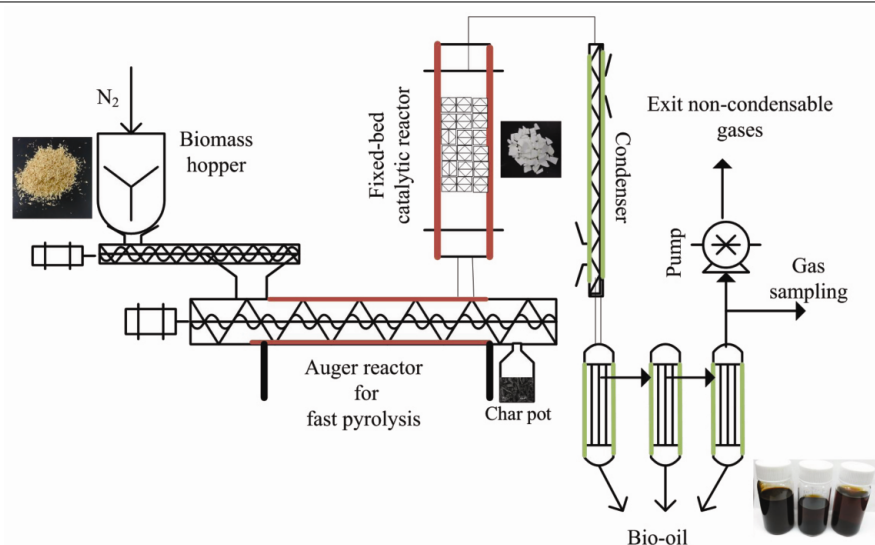
Altering bio-oil composition by catalytic treatment of pine wood pyrolysis vapors over zeolites using an auger - packed bed integrated reactor system

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HIGHLIGHTS

- An integrated reactor system is reported for catalytic pyrolysis of pine wood.
- Five zeolites with different acidity, pore sizes, and pore structures were studied.
- Bio-oil composition was a function of catalyst's surface area and pore properties.
- ZSM-5 in H form, with its shape-selective catalysis, produced best quality bio-oil.

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ABSTRACT

Pine wood pyrolysis vapors were catalytically treated using zeolite catalysts. An auger fed reactor was used for the pine wood pyrolysis while a packed bed reactor mounted on the top of the auger reactor housed the catalyst for the treatment of pine wood pyrolytic vapors. The pyrolytic vapors produced at 450 °C were passed through zeolite catalysts maintained at 425 °C at a weight hourly space velocity (WHSV) of 12 h⁻¹. Five zeolites, including ZSM-5, mordenite, ferrierite, zeolite -Y, and zeolite-beta (all in H form), were used to study the effect of catalyst properties such as acidity, pore size, and pore structure on catalytic cracking of pine wood pyrolysis vapors. Product bio-oils were analyzed for their chemical composition (GC-MS), water content, density, viscosity, acid value, pH, and elemental compositions. Thermogravimetric analysis (TGA) was performed to analyze the extent of coking on zeolite catalysts. Application of catalysis to biomass pyrolysis increased gas product yields at the expense of bio-oil yields. While all the zeolites deoxygenated the pyrolysis vapors, ZSM-5 was found to be most effective. The ZSM-5 catalyzed bio-oil, rich in phenolics and aromatic hydrocarbons, was less viscous, had relatively lower acid number and high pH, and possessed oxygen content nearly half that of un-catalyzed bio-oil. Brønsted acidity, pore size, and shape-selective catalysis of ZSM-5 catalyst proved to be the determining factors for its activity. TGA results implied that the pore size of catalysts highly influenced coking reactions. Regeneration of the used catalysts was successfully completed at 700 °C.

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1. Introduction

The depleting fossil fuel resources and emphasis on decreasing greenhouse gas emissions initiated the quest for renewable/green fuels. Lignocellulosic biomass is an abundant renewable resource that could be converted to liquid and gaseous fuels by thermochemical conversion technologies. Pyrolysis is an effective thermochemical conversion technology to produce liquid fuel called bio-oil from a variety of feedstocks. Bio-oil offers advantages compared to biomass in terms of its energy density and ease of transportation. However, compared to petroleum and diesel, bio-oil has substantially less calorific value while also being highly corrosive and thermally unstable making it unsuitable as a transportation fuel. Bio-oil's high oxygen content, in the form of more than 300 chemical compounds including water, carboxylic acids, esters, aldehydes, ketones, phenolics, etc., is responsible for its deleterious physical and chemical properties. Bio-oil can partially substitute fossil fuel if it is upgraded and stabilized to a high value end product by converting the high oxygen content intermediates to more stable hydrocarbons.

Catalytic pyrolysis of biomass to produce bio-oil followed by catalytic hydroprocessing of bio-oil is the most commonly followed upgrading route (Elliott et al., 2012; Wang et al., 2013; Zacher et al., 2014). Formation of low organic liquid yields and the transfer of fixed carbon to thermal (due to bio-oil instability when heated to hydroprocessing temperatures) and catalytic coke are the major problems associated with this process (Gayubo et al., 2005). To overcome the thermal instability problems of bio-oil as well as to attenuate catalyst deactivation by reducing the formation of excessive thermal and catalyst coke, application of catalysis to fast pyrolysis was proposed (Diebold and Scabill, 1988). Catalytic pyrolysis (catalytic treatment of pyrolysis vapors) is a promising alternative with better economics through the elimination of the costly condensation/re-evaporation step otherwise required for upgrading bio-oil in a secondary hydroprocessing reactor.

Catalytic pyrolysis has been studied using various catalysts (Dickerson and Soria, 2013; Liu et al., 2014). The properties of product bio-oils were dependent on starting biomass material (Zhang et al., 2007; Carlson et al., 2009; Bae et al., 2011; Thangalazhy-Gopakumar et al., 2011), reaction conditions (Meng et al., 2008), and the catalyst type (Aho et al., 2007; Iliopoulou et al., 2007; Aho et al., 2008; Lu et al., 2009; Uzun and Sarioglu, 2009; Lee et al., 2011; Mihalcik et al., 2011). High reaction temperatures and high surface area catalysts lowered the liquid yields (Twaiq et al., 2003). Zeolites, especially ZSM-5 in H form, were effective in converting pyrolysis vapors to liquid fuel rich in phenolic compounds and aromatic hydrocarbons (Heo et al., 2011). However, the product distribution significantly varied with the type of reactor employed in the studies (Chen et al., 1988; Aguado et al., 2000; Aho et al., 2007; Wang et al., 2010). While fluidized bed reactor was the widely used reactor configuration (Chen et al., 1988; Park et al., 2006; Aho et al., 2008; Rabinovich et al., 2010; Zhang et al., 2013), most of the catalytic pyrolysis studies involved the use of pyrolysis gas chromatography mass spectrometry (Py-GCMS) (Lu et al., 2010; Mihalcik et al., 2011; Thangalazhy-Gopakumar et al., 2011; Liu et al., 2014) or molecular beam mass spectrometry (MBMS) (French and Czernik, 2010). MBMS and Py-GCMS, though offers rapid catalyst screening and online analysis of product bio-oils, the yields and product distribution of catalytic pyrolysis cannot be ascertained. Moreover, these studies involve the use of very high heating rates (1000 °C/min) and high catalyst to biomass ratios (15-20) (Carlson et al., 2008; Carlson et al., 2009; French and Czernik, 2010). Use of such high heating rates and catalyst to feed ratios is not quite feasible in conventional processes. Therefore, the composition of product bio-oils from Py-GCMS μg to mg-scale studies vary from the product bio-oils obtained using conventional bench scale reactors (Torri et al., 2010; Compton et al., 2011). Augers fed reactors are relatively recently developed reactors for pyrolysis processes. The auger design is portable and is well suited for pyrolysis systems in a highly decentralized biomass processing scheme. The auger fed reactors are compact, do not need a carrier gas, but heat transfer rates and liquid yields are relatively lower. However, characterization studies of bio-oil obtained from fast pyrolysis of pine wood using auger reactor at Mississippi State University (MSU) showed that their chemical composition was similar to the bio-oils produced using conventional fluidized bed reactors (Ingram et al., 2008; Hassan et al., 2009). The combination of an auger reactor for fast pyrolysis and a packed-bed catalytic reactor for catalytic upgrading of pyrolysis vapor has not been much explored.

In this study, we report the use of an integrated reactor system, including an auger reactor for pine wood pyrolysis and a packed-bed reactor for upgrading

pyrolysis vapors coming out of the auger reactor, to convert pine wood biomass to deoxygenated bio-oils using zeolite catalysts. Five zeolites, each with different surface area, pore size, and pore structure, were tested for their efficacy in producing deoxygenated bio-oils from catalytic pyrolysis of pine wood. The effects of catalyst's surface area, Brønsted acidity, pore size, and pore structure on the product distribution were also determined.

2. Materials and Methods

2.1. Reactor configuration

An auger reactor pipe of 3" in diameter and 40" in length was employed for the purpose of producing bio-oil vapor. The distance between the screws (i.e., between the augers) was about 3". The auger speed was 11-12 RPM at the desired auger pyrolysis temperature. The particle size of the pine sawdust used in the pyrolysis was ~ 0.1 ". The auger reactor had four temperature zones. The feed first passed through a 4" heating (preheating) zone kept at ~ 200 -220 °C, then entered two pyrolysis zones, 10" and 8" in length, respectively, with temperatures in the range 450 °C, and finally reached an 8" zone kept at ~ 150 -175 °C. Initial feed was converted to char by the time it reached the 8" fourth zone. Upon exit, the char was collected in a collection pot through a 3" long insulated zone. The pyrolysis vapors from biomass pyrolysis then passed through a 1" I.D., 24" long packed bed reactor (PBR) mounted on the top of the auger reactor. This PBR was enclosed in a three zone furnace. The first two zones were kept at the desired catalytic upgrading reaction temperatures (425 °C) whereas the third zone was maintained at a temperature lower (by 50-75 °C) than the first two to start cooling of pyrolysis vapors before reaching the condensers. A schematic of the reactor system used in our study is shown in Figure 1.

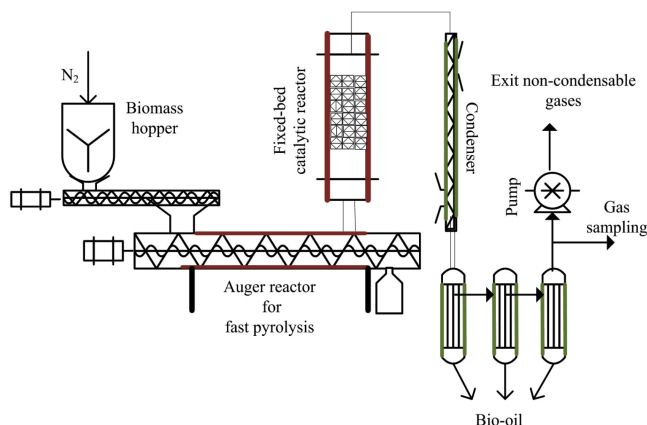


Fig.1. Schematic of the integrated auger-packed-bed reactor system.

2.2. Feedstock

Loblolly pine wood tree stems were debarked and then reduced to 0.75-1.25" sized paper chips. The chips were ground to smaller sized particles in a hammer mill and finally sieved to the required particle sizes (~ 0.1 ") for the pyrolysis experiments. The pine wood chips were oven dried at 105 °C overnight to about 8-10% moisture content and stored in sealed plastic buckets prior to use in the experiments.

2.3. Catalysts employed

Five zeolites, including ZSM-5, mordenite (ZM), ferrierite (ZF), zeolite-Y(ZY), and zeolite-beta (ZB) were used for the catalytic treatment of pyrolysis vapors. All the zeolites were commercially purchased from Zeolyst International in ammonium form. Prior to use, the catalysts were

Table 1.
Catalysts used for the treatment of pine wood pyrolysis vapors.

Catalyst	SiO ₂ /Al ₂ O ₃ ratio	Surface area (m ² /g)	Average pore size (nm)	Structure
CBV2314- ZSM-5	23	425	0.53	3-D pore system; Cubic crystal structure with straight 10-membered ring channels (5.3 × 5.5 Å) connected by sinusoidal channels (5.1 × 5.5 Å)
CBV814C- Beta	38	680	0.61	3-D pore system; Tetragonal crystal structure with straight 12-membered ring channels (7.6 × 6.4 Å) with crossed 10-membered ring channels (5.5 × 6.5 Å)
CBV21A- Mordenite	20	500	0.58	Orthorhombic crystal structure with straight 12-membered ring channels (6.5 × 7.0 Å) with crossed 8-membered ring channels (2.8 × 5.7 Å)
CP914C- Ferrierite	20	400	0.51	Orthorhombic crystal structure with straight 10-membered ring channels (5.4 × 4.2 Å) with crossed 8-membered ring channels (4.8 × 3.5 Å)
CBV720- Zeolite Y	12	730	0.72	3-D pore system; Cubic crystal structure with 12-membered ring channels (7.4 Å) connecting spherical 11.8 Å cavities (supercages)

calculated in air at 500 °C to convert the ammonium form to the active proton form of zeolites. **Table 1** shows the SiO₂/Al₂O₃ ratios, surface areas, pore sizes, and pore structures of the zeolites used in our study.

2.4. Experimental set-up

Pine wood pyrolysis was carried out at 450 °C. The catalytic treatment of pyrolysis vapors was performed at 425 °C maintaining the weight hourly space velocity (WHSV) of 12 h⁻¹. The catalytic pyrolysis experiments had the same amount of catalyst loading (50 g). A flow of N₂ gas controlled at 1 L/min by a mass flow controller was used to maintain inert atmosphere and to facilitate the pyrolysis vapor flow through the catalyst bed. A blank run, where the PBR was not loaded with any catalysts, was performed to compare the thermal treatment of pyrolysis vapors with the catalytic pyrolysis experiments.

The effluent pyrolysis vapors from the PBR were condensed by passing them through a 5' long stainless steel tube (½" I.D) enclosed by a jacket of coolant (50% ethylene glycol solution maintained at -8 °C) before reaching a set of glass condensers kept in the constant temperature bath having coolant maintained at -8 °C.

2.5. Characterization of upgraded pyrolysis products

Gas products were analyzed using a GC (Shimadzu) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The initial temperature of the molecular sieve column was maintained at 35 °C, followed by 10 °C ramping to a final temperature of 180 °C and held for 30 min. Gas samples, collected using 0.5 L Tedlar[®] gas sampling bags, were collected at different time intervals to check the effect of run-time on the catalysts activity. Product bio-oils were analyzed using a Hewlett Packard 5890 series II GC/5971 series A mass spectrometer. The injector temperature was 270 °C. A 30 m × 0.32 mm internal diameter × 0.25 μ film thickness silica capillary columns coated with 5% phenylmethylpolysiloxane was used at an initial temperature of 40 °C for 4 min followed by heating at 5 °C/min to a final temperature of 280 °C for 15 min. The mass spectrometer employed a 70 eV electron impact ionization mode, a source detector temperature of 250 °C, and an interface temperature of 270 °C.

The percent water, viscosity, density, pH, and acid values of the product bio-oils were determined. Karl Fisher titration (Cole-Parmer Model C-25800-10 titration apparatus) was carried out to measure the water percentage. A 200 5B viscometer (Stony Brook Scientific) was used to measure the viscosity and the pH was acquired with an expanded ion analyzer EA 920. Density was calculated according to ASTM standard D4052. The acid values were determined by titrating 1 g of the bio-oil fractions dissolved in 50/50 v/v isopropanol/water with 0.1 N NaOH to a pH 8.5.

3. Results and Discussion

3.1. Catalytic effects on the yields of pyrolysis products

Figure 2 shows the product distribution of the catalytic pyrolysis experiments. Catalysts did not influence the production of char since it is a pyrolysis byproduct produced in the auger reactor. The amount of char

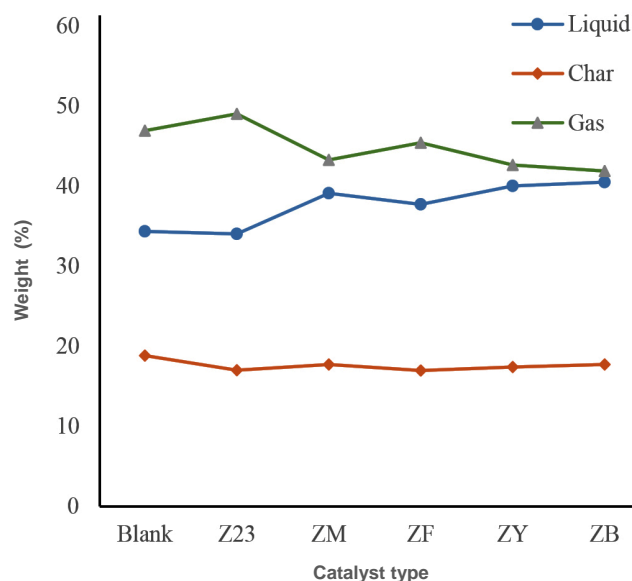


Fig.2. Influence of catalysts on the yields of pyrolysis products.

produced was uniform in all the experiments except the thermal treatment. This may be due to the presence of slightly bigger feed particles that led to a slight increase in the weight percentage of the char produced.

All the catalysts, except ZSM-5, improved liquid product yields compared to the thermal treatment of pyrolysis vapors, indicating that the thermal treatment leads to secondary cracking of the primary pyrolysis vapors, and therefore, converts the volatile compounds to non-condensable gases (NCG's). The liquid yield obtained using ZSM-5 was similar to the yields from the thermal treatment. Among the tested catalysts, ZSM-5 catalyst had the highest density of Brønsted acid sites (**Table 2**). Decrease in the silica content leads to higher charge imbalance and hence increases the Brønsted acidity. Higher Brønsted acidity increases the cracking of pyrolysis vapors to low molecular weight volatile compounds and, with increasing space time, to NCG's. The catalytic experiments showed significant increases in the formation of GC-MS quantifiable target compounds (**Table 3**). This shows that the thermal treatment either substantially reduced the formation of target compounds or converted the pyrolysis vapors to noncondensable gases.

Among the catalysts, ZSM-5 increased gas yields at the expense of liquid product yields. High surface area catalysts, ZB (680 m²/g) and ZY (730 m²/g), produced higher liquid yields than the low surface area catalysts ZM (500 m²/g) and ZF (400 m²/g). This observation is in contrary to what [Twaik et al. \(2003\)](#) observed (increasing catalysts surface area decreased liquid yields) using MCM-41 catalyst for cracking palm oil. However, their study used mesoporous catalysts and a different feedstock (palm oil versus pine wood pyrolysis vapor). The distribution of liquid yields can also be

Table 2.
Distribution of weak, medium, and strong Brønsted and Lewis acid sites in the zeolites used in the present study (Aho et al., 2008).

Catalyst	SiO ₂ /Al ₂ O ₃ ratio	Brønsted acid sites (μmol/g)			Lewis acid sites (μmol/g)		
		250 °C	350 °C	450 °C	250 °C	350 °C	450 °C
ZSM-5	23	416	395	284	36	8	3
ZB	25	219	187	125	82	43	25
ZM	20	378	305	153	30	12	3
ZY	12	255	205	129	123	75	58

Table 3.
GC-MS quantitative results of target compounds (μg/ml methanol).

Catalyst	Blank	Z23	ZM	ZF	ZY	ZB
Furfural	166.23	237.26	384.21	399.78	303.80	276.55
2-met, 2-Cyclopenten-1-one	30.30	130.75	106.85	103.42	115.36	84.13
Furfural, 5-methyl	62.73	201.84	775.34	427.91	404.5	280.05
3-met, 2-Cyclopentenone	27.61	198.49	144.15	161.90	167.17	95.99
Phenol	302.43	585.81	483.73	471.22	479.14	346.35
3-met,1,2-Cyclopentane dione	-	63.26	103.93	93.59	111.22	91.10
Phenol, 2-methyl	191.32	1248.47	333.81	348.87	384.01	272.01
Phenol, 3-methyl	275.14	634.93	679.04	675.53	631.43	343.95
Guaiacol	1.08	7.95	36.03	8.45	16.49	32.37
Phenol, 2,6 dimethyl	21.33	85.42	54.07	50.34	54.98	31.99
Levogluosenone	-	7.76	18.20	0.97	35.85	16.54
Phenol, 2,4 dimethyl	124.02	375.97	370.73	355.77	384.82	258.31
Phenol, 3-ethyl	75.40	278.55	291.65	301.96	299.91	189.28
Phenol, 2,3 dimethyl	19.17	34.99	34.95	37.13	41.29	25.62
Phenol,4-methyl,2-methoxy	0.18	1.76	3.63	4.67	10.59	53.76
Catechol	-	1373.58	1841.43	2067.55	1443.38	907.57
Catechol, 3-methyl	-	410.49	479.63	483.63	450.16	272.16
Phenol, 4-ethyl, 2-methoxy	-	5.13	9.20	8.09	12.37	20.93
Catechol, 4- methyl	0.96	1479.24	1745.2	1759.43	2284.1	828.19
Phenol, 2,6-dimethoxy	-	-	-	-	0.06	0.48
Eugenol	-	0.60	5.59	0.71	6.14	16.83
Phenol, 2-methoxy,4-propyl	-	0.26	14.97	1.37	1.26	4.25
Vanillin	-	1.06	4.34	1.86	7.76	20.44
cis- Isoeugenol	-	4.48	13.43	2.82	25.75	239.92
3,4-Dimethylbenzoic acid	-	0.62	1.18	1.02	0.30	0.76
Resorcinol, 4-ethyl	-	9.27	7.26	7.62	5.69	3.42
Anhydrosugars	17.98	65.8	265.63	164.18	166.91	213.58
Acetovanillone	1.40	0.13	2.03	0.27	5.12	11.16
Oleic acid	-	0.75	51.81	6.50	42.67	47.68

related to the acidity of the zeolites. The yields of liquid products decreased, following the order ZSM-5 < ZF < ZM < ZY = ZB, with increasing catalyst acidity. As shown in Table 2, the Brønsted acidity of the catalysts followed the order: ZSM-5 > ZM = ZF > ZY > ZB. The strong Brønsted acid sites (at 450 °C) were found to be similar in ZB and ZY with densities of 125 and 129 μg/mol, respectively (Aho et al., 2007 and 2008). This could be the reason why ZB and ZY produced similar liquid yields (40.5 and 40%, respectively). One exception noticed was that though ZM and ZF had similar SiO₂/Al₂O₃ ratio and therefore, assumed to possess similar acidity, ZM (39%) gave a higher liquid yield than ZF (37.7%). This indicates that factors other than SiO₂/Al₂O₃ ratio influences the catalyst acidity (Costa et al., 2000), and therefore, the distribution of pyrolysis product yields.

To further study the influence of catalysts on the pyrolysis products, the GC-MS detected chemical composition of the upgraded bio-oils was categorized into hemicellulose and cellulose derived and lignin derived compounds. Furthermore, as the number of compounds formed from lignin breakdown is high; they are further classified based on the function groups (guaiacols, diols, and phenols) of the compounds.

3.2. Catalytic effects on the distribution of hemicellulose and cellulose derived compounds

Figure 3 shows the influence of catalysts on the distribution of cellulose and hemicellulose derived compounds. While anhydrosugars are fragmentation/depolymerization products of pyrolysis reactions, the lower molecular weight furans and hydrocarbons are predominantly formed from catalytic treatment of pyrolysis vapors. Since the decrease in SiO₂/Al₂O₃ ratios increases the catalysts' Brønsted acidity (Corma, 1995; Su et al., 2002; Kasim et al., 2007) and therefore, the cracking efficiency, the catalysts with increasing acidity produces lower yields of anhydrosugars while increasing the formation of furan compounds (furfural and 5-methyl furfural).

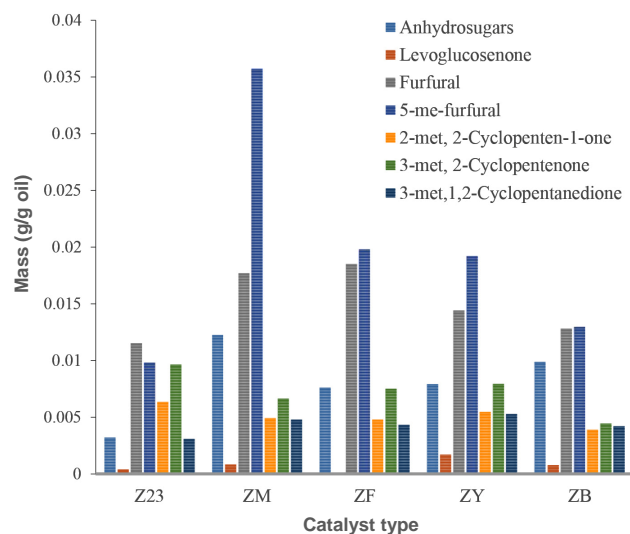


Fig.3. Breakdown of cellulose and hemicellulose.

The density of the Brønsted acid sites decreased in the order: ZSM-5 > ZM = ZF > ZY > ZB (Table 2). The yields of anhydrosugars increased with decreasing catalyst acidity, except in the case of ZM, while no linearity was observed in the formation of furan compounds. Of the tested catalysts, mordenite produced the highest yields of anhydrosugars and 5-methyl furfural. And among ZF, ZY, and ZB catalysts, the yields of furan compounds decreased with catalyst acidity. ZSM-5, despite having the highest density of Brønsted acidic sites, produced the least amount of furan compounds. This might be either due to the secondary cracking of these low molecular weight compounds to NCG's (CO, CO₂) or their conversion to aromatic hydrocarbons as shown by Carlson et al. (2009). Zhu et al. (2010) also showed the formation of aromatic hydrocarbons by catalytic pyrolysis of xylan using a ZSM-5 catalyst in H form.

3.3. Catalytic effects on the distribution of lignin derived compounds

Pyrolysis of pinewood biomass results in depolymerization of lignin polymer into its three principle fractions namely 4-hydroxyphenyl, guaiacyl (4-hydroxy-3-methoxyphenyl), and syringyl (4-hydroxy-3,5-dimethoxyphenyl) (Dorrestijn et al., 1999). These fractions, due to thermal and thermo catalytic effects (temperature, space time, catalytic activity, etc.), further get converted to phenols, diols, guaiacols, polyaromatic hydrocarbons (PAH's), coke, etc. The formation of monomeric compounds start during pyrolysis but their distribution and further breakdown to lighter compounds is strongly influenced by the presence of catalysts.

Thermal treatment considerably decreased or eliminated most of the useful lignin compounds (Table 3) either to low molecular weight compounds/gaseous products or to thermal coke. Though, aromatic hydrocarbons are produced, complete elimination of the phenolics and hydrocarbon precursors like guaiacols and catechols (diols) prove that thermal treatment is not an effective pathway to upgrade pyrolysis vapors.

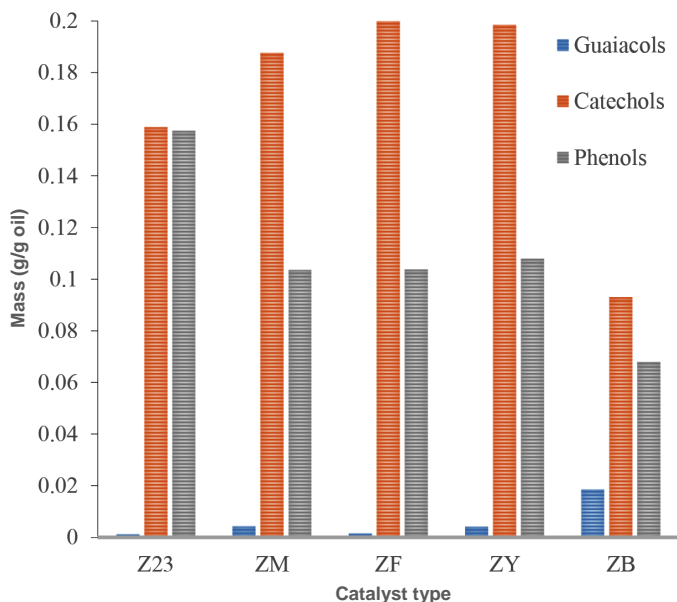


Fig.4. Influence of catalysts on the distribution of lignin breakdown compounds.

The composition of lignin derived compounds in the upgraded bio-oils varied with catalyst composition. Since the formation of low molecular weight compounds follow the route: lignin polymer → guaiacols, eugenols, vanillins → diols → phenols → hydrocarbons → low molecular weight compounds, the catalyst's efficacy can be interpreted by its ability to produce the highest amount of deoxygenated lighter compounds. ZSM-5 decreased guaiacols and diols with significant formation of phenols. ZM, ZF, and ZY decreased guaiacols but not diols and ZB could not convert guaiacols to low molecular weight compounds (Fig. 4). Therefore, the ZB catalyzed bio-oils had highest concentrations of guaiacols and lower amounts of diols and phenols.

Figures 5, 6, and 7 show the distribution of guaiacols, eugenols and vanillins, and diols in the bio-oils from the catalytic pyrolysis

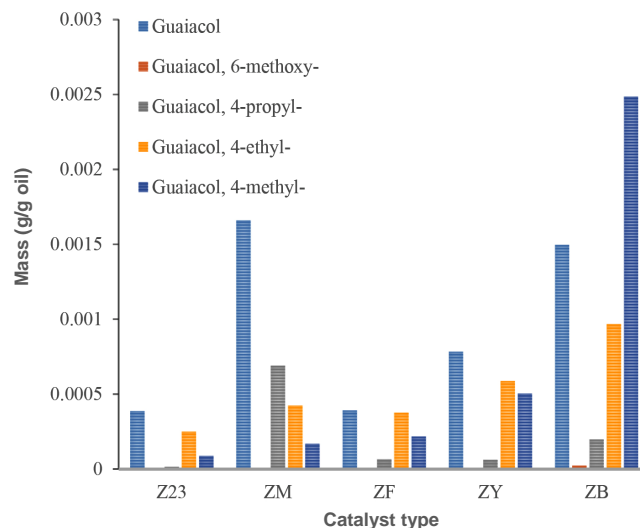


Fig.5. Distribution of guaiacols in the catalyzed bio-oils.

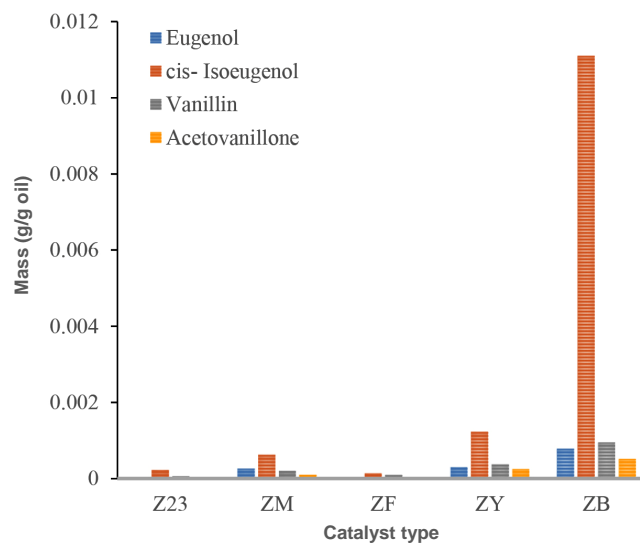


Fig.6. Distribution of eugenols and vanillins in the catalyzed bio-oils.

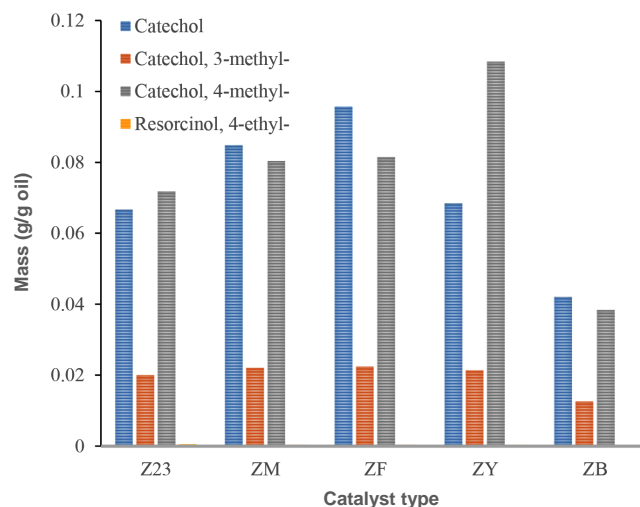


Fig.7. Distribution of diols in the catalyzed bio-oils.

experiments. Guaiacols, eugenols, and vanillins were relatively easier to convert to lighter compounds. Catechols (1,2-diols) were the most dominant compounds present in all the catalyzed bio-oils thereby showing their resistance to the thermocatalytic reactions at the employed reaction conditions (425 °C, WHSV of 12 h⁻¹). ZSM-5 showed the highest activity in the conversion of all the heavy compounds, including diols. The presence of lower amounts of diols in the ZB-catalyzed bio-oil may not be due to the catalyst's efficacy in cracking the diols but due to the lower conversion of guaiacols and eugenols to diols. Though the catalysts ZF and ZM had a similar SiO₂/Al₂O₃ ratio (20) and closely related crystal structures (orthorhombic), ZF exhibited a higher activity in the conversion of guaiacols, eugenols, and vanillins to diols. This could be due to the difference in the pore size distribution (large pores in mordentite vs. medium pores in ferrierite) in the catalysts, which hints that pore size also impacts product distribution.

3.3.1. Catalytic effects on the distribution of phenols

Phenols, due to their applications as value-added chemicals, are the products of high interest from biomass pyrolysis. Formation of phenols may occur through multiple pathways: 1) due to the thermal/pyrolytic breakdown of the phenyl-phenyl bond of 4-hydroxyphenyl fraction of the lignin polymer; 2) hydrogenolysis/cracking reactions, mostly catalytic, involving the cleavage of the aromatic C-C and C-O bond in vanillin or cleavage of the aromatic C-O bond in the guaiacols to produce phenols (Vuori and Bredenberg, 1984); 3) a step-wise approach including the reactions, dehydration of vanillins to guaiacols which further hydrolyze to diols and then the acid catalyzed dehydration of diols to phenols (Samolada et al., 2000). Therefore, the higher the amount of phenols in the upgraded bio-oils, the greater is the ability of the respective catalyst to crack the heavier compounds.

Table 3 shows that the thermal treatment significantly reduced the formation of phenols compared to the catalytic experiments. At the pyrolysis temperature of 450 °C and PBR temperature of 425 °C, phenols could either be converted to hydrocarbons or to carbon residue but not completely to NCG's. This implies that thermal treatment converted most of the lignin compounds including phenols to carbon residue and, to a very low extent, to hydrocarbons and lower molecular weight compounds. Figure 8 clearly shows that among the catalysts, phenols were most predominantly formed using ZSM-5, and others following the order ZM = ZF > ZY > ZB. Formation of phenols decreased with catalyst acidity, and therefore, clearly a function of catalyst's Brønsted acidity.

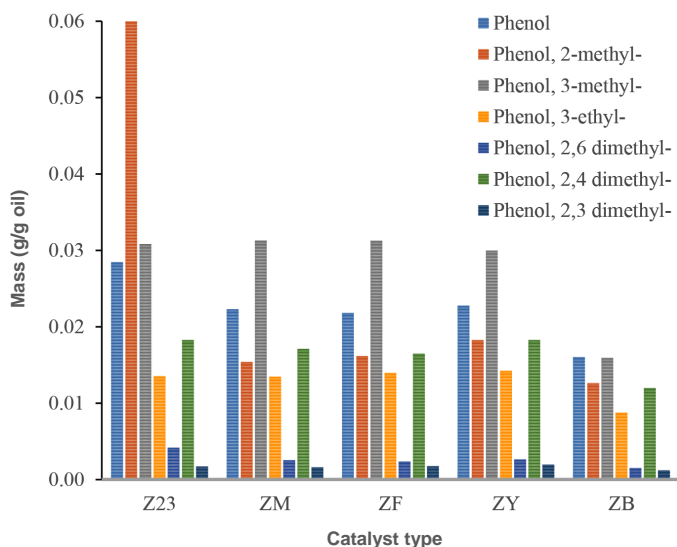


Fig.8. Distribution of phenols in the catalyzed bio-oils.

3.3.2. Catalytic effects on the formation of hydrocarbons

The presence of aromatic hydrocarbons, with toluene and xylene being most common, was noticed in all the catalyzed bio-oils. While all the catalysts deoxygenated the pyrolysis vapors to produce hydrocarbons, the ZSM-5

catalyzed bio-oils showed clear dominance in the number and amount of hydrocarbons formed. The catalytic activity for the formation of hydrocarbons followed the order: ZSM-5 >> ZB > ZY > ZM > ZF.

The higher activity of ZSM-5 catalyst was due to its acidity, pore structure, and activity towards shape-selective hydrocarbon reactions (Sigmund, 1984; Chen and Garwood, 1986; Corma, 1995). The activity of ZB in the formation of aromatic hydrocarbons was next only to ZSM-5. ZM and ZF catalysts, though exhibited higher acidity than the ZY and ZB catalysts and had the pore size distribution similar to ZSM-5, did not show a high activity towards the production of hydrocarbons. This difference in behavior could be due to two reasons: 1) both catalysts had orthorhombic crystal structure, which varied from the crystal structures of the other catalysts; and 2) ZF pore size was smaller compared to the other catalysts, and therefore, diffusion limitations caused the restriction of molecules into the pores for hydrocarbon reactions to occur. In a separate study carried out by Mihalcik et al. (2011) using py/GC-MS, similar trend was observed except that ZY and ZF exhibited similar activity towards the formation of hydrocarbons.

3.4. Chemistry of the cracking activity of Zeolites

Fast pyrolysis of pine wood biomass produces volatile organics, gases, and solid char by homogenous thermal decomposition (free radical mechanisms). The volatile organics undergo dehydration reactions at elevated reaction conditions present in the pyrolysis reactor to produce water and the dehydrated species. The dehydrated species, upon contact with active sites of the catalyst, undergo different reactions depending on the catalyst properties. Predominantly, these reactions involve acid catalyzed oligomerization, isomerization, hydrogenation, dehydration, decarboxylation, and decarbonylation reactions. The resultant products are NCG's (CO, CO₂, H₂, and C₂₊), water, low molecular weight oxygenates, aliphatic and aromatic hydrocarbons, and coke. The product distribution depends on the acidity, pore size, and pore structure of the catalysts.

In case of zeolites, the formation of hydrocarbons generally takes place through carbocation/carbenium ion reaction intermediates (Corma, 1995). The Brønsted acid sites of the zeolites are believed to be the catalytic active sites. The donation of an acidic proton (present at the active reaction site) to the visiting pyrolytic substrate, such as an oxygenated compound or a hydrocarbon, forms a carbocation intermediate. This is followed by the formation of olefins through β-scission process. These olefins undergo oligomerization, cyclization, isomerization, hydrogenation, etc. reactions to form aromatics. In addition, zeolites are known for shape selective catalytic reactions that includes diffusivity, reactant and product shape selectivity, restricted transition state-type selectivity, and molecular traffic control (Sigmund, 1984). The formation of polyaromatics causes catalyst coking, the extent of which depends on the pore size, acidity, and pore structure of the catalyst. The bigger pore diameter of Y zeolites was proved to be responsible for their higher coking activity (Bhatia et al., 1989).

Our results indicated that the hydrocarbon production vastly depended on pore size, pore structure, and acidity of the catalysts. ZSM-5, being the most acidic among the tested catalysts, effectively produced highest yields of aromatic hydrocarbons. ZSM-5 catalysts in H form are widely known for their shape selective catalytic reactions (Rollmann and Walsh, 1979). ZF was least effective in the production of hydrocarbons. Its relatively small pore size might have caused diffusion limitations of reactant molecules to enter the catalyst pores for hydrocarbon reactions to occur. This is supported by the fact that no hydrocarbons with more than one aromatic ring were produced using ZF catalyst (Table 4). The TGA studies carried out herein indicated high coking activity of the ZY catalyst, attributing to its large pore diameter (7.4 Å).

3.5. Catalytic effects on the physical properties of the upgraded bio-oils

3.5.1. Elemental composition

Table 5 shows the elemental composition and the C/H, O/C ratios of the catalyzed bio-oils. Since the hydrogen content of all the catalyzed bio-oils were close to each other (6.9-7.6%), C/H ratio was used to interpret the oil retaining higher carbon content after losing oxygen through catalysis. O/C ratio explains that the oils having the least value contain the least amount

Table 4. Qualitative report (GC peak area %) of the hydrocarbons in the catalyzed bio-oils.

Hydrocarbon	Z23	ZM	ZF	ZY	ZB
Toluene	3.49	1.82	1.78	1.21	1.53
Ethyl Benzene	1.11	-	-	0.29	-
o-Xylene	3.5	-	1.04	1.01	1
p-Xylene	1.29	1.11	-	0.59	0.85
Benzene,1-ethyl-3-methyl	0.97	1.21	1.2	-	-
Benzene,1-ethyl-4-methyl	1.94	-	-	1.18	-
Benzene,1-ethyl-2-methyl	-	-	-	-	1.05
Benzene,1,2,3-trimethyl	2.11	-	-	-	-
Benzene, 2-propenyl	-	-	-	-	-
Benzene, 2-butenyl	-	-	-	-	-
Benzene, 1-me-3-propyl	-	-	-	-	-
Styrene	-	1.01	1.12	-	-
Indane	1.15	-	-	-	-
Indene	0.98	0.78	-	0.45	-
1H-Indene, 1-methyl	-	-	-	-	-
Naphthalene, 1-methyl	2.81	0.82	-	1.3	2.06
Naphthalene, 1-ethyl	1.21	-	-	-	-
Naphthalene, 1,6-dimethyl	2.32	-	-	1.13	1.11
Naphthalene, 2,6-dimethyl	1.15	-	-	0.47	0.92
Anthracene	-	-	-	-	-
Phenanthrene, 1-methyl	-	-	-	-	2.1
Total	24.03	6.75	5.14	7.63	10.62

Table 5. Elemental composition of the un-catalyzed and catalyzed bio-oils.

Catalyst	% C	% H	% N	% O	C/H	O/C	% Ash
Pine wood*	52.64	7.53	0.09	39.52	6.99	0.75	0.197
Blank	52.12	8.81	0.20	38.87	5.92	0.75	-
Z23	69.40	7.23	0.23	23.14	9.60	0.33	-
ZM	64.41	7.36	0.32	27.91	8.75	0.43	-
ZF	64.55	7.19	0.00	28.26	8.98	0.44	-
ZY	62.31	7.03	0.00	30.66	8.86	0.49	-
ZB	63.06	7.60	0.25	29.09	8.30	0.46	-

* Taken from Ingram et al. (2008), whose study also employed the same pine wood feedstock used in this work.

of oxygen and the highest amount of carbon, thereby having highest heating value.

The product bio-oil from thermal treatment had the least amount of carbon (52%) and highest amount of oxygen (39%), showing that this method resulted in loss of carbon in the form of carbon residue and gases like CO. This conclusion was also supported by two other observations: 1) GC-MS data showed the elimination of most of the chemical compounds; and 2) loss of carbon in the form of CO₂ would have resulted in decreased amount of oxygen content in the bio-oil. Among the tested catalysts, ZSM-5 was most effective in decreasing the oxygen content of the pine wood pyrolysis vapor. Raw bio-oil has an oxygen content of 40-45% (Mohan et al., 2006), whereas the ZSM-5-catalyzed bio-oil, despite having 7.4% dissolved water, had only 23% oxygen content (O/C=0.33) while possessing 70% carbon. The ZSM-5-catalyzed bio-oil also had the highest C/H ratio and the least O/C ratio, indicating that this bio-oil possessed the highest heating value. This data, along with GC-MS characterization results, proved that ZSM-5 was the most

effective catalyst in catalyzing the pyrolysis vapors to partially deoxygenated liquid fuel. The C/H and O/C ratios showed that ZM and ZF performed similar whereas ZB (29%) fared slightly better than ZY (30.66%) in reducing the oxygen content. These results are strong evidence that the SiO₂/Al₂O₃ ratio and therefore, catalyst acidity strongly influence the cracking of pyrolysis vapors.

3.5.2. Water content, density, viscosity, acid value, and pH

The catalyzed bio-oils had varied amounts of dissolved water ranging from 7.4% (ZSM-5) to 14.7% (ZB). The product bio-oil from thermal treatment had the highest amount of water content, i.e. 15.6 %, showing that thermal treatment promotes secondary cracking (condensation) reactions. Increases in polarity of bio-oil could also favor the presence of dissolved water. From Table 6, it could be noticed that the acid values and the water contents of the catalyzed bio-oils were linear to each other.

Table 6. Physical properties of the un-catalyzed and catalyzed bio-oils.

Catalyst	Water content (%)	Acid value	pH	Density (g/ml)	Viscosity (Pa-S)
Blank	15.69	30.12	3.85	1.01	-
Z23	7.37	34.95	3.35	1.08	12.56
ZM	13.19	50.40	3.01	1.10	17.92
ZF	11.43	46.38	3.21	1.10	19.50
ZY	12.36	47.41	2.78	1.13	22.28
ZB	14.67	51.50	2.86	1.12	27.82

The ZSM-5-catalyzed bio-oil had the lowest acid value, among the catalyzed bio-oils, showing that ZSM-5 decreased the polarity of bio-oil and therefore, the amount of bound water. Decreases in catalyst acidity should reduce condensation reactions and therefore, the amount of water content. But, the bio-oils from less acidic ZY- and ZB-catalyzed reactions had more water contents. This might be either due to the higher polarity of the respective bio-oils or due to the domination of thermocatalytic reactions (higher secondary cracking) over catalytic reactions. The viscosities of the catalyzed bio-oils were found to be a true function of catalyst acidity. The ZSM-5-catalyzed bio-oil had the lowest viscosity while the ZB-catalyzed bio-oil, despite having high water content, possessed the highest viscosity. It is to be noted that the ZB-catalyzed bio-oil had the highest amounts of heavy compounds such as guaiacols, and the least amounts of phenols (Figs. 4 and 8). In regard to the densities of the catalyzed bio-oils, a close similarity was observed. The bio-oil with least density was obtained from thermal treatment (1.01), which was quite obvious as thermal treatment eliminated or converted the heavy compounds of bio-oil fraction to NCG's or carbon residue. The densities of the catalyzed bio-oils followed the same pattern as the viscosities. The densities and viscosities of the ZM and ZF catalyzed bio-oils were almost similar.

3.6. Distribution of gas products

The catalytic treatment of pine wood pyrolysis vapors resulted in significant production of gases (up to 49% using ZSM-5 catalyst) at the expense of liquid products. In general, fast pyrolysis of biomass results in ~15% non-condensable gases (Mohan et al., 2006; Bulushev and Ross, 2011). This significant enhancement in the yields of NCG's was due to a collective set of reactions such as secondary cracking of pyrolysis vapors, catalytic cracking, and increased residence time due to the presence of a catalyst bed. Various studies have also shown that catalytic treatment enhances the yields of NCG's (Samolada et al., 2000; Adam et al., 2005; Park et al., 2007; Pütün et al., 2009; Park et al., 2010). In addition, our experiments were performed at a low WHSV (12 h⁻¹), which could increase the production of non-condensable gases by promoting secondary cracking reactions.

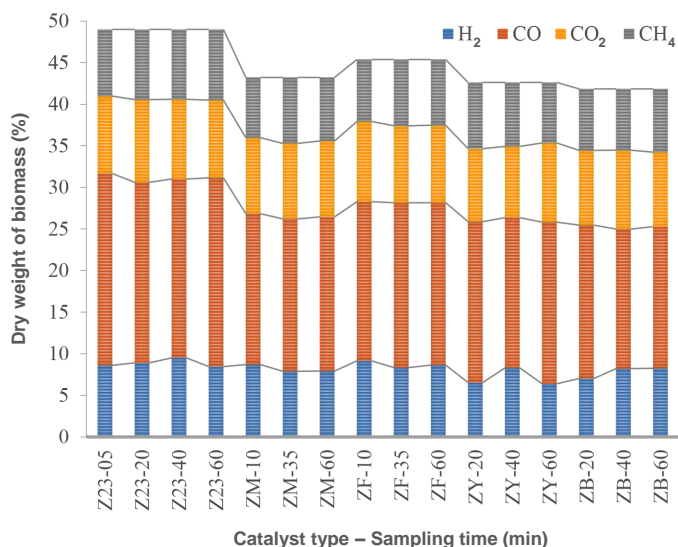


Fig.9. Yields of non-condensable gases from catalytic treatment of pine wood fast pyrolysis vapors.

Gas sampling was performed at different reaction times on stream (at 5, 20, 40, and 60 min for ZSM-5; at 10, 35, and 60 min for ZM and ZF; at 20, 40, and 60 min for ZY, ZB) to study the effect of run time on catalyst activity. Analyses was performed using a GC equipped with FID and TCD detectors. The major components of the gas fraction were CO, CO₂, CH₄, and H₂ along with minor quantities of C₂₊ hydrocarbons. Since the detectors were not calibrated for the C₂₊ gaseous hydrocarbons, no quantitative results of hydrocarbons apart from methane could be presented. Figures 9 and 10 shows the conversion of starting feed material to respective gas components and the quantitative compositions of the gas samples.

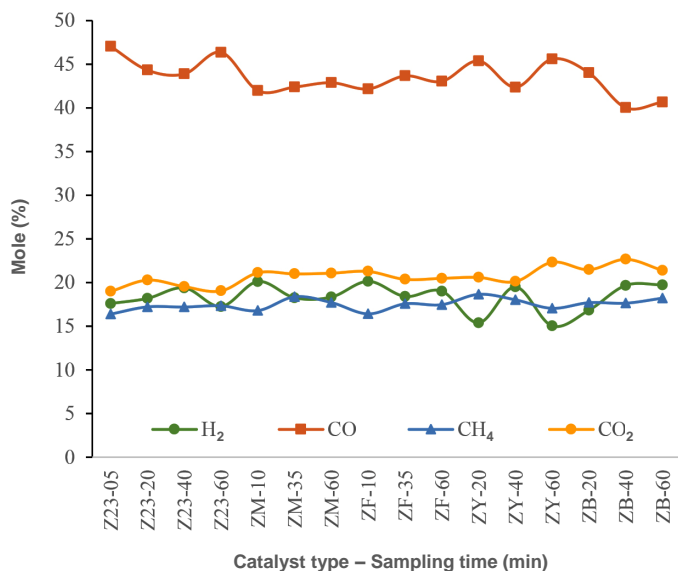


Fig.10. Compositions (mole%) of the gas samples.

The main route for deoxygenation of pyrolysis vapors, *via* gaseous products, was through the elimination of oxygen in the form of carbon monoxide (CO). The ZSM-5-catalyzed experiments showed highest amounts of CO in the gas fractions. This observation can be supported by the presence of least amount of anhydrosugars, furan compounds, and cyclopentenones in the ZSM-5-catalyzed bio-oils. No specific trend was observed with regard to the effect of run-time on the evolution of NCGs. The gas compositions of the samples collected at different run times remained almost uniform. This implies that the

evolution of NCGs primarily occurred through the homogenous thermal decomposition (primary pyrolysis) reactions and the secondary cracking of the pyrolysis vapors.

3.7. Thermogravimetric analysis (TGA)

A TGA-50 Shimadzu instrument was used to perform the TG analysis. A required amount of catalyst was placed on an alumina pan and the temperature was ramped from room temperature to 1000 °C (at 5 °C/min) under air flow of 30 mL/min. The amount of residual carbon on the catalyst was quantified by calculating the difference between the initial and final weight (total weight loss) of catalyst.

Figure 11 shows that weight loss (by the decomposition of residual compounds from catalysts' surface) occurred between 425-670 °C for all catalysts except for ZM and ZF catalysts. Weight loss occurred between 500-670 °C and 500-750 °C for ZF and ZM, respectively. High temperature regeneration of ZM indicated the deposition of high-boiling point compounds on the catalysts surface/within the pores. The weight loss of the used catalysts followed the order: ZY > ZSM-5 > ZB > ZM > ZF.

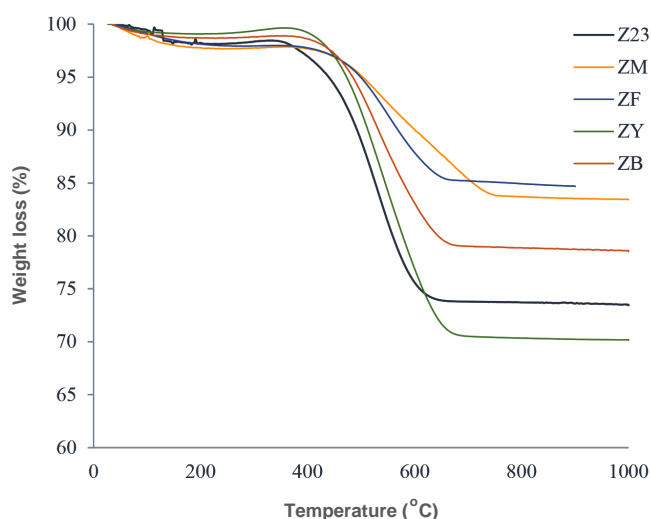


Fig.11. TGA of the used catalysts.

Maximum weight loss was noticed with ZY catalyst. Presence of large pore diameter (7.4 Å), which favors the formation of coke precursors like polyaromatic hydrocarbons (PAH's), and large surface area (730 m²/g) could be attributed to ZY high coking activity. Previous studies also proved that, while rapid coking (deactivation) occurs in large-pored zeolites due to minimal steric constraints, medium-pore zeolites inhibit coking reactions and slowly deactivate in hydrocarbon reactions (Chen and Garwood, 1986). The maximum weight loss next to ZY was noticed with ZSM-5 catalyst. High acidity and the shape selective hydrocarbon reactions (Sigmund, 1984) favored the deposition of carbon residue both on the surface and within the pores of ZSM-5 catalyst (Rollmann and Walsh, 1979). Following ZSM-5, ZB showed the next highest weight loss. High surface area (680 m²/g), large pore diameter (0.62 nm), and high activity for the formation of hydrocarbons (next to ZSM-5 catalyst – Table 4) could be the reasons for coking of the ZB catalyst. ZF and ZM catalysts, though more acidic than ZY and ZB, exhibited lower coking activities. Their low surface areas (400 m²/g for ZF and 500 m²/g for ZM) and small-sized pores could have restricted the formation of coke precursors (PAH's). ZF, having the lowest surface area (400 m²/g) and smallest diameter pores (0.39 – 0.51 nm), showed the least coking activity. TG characterization of the used catalysts showed that the catalyst coking depended on acidity, pore size, and the surface area of the catalysts. Pore structure also plays a huge role in catalyst coking (Bhatia et al., 1989).

4. Conclusions

Zeolites were successfully employed for the deoxygenation of pinewood fast pyrolysis vapors. The catalysis of pyrolytic vapors decreased bio-oil yields and increased gas yields. Among the tested catalysts, ZSM-5, due to the presence of high density of Brønsted acid sites, was most efficient in producing partially deoxygenated liquid rich in aromatic hydrocarbons. Compared to uncatalyzed bio-oil, catalysis decreased oxygen content of bio-oil by approximately 50%; the acid values and viscosities were also significantly reduced. Deoxygenation of pyrolytic vapors mainly occurred through decarbonylation, decarboxylation, and dehydration reactions. The activity of catalysts in the formation of aromatic hydrocarbons followed the order ZSM-5 > ZB > ZY > ZM > ZF. Catalyst properties such as pore size, pore structure, and Brønsted acidity were crucial in determining the end product selectivity. The spent catalysts could be regenerated completely at 700 °C.

The drawbacks of the results obtained in the present study were low liquid yields and low selectivity towards aliphatic and aromatic hydrocarbons. Further catalytic studies by varying the process variables like WHSV and temperature would provide more data, and therefore, better understanding to optimize the catalytic pyrolysis process.

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