



## Catalytic upgrading of bio-oil from bagasse: Thermogravimetric analysis and fixed bed pyrolysis

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### ABSTRACT

The objective of this work was to upgrade bio-oil from bagasse by pyrolysis using catalyst/biomass of three different compositions (5, 15 and 20 wt% HZSM-5 loadings). The thermal analysis and product distribution experiments were carried out in a thermogravimetric analyzer (TGA) and a fixed bed reactor, respectively. In TGA, the pyrolysis of catalytic runs shifted the thermograph curves to the lower temperatures and generated high yield residues compared to that obtained from non-catalytic run. From a fixed-bed condition, the maximum bio-oil yield from non-catalytic and catalytic runs at a temperature of 500 °C at 15% ZSM-5 catalyst concentration were 49.4% and 21.1 wt% respectively. Aromatics, phenols and oleic acids are the main chemical components deduced from gas chromatography/mass spectrometry (GC–MS) analysis of the bio-oil. Bio-oil from catalytic pyrolysis had more aromatics (desirable component) and less oleic acid (undesirable component) than the bio-oil from non-catalytic pyrolysis. The study of bio-oil from catalytic bagasse pyrolysis enhances desirable component when used as transportation fuel. Besides addition of catalyst improving the degradation mechanism of biomass also alters the product composition closer to the aromatic range hydrocarbon.

### 1. Introduction

The depleting fossil deposits and consequent rise in the price of petroleum produced coupled with the attendant environmental challenges and the drive for serene environment have stimulated the search for alternative and renewable energy source. Currently, biomass constitutes about 14% of the global energy consumption and known to be fourth largest source of energy after coal, natural gas and petroleum oil (Bridgwater et al., 1996). Biomass is predominantly composed of cellulose, hemicellulose, and lignin as a non-food material. Other compositions of biomass include organic compound (extractive), ash, inorganic compound and hetero-atom (oxygen, hydrogen, sulfur and nitrogen). Although the oxygen and hydrogen contents of biomass are higher than that found in fossil, its low contents of nitrogen and sulfur make them relatively benign and safe to handle. The benign energy resource from biomass via various conversion processes is an epitome of solid (char), liquid (bio-oil) and gaseous fuels, as well as value added chemicals (Garba et al., 2006).

Thermochemical conversion of biomass can be carried out via combustion, gasification, carbonization, liquefaction and pyrolysis

(Diebold, 2000). Among the thermochemical conversion routes, pyrolysis is the core reaction for the production of bio-oil, char and gaseous product. Pyrolytic decomposition is closely associated to various reactor types, pyrolysis conditions and fuel types. For the case of reactor types, pyrolysis can be study on both micro-scale (TGA) and macro-scale reactors (furnace – fixed bed, packed bed etc). Each of these reactor-scale has its advantage and disadvantage. Although TGA offer the advantage of not being limited by heat transfer because of its very small mass (~10 mg), the gases evolved were limited to carry out any quantitative analysis (Garba et al., 2016; Garba et al., 2018). Macro-scale experiments has disadvantage of heat transfer as a limiting factor, however, higher biomass mass loading evolved more gases so that meaningful quantitative analysis can be carry out. Pyrolysis conditions such as temperature and heating rate influence the distribution and composition of char, bio-oil and gas. The char obtained is high in calorific value and can be used in the production biomass briquettes. Bio-oil is a free-flowing, highly oxygenated, dark brown organic liquid fuel which can be used in furnace and boilers. It can also be used as a feedstock in the production of value added chemicals while the gaseous products can be harnessed for the production of biogas, producer gas

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and substitute natural gas (Zuo et al., 2012; Yang et al., 2006).

Bio-oil can be used as a fuel in heating boilers, slow-speed diesel engines and gas turbines. The major obstacles militating against direct use of bio-oil as a fuel is its high oxygen content about 35–40 wt%, owing to oxygen-rich constituents such as water, ketones, acids, phenols, aldehydes and sugar derivatives. These constituents make bio-oil to have low heating value, high viscosity, and corrosiveness and low oxidation stability. In this manner, it is hard to utilize bio-oils directly as a transportation fuel. Therefore emphasis is laid in the elimination of oxygen in order to improve the quality of bio-oil (Karimi et al., 2014). Catalytic biomass pyrolysis has been employed as a means of upgrading the quality of the bio-oil. Catalyst is utilized to selectively alter the product yields, thereby affecting the physical and chemical properties of the bio-oil (Babich et al., 2011).

Many catalysts such as mesoporous materials, metal oxides and zeolites were used for biomass pyrolysis application. Among these catalysts, zeolites have been used successfully for the conversion of biomass oxygenates via deoxygenation to aromatic. ZSM-5 has high efficacy for reducing biomass-derived oxygenates and enhancing aromatic formation because of their acid sites, pore size, shape selectivity and high surface area (Vichaphund et al., 2014).

TGA and Fixed bed reactor are the most commonly applied pyrolysis technology for thermal study of biomass (Williams & Nugranad, 2000). The product yield and distribution of different biomass such as rice husk (Paul and Nittaya, 2000), industrial sugarcane bagasse (Tsai et al., 2006; Asadullah et al., 2007), coconut shell (Tsai et al., 2006), empty fruit punch (Auta et al., 2014), *Jatropha curcas* shells (Prasanta et al., 2015) and Karanja seed (Shadangi and Mohanty, 2014) were deeply investigated in fixed-bed reactors. The upgrading of bio-oil from fixed bed catalytic pyrolysis of different kind of biomass and catalyst such as wood and HZSM-5 (Sharypov et al., 2002), *Laminaria japonica* over hierarchical meso-MFI zeolite (Meso-MFI) (Wang et al., 2011), bagasse and HZSM-5 (Foster et al., 2012), corn stalk and HZSM-5 (Gayubo et al., 2004), wheat straws and solid acid catalyst (Iliopoulou et al., 2012) were intensely studied. Similarly, the thermal behavior of biomass and biomass/catalyst under TGA has rarely been investigated (Zhang et al., 2016). These studies focused mostly on the maximum bio-oil yield as well devolatilization kinetics, so that the decomposition characteristic and reaction pathways during catalytic pyrolysis process are not much accounted. Precise decomposition pathway will make it possible to understand the efficiency of catalytic and predict the quality of bio-oil. The decomposition pathway of very small mass of biomass/catalyst, has not been investigated with the aim of correlating it to the decomposition characteristics of higher mass loading. This approach could be useful in optimization of industrial processes. Therefore, comparative investigation of pyrolysis behaviors and distribution of pyrolysis products was performed for bagasse in a TGA and a fixed-bed pyrolyzer.

## 2. Experimental device and methods

### 2.1. Materials

The chewing sugarcane bagasse will be used for this study. It is softer and contains more water and less sucrose when compared to industrial sugarcane. This type of variety has the ability to withstanding drought. It constitutes up to 60% of sugarcane available in Nigeria due to its high rate of public consumption (Gana, 2011). Consequently, resulting in the generation of large quantity of bagasse as waste on a number of streets in Nigerian cities. In Nigeria, It has been reported that over 1,412,070 tonnes sugarcane bagasse is generated annually (F.A.O., 1999). Although some reports have been documented on the production of bio-oil from industrial sugarcane bagasse (Tsai et al., 2006; Asadullah et al., 2007). No such reports have appeared on chewing sugarcane bagasse despite in relative abundance.

The bagasse used as feedstock for this study was obtained locally from Minna, Nigeria. The bagasse was dried at 105°C for 2 h and then

sieved to a particle size less than 0.3 mm. This particle size has been demonstrated to be suitable for preventing the effects of heat and mass transfer during the experiments. A commercial grade Zeolite with a ratio  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  of 80 and surface area of  $425 \text{ m}^2/\text{g}$  was obtained from Zeolyst international used in this study. A known amount of 100 g of ZSM-5 was slowly added to ammonium hydroxide and the mixture was stirred for 20 min and filtered (Garba et al., 2018). The filtered ZSM-5 was dried at 105 °C for 3 h and calcined at 500 °C for 1 h in a muffle furnace. The ZSM-5 was sieved to particle size of less than 150  $\mu\text{m}$ . The experiment on the non-catalytic run (NC) and catalyst/biomass of three different compositions (5, 15 and 20 wt% HZSM-5 loadings).

### 2.2. Pyrolysis experiments under TGA

The thermogravimetric analysis (TGA) was used to conduct proximate analysis of the bagasse with the aid of Paris analyzer (Perkin Elmer STA6000). The analysis was carried out by heating 5 mg bagasse to a temperature of 900 °C at the heating rate of 10 °C/min under nitrogen inert atmosphere (20 mL/min). The moisture content, volatile matter and ash of the bagasse were extracted from the TGA curve. The TGA on the catalyst/biomass of three different compositions (0.05C, 0.15C and 0.20C of HZSM-5 loadings).

### 2.3. Pyrolysis experiment under fixed-bed reactor

The experiment under fixed-bed reactor used in this investigation allows the pyrolysis of higher loading of biomass compared to TGA. Combining TGA and fixed-bed reactor allows a complete and systematic investigation of pyrolysis process. Briefly, the experiments were performed in fixed-bed reactor under the flow of nitrogen (as a sweeping gas) is shown in Fig. 1. The fixed-bed reactor was made up of a nitrogen steel cylinder, reactor, rotameter and condensation collection unit. The steel cylinder contain nitrogen which was used to supply inert gas into the reactor. The reactor was made up of a glass tube pyrolyzer and horizontal clamp furnace. Detailed of the reactor configuration can be find in Garba et al. (2017).

The reactor outlet was connected by a steel tube to a round bottom flask which served as the condensing phase (bio-oil) collector. The reactor was inertly maintained by a continuous flow of nitrogen gas at 40 mL/min. Before pyrolysis, bagasse was grinded and sieved with 100  $\mu\text{m}$  mesh size. 10 g of the sieved bagasse was loaded into the reactor and the resultant bio-oil and char was weighed. Effect of temperature on the bagasse pyrolysis was varied from the temperature of 400–600 °C at the interval of 100 °C for 10 min. The experiment was repeated in the presence of catalyst at 500 °C. The condense phase (bio-oil) product was collected in the round bottom flask under the temperature 5 °C in an ice bath. In the case of catalytic pyrolysis, 5 wt% catalyst (H-ZSM-5) was physically mixed with 10 g of sieved bagasse before introducing into the reactor. The procedure was repeated with 10 wt% and 15 wt% catalyst with 10 g of dried bagasse. The experiments were performed in duplicate to ensure that the reactions is reproducible and stable. The products (bio-oil, char and gas) obtained from catalytic and non-catalytic pyrolysis were determined in terms of

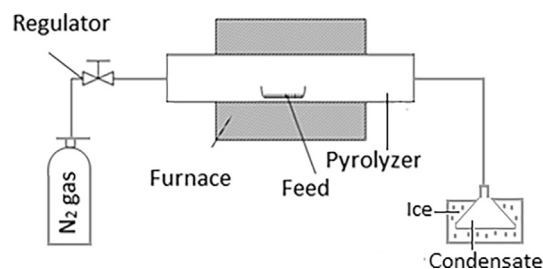


Fig. 1. Schematic diagram of the experiment set-up.

weight percent: the char yield–ratio of char product (g) to the initial bagasse feed (g); bio-oil yield –ratio of bio-oil product (g) to the initial bagasse feed (g); the gas yield–ratio of difference between initial bagasse feed (g) and total yield of bio-oil and char to initial bagasse feed (g). After the pyrolysis experiment, the bio-oil obtained were analyzed using gas chromatograph–mass spectrometry (GC–MS) analysis.

#### 2.4. Chemical composition of the bio-oil

Detail analysis of the chemical composition of the bio-oil analysis was conducted with GC–MS analyzer (Perkin Elmer Clarus 600) equipped with a capillary column (30 mm × 0.25 mm × 0.25 μm) and mass selectivity detector. The peaks GC were identified by comparing with National Institute of Standards and Technology (NIST) standard.

### 3. Results and discussion

#### 3.1. Pyrolysis characteristics under TGA

The TGA of non-catalytic run at 10 (°C/ min<sup>−1</sup>) bagasse was carried out between room temperature and 900 °C under nitrogen atmosphere for non-catalytic run (NC) and catalytic runs of three different compositions of catalyst/biomass (0.05C, 0.10C and 0.15C of HZSM-5 loadings). The thermal decomposition was observed to be divided into three distinct stages: moisture removal, main devolatilisation and slight devolatilisation as shown in Fig. 2a and b. The first weight loss in the TG curve was observed at temperature above 100 °C in Fig. 2a. This was attributed to vaporization of inherent moisture contained in the bagasse. The second stage is usually the main devolatilisation (between 167 and 407 °C) in pyrolysis where volatile materials derived from hemicellulose and cellulose were essentially converted to bio-oil (Lim and Andresen, 2011; Uzun et al., 2009). The second stage of mass loss showed in Fig. 2a corresponds to the degradation of lignocellulosic components (hemicelluloses, cellulose and lignin). Hemicelluloses commonly degrade between 160 and 240 °C, whereas cellulose decomposes at the higher temperature between 257 and 360 °C. The decomposition of lignin occurs slowly over a wide temperature range of 160–627 °C. Finally, in the last stage (> 407 °C), a minor weight loss is observed beyond 407 °C. The total residue remaining (composing of char, coke and ash) at the final temperature of 877 °C is 21.3% and 27.6% for non-catalytic and catalytic run (5%) of bagasse samples, respectively. Total residues from catalytic runs are comparatively lower than that obtain from to non-catalytic run. Higher catalyst loadings resulted in decomposition at lower temperatures which implies longer residence times and less energy in the TGA. Zhang et al. (2016) have pointed out that that less energy is needed to decompose the biomass under the influence of catalyst, since the thermograph curves of catalyzed biomass shifted to lower temperatures compared to the curves of uncatalyzed biomass. Longer residence time might aggravate chars formation by cracking, dehydration, decarbonylation, and

decarboxylation during the degradation reactions. The increment is mainly attributed to the coke formation on the catalyst which actually is the obstacle militating against the effectiveness of the catalytic process. The course of catalytic degradation and product composition were reported in many articles (Sharypov et al., 2002; Iliopoulou et al., 2012).

The DTG curve in Fig. 2b shows the temperature where the maximum rate of decomposition occurred through the peak positions in the curve. The minor change in TG curve is magnified by DTG curves. The DTG in Fig. 2a magnifies large differences in their decomposition behavior of catalytic runs as compared to non-catalytic run. In a non-catalytic run, heat transfer material is generally assumed to be passive and biomass transformation to ketones, furans and phenols is accompany with intermediate oxygenates. It is not the case with catalytic run where the inert environment is substituted with a solid catalyst with pores. Catalytic process allows these intermediates to diffuse into it pores to form both monocyclic aromatics and olefins through a series of dehydroaction, decarboxylation, oligomerization and decarboxylation reactions. However, as aromatics were being formed, other competing reactions also lead to the coke formation from the polymerization of other intermediate oxygenates (such as furans) from hydrocarbon pool. As these reaction competes, aromatics selectivity is inhibited and catalyst deactivation is promoted.

#### 3.2. Characteristics of pyrolysis in a fixed bed reactor

The pyrolysis temperature of bagasse was varied from 400 to 600 °C to evaluate the effect of temperature on products yield from the bagasse. The effect of product yield on the non-catalytic pyrolysis is presented in Fig. 3. The amount of char exhibited a declining trend with increase in pyrolysis temperature while the gaseous products show a concurrent increase with increase in pyrolysis temperature. At low temperature of 400 °C, (as indicated in the TG profile, Fig. 3) the yield of char was high due to non-cracking of high molecular weight compound. The result of char and gaseous products yields were in accordance with the trend of the previous findings (Abdullah et al., 2010; Sensoz and Angin, 2008; Wang et al., 2010a,b). Secondary cracking of high molecular weight compound often promotes the yield of gaseous product formed due to decomposition of char at higher temperatures (Sukiran et al., 2009). The bio-oil yield was observed to increased from was 38.2% at 400 °C to a maximum yield of 49.4% at 500 °C (This result is consistent with TGA profile) and latter began to decline until it reaches 39.6 wt% at 600 °C. The results revealed that most of the devolatilisation from the biomass evolved at temperatures of about 500 °C. This observation bears close similarity to other biomass materials reported in the literature (Tsai et al., 2006; Asadullah et al., 2007; Putun et al., 1999, Onay et al., 2001, Ates et al., 2004).

Larger primary degradation of biomass feedstock and secondary degradation of bio char as the temperature increased may have enhanced the bio-oil yield (Velghe et al., 2010). At low temperature such

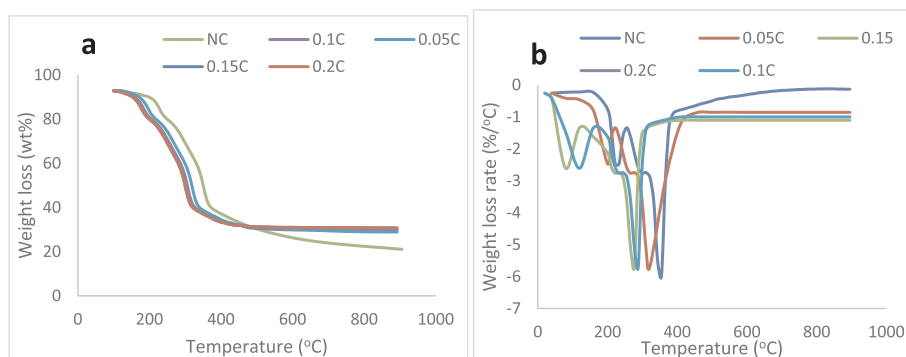


Fig. 2. Thermograph curves ((a) TG and (b) DTG) showing the characteristic of catalytic pyrolysis of bagasse under nitrogen condition.

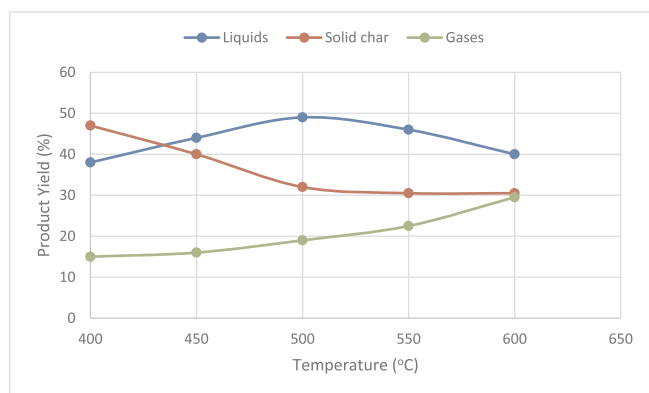


Fig. 3. Effect of temperature on the product yield from non-catalytic biomass pyrolysis.

as 400 °C, where the decomposition of bagasse just started (as shown in the TGA curve, Fig. 2a and b). The gas yield was only 15.3%. At this temperature most of the carbon in the bagasse were not converted to char. However, as the pyrolysis temperature increased carbons were continuously converted to gas product volatile until the highest gas yield of 29.5% was obtained at 600 °C. Fig. 2 shows a declining trend of char as the pyrolysis temperature increased from 400 to 600 °C due to the progressive pyrolysis conversion at the higher temperature.

Furthermore, it is observed that the remaining residue from TGA experiments were higher compared to those obtained from the fixed-bed reactor experiments. Quan et al. (2014) have illustrated that the higher loading in fixed-bed reactor experiments would add to increase the contact time between fuels and their volatiles in such a way accounting for some gas–solid reactions which were excluded under TGA.

### 3.3. Effect of catalyst loading on bio-oil yield from pyrolysis

ZSM-5 was used as catalyst in order to increase the bio-oil yield and upgrade the quality of bio-oil, the ZSM-5 was used as a catalyst. The result of the effect of ZSM-5 concentration (5, 10 and 15 wt%) on bagasse pyrolysis product investigated at constant pyrolysis temperature of 500 °C for 10 min are shown in Fig. 4. As can be seen from Fig. 5, the catalytic effect of ZSM-5 at 5 wt% catalyst was not pronounced as only marginal bio-oil yield was observed. The bio-oil yield in the presence of 5 wt% ZSM-5 reached the maximum value of 49.7% as against 49.2% without the application of ZSM-5. This findings obviously show that the bio-oil oil yield does not show any significant change under 5 wt% catalytic pyrolysis conditions. Further increase in the ZSM-5 concentration to 10 wt% and 15 wt% respectively resulted in a decrease in the bio-oil yield to 41.5% and 21.1% respectively. Similar observation was earlier reported by Onay, (2014) on catalytic pyrolysis of waste tire

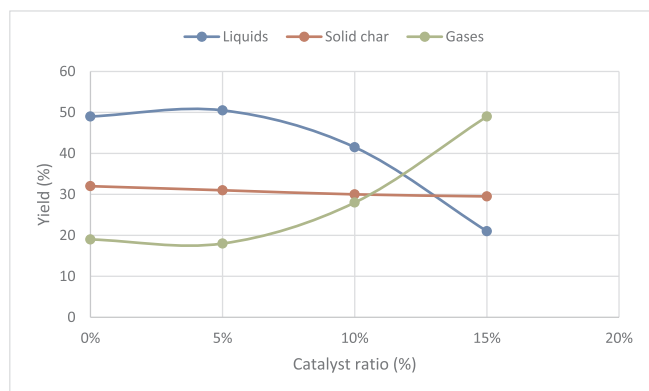


Fig. 4. Effect of ZSM-5 loading on bagasse pyrolysis product yield at 500 °C.

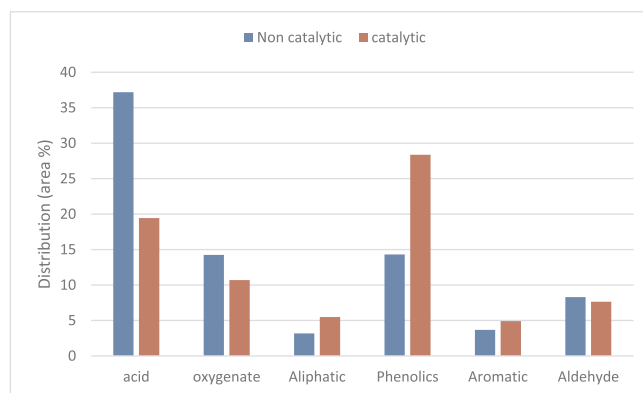


Fig. 5. Product distributions of bio-oil from pyrolysis of chewing sugarcane bagasse by catalytic pyrolysis at 500 °C at 10 wt% catalyst concentration.

and pistachio seed using Criterion 424 as catalyst. According to this authors the influences of catalyst 5 wt% catalyst shows negligible effect on the bio-oil yield while higher catalyst concentration (10–25 wt%) resulted into a remarkably decrease in bio-oil yield. According to Ates et al. (2004) the decrease in bio-oil yield at higher catalyst concentration can be attributed to the secondary cracking of the lignocellulose materials into volatile products. Based on previous research carried out by Foster et al. (2012) and Kim et al. (2015) catalyst produced CO and CO<sub>2</sub> through decarbonylation and decarboxylation reactions.

It can be seen from Fig. 4 that there is no visible change in the char yields with ZSM-5 catalyst addition. While the gaseous product yield increase with increase in ZSM-5 concentration. The lowest gas yield (18.5%) was obtained at a catalyst concentration of 5 wt% and this increase with increase in catalyst concentration until a maximum yield of 49.0% was obtained at a ZSM-5 concentration of 15 wt%.

### 3.4. Gas chromatograph–mass spectrometry (GC–MS) analysis

Retention time and peak area are important criteria for quantitative determination of the composition of the bio-oil from GC–MS analysis. The GC–MS analysis results of the liquid products from non-catalytic and catalytic degradation of sugarcane bagasse are presented in Table 1. The main constituents of non-catalytic pyrolysis is mainly

Table 1  
Percentage (area %) pyrolysis compounds in the bio-oils.

Name of compound	Formula	Peak area (%)	
		Non catalyzed Bio-oil	catalyzed Bio-oil
Hexamethylene oxide	C <sub>6</sub> H <sub>12</sub> O	2.23	4.34
2-Aminopyrimidine-1-oxide	C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O	0.95	1.14
Phenol	C <sub>6</sub> H <sub>6</sub> O	2.93	8.12
4-Methoxy-3-(methoxymethyl)-phenol	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	2.49	4.94
Phenol, 2,6-dimethoxy-	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	6.12	10.38
2-Methoxy-4-ethyl Phenol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	1.07	2.13
1,2-Cyclopentanedione-3-methyl	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	3.92	6.02
Hydroxymethylcyclopentane	C <sub>4</sub> H <sub>8</sub> O	17.01	18.43
Phenol-4-ethyl	C <sub>8</sub> H <sub>10</sub> O	1.70	2.80
4-Methyl-1-Hexanol	C <sub>7</sub> H <sub>16</sub> O	4.37	4.98
1,2-Benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	3.67	4.92
2-Methylphenyl ester	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	2.37	1.74
1,3-Dimethyl ether	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	3.79	2.89
Benzaldehyde	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	3.38	2.30
1,2,3-Trimethoxybenzene	C <sub>9</sub> H <sub>12</sub> O <sub>3</sub>	4.91	5.34
3,4-Dimethylphenyl ether	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	1.77	1.95
1,6-Anhydro-beta-D	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	6.32	4.12
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	37.19	19.44



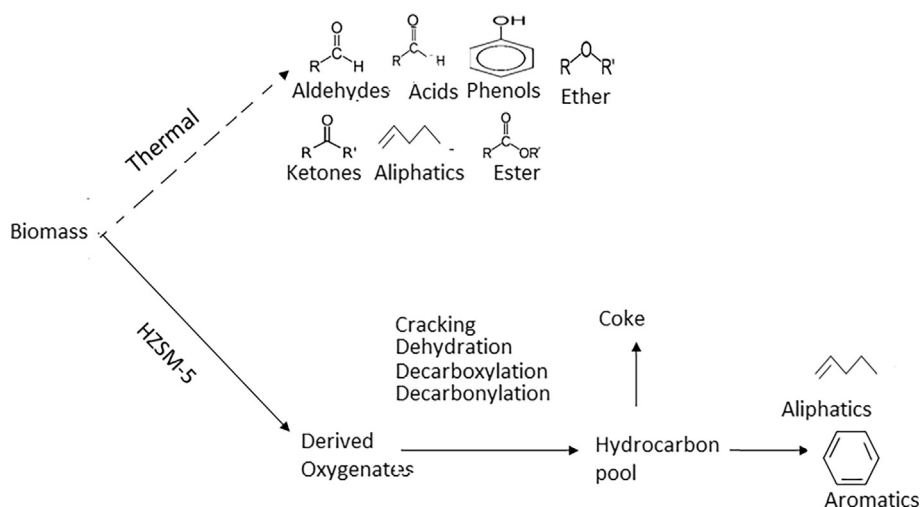


Fig. 6. Proposed reaction pathway for ZSM-5 catalyzed pyrolysis of Sugarcane Bagasse.

composed of phenol and phenolic derivatives (13.21%), aldehyde (10.52%) and oleic acids such as 9-octadecenoic (37.19%). Others include ether (5.56%), ester (2.37%), aliphatic (2.23%) and alcohol (4.37%). These results show that the major compositions from non-catalytic fast pyrolysis were mainly oleic acid and oxygenated compounds (alcohols, esters, aromatics, aliphatic, phenolic and ethers). The findings from this analysis are in accordance with the report of Lee et al. (2011) on the fast pyrolysis of microalgae but differ significantly with the work of Tsai et al. (2006) who reported the non-catalytic pyrolysis of industrial sugarcane bagasse. The observed variation in composition might be probably due to difference in sugarcane varieties, pyrolysis operating conditions. According to Amin et al. (2012) the presence of acids (oleic acids) in bio-oil are known to cause corrosion while the presence of oxygenated compounds such as ether and ester can substantially decrease the heating values of bio-oil. These will eventually lead to poor quality bio-oil (Tsai et al., 2006; Asadullah et al., 2007). On the other hand, aliphatic and aromatic hydrocarbons are desirable compositions of bio-oils as a fuel. This is because the presence of these compounds results in an increase in the higher heating value of the bio-oil. Aldehyde and ketones cause poor storage stability of bio-oil.

In the catalytic pyrolysis of sugarcane bagasse using HZSM-5, the undesirable oleic acids and oxygenated compounds (ether and ester) were significantly reduced to 19.44% and 10.7% respectively as against 37.19% and 14.25% obtained for the non-catalytic pyrolysis while the desirable products such as aliphatic and aromatics increased from 5.48% and 4.92% in the presence of HZSM-5 as shown in Fig. 5. This result is similar to the report by Wang et al. (2010a,b) on the use of HZSM-5 as catalyst for pine wood pyrolysis in a fixed-bed. The observed reduction in acidic groups of the bio-oil can be attributed to the ability of the catalyst to neutralize the carboxylic groups present in the hemicellulose part of the biomass (Wang et al., 2010a,b; Auta et al., 2014). The results show that HZSM-5 catalysts significantly enhanced the conversion of oxygenated compounds into the formation of aromatics and aliphatics respectively. Vichaphund et al. (2014) reported that the volatile oxygenated species usually diffuse into the pores of HZSM-5 and react with the active protons through dehydration, oligomerization, decarbonylation, decarboxylation and dehydrogenation thereby leading to the production of aromatics, carbon dioxide, carbon monoxide and water.

### 3.5. The proposed reaction pathway of catalytic pyrolysis

In general, thermal degradation is the traditional reaction pathway leading to the formation of oxygenated compounds (Paul and Nittaya, 2000; Corma et al., 2007; Abnisa and Daud, 2014). The proposed

reaction pathway for thermal and catalytic pyrolysis of biomass is shown in Fig. 6. The broken lines in the figure represent the non-catalytic reaction pathway which shows the formation of oxygenated products such as oleic acid, aldehydes, alcohols, esters and ethers through non-catalytic pyrolysis as illustrated in Table 1. For the case of catalytic pyrolysis (see Fig. 6), these oxygenates are formed as intermediates which then diffuse into the pores of zeolite catalyst undergoing reactions such as cracking, dehydration, decarbonylation, and decarboxylation to form aromatics and short chain olefins. After the addition of HZSM-5, the traditional reaction mechanisms have been changed as shown by the solid lines in Fig. 6. These changes were elucidated by the shifting of thermograph curves to lower temperatures as the catalyst loadings increased in Fig. 2a and b. However, there are other reactions which compete with the formation of aromatic compounds and short chain olefins according to Liu et al. (2014). These reactions form coke either from intermediate oxygenates in the hydrocarbon pool or through the polymerization of furans which leads to catalyst poisoning and deactivation.

## 4. Conclusion

Proximate, fiber and TGA analyses were evaluated prior to pyrolysis experiment in a fixed bed reactor. The study evaluated the effect of pyrolysis temperature and catalyst loading on the product yield and chemical compositions of bio-oil. The results revealed that bagasse has high volatile matter, low ash, high cellulose and lignin contents which make it a good candidate for quality bio-oil production. The optimum temperature for production of bio-oil from non-catalytic and catalytic pyrolysis was 500°C, respectively. Detailed analyses of the chemical composition reveal the presence of phenols and oleic acids as the components in the bio-oil. Bio-oil from catalyzed pyrolysis had more phenolic and less oleic acid components than the bio-oil from non-catalyzed pyrolysis. The study on bio-oil from catalytic biomass pyrolysis enhances their potential for liquid fuel production.

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