Catalytic Valorisation of Sugarcane Bagasse to Energy Carriers

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Research Article

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Abstract

Sustainable processes have continued to be of interest to both academia and industries. The sugar industry in this regard has explored the potential of using sugar cane bagasse as a fuel within the industry so as to enhance the economics of the process. In addition to its fuel potential, bagasse has the prospects of being converted to chemical compounds that could serve as both raw materials as well as energy carriers. In this work, we investigated the potential of adding value to sugarcane bagasse by catalytic and non-catalytic thermal conversion processes; hydrothermal liquefaction (HTL) and pyrolysis. HZSM-5 was used as a catalyst for both the hydrothermal liquefaction and pyrolysis processes. The HTL operating temperature and heating times were varied between 220–373°C and 30–60 mins respectively while the catalyst type, reactor volume loading and feedstock to water ratio remained fixed. The pyrolysis was carried out at temperatures of 400°C, 450°C and 500°C and the effect of catalyst to biomass (0.1:1 g/g, 0.25:1 g/g and 0.5:1 g/g) on the product yield and distribution was also investigated. The results showed that various compounds were obtained as the hydrothermal conditions were varied. Interestingly, the aliphatic hydrocarbons were relatively lower in concentration when compared to the substituted hydrocarbons. The highest amount of hydrocarbons (a little over 6 wt. %) was obtained when the bagasse was hydrothermally converted using a catalyst at 300°C for 45 minutes. Esters accounted for about 80 wt. % when the process was carried out at 373°C and 45 minutes in the presence of ZSM-5, this is more than double the amount obtained when the same conditions were used in the absence of a catalyst. Findings from this study also revealed that the bio-oil yield was significantly affected by pyrolysis temperature and catalyst to feedstock ratio. A higher yield of pyrolytic bio-oil and higher conversion of sugarcane bagasse was produced with the HZSM-5 catalyst when compared to the non-catalytic pyrolysis process. Aromatization of produced bio-oil was enhanced by the higher catalyst loading during the pyrolysis of sugarcane bagasse.

1. Introduction

Global energy demand has increased significantly as a result of rapid industrialization and urbanization taking place around the world. Although non-renewable fossil energy sources and other conventional energy sources are rapidly becoming exhausted, statistics show that there is still a significant dependence on these non-renewable energy sources to fulfil global energy utilization requirements (Fatima et al., 2021; Ben Jebli & Kahia, 2020). Access to these resources may be costly, and challenging owing to shortages, or fraught with ecological dangers. As a result of environmental concerns and the growing demand for clean energy around the world, renewable energy has received much interest lately. The continuous widening gap between energy supply and demand coupled with the negative environmental effect of fossil fuel utilization has necessitated the need for new alternative energy sources (Deora et al., 2022; Anekwe et al., 2021). Consequently, there is a considerable focus on the generation of energy from low-cost, sustainable, and eco-friendly sources.

Biomass is one of the most potent organic feedstocks. Biomass has a plentiful supply, low prices, a renewable nature, and lower nitrogen and sulfur components than other fuels. Biomass is a feedstock
that can come from a variety of sources, including agriculture, forests, and energy crops (Saxena et al. 2009), and is one of the many renewable energy solutions available. Non-edible plant waste is generated in large quantities each year (with the majority of it being disposed of) (Sanderson 2011). Due to its low pollution emissions, biomass is widely identified as a significant sustainable energy source. World sugar cane production is around 540 million tons per year, with an estimated 280 kg of bagasse obtained for every 1000 kg of sugar cane processed (Ahmed et al. 2018). Sugarcane bagasse can be transformed into a variety of fuels, such as solid fuels (bio-char or hydrochar), liquid fuels, and gaseous fuels (H\textsubscript{2} and CH\textsubscript{4}) (Demirbas 2008). Research is ongoing to explore potential technologies for the conversion of the underutilized sugarcane bagasse biomass into transportable, high-energy-density liquid fuels. However, there is still much work to be done in this area (Pexa et al. 2016; Zhang et al. 2016; Yamada et al. 2017).

The synthesis of biofuels and chemicals from biomass (agricultural waste) can be accomplished by thermochemical technologies including pyrolysis and liquefaction (Chumpoo and Prasassarakich 2010), which are currently being investigated. Pyrolysis and hydrothermal liquefaction (HTL) as biomass transformation technologies can convert biomass into liquid energy carriers and chemicals. An increased operational temperature (673–873 K), without an O\textsubscript{2} source and biomass with low moisture (< 10%) are all required for pyrolysis. Aside from that, low heat value and low quality of produced bio-oils are limitations of the pyrolysis technique (Li, Li, et al. 2015), and as a result, hydrothermal liquefaction is favoured over pyrolysis. However, HTL is performed at fairly mild temperatures (523–673 K) and increased pressures (50–300 bar) in various solvents. Indeed, the type of solvent used during liquefaction has a significant impact on total transformation and the characteristics of the produced bio-oil, product yield and distribution (Aysu and Durak 2015; Huang and Yuan 2015). The HTL technique entails thermal depolymerization in H\textsubscript{2}O or an organic medium, with or without a catalyst. When compared to pyrolysis (at greater temperatures but mild pressures), the liquefaction process has the fundamental benefit of being able to process wet biomass thereby reducing the need for the initial drying expenditures (Cao et al. 2020; Kumar 2013). In addition, the working conditions utilized in HTL enable the generation of hydroxyl and hydrogen ions, which aid in the scission of biomass bonds and the conversion of desired products to their respective forms.

Several research has been carried out to study the viability of pyrolysis as a method of utilizing sugarcane bagasse. In the study on the pyrolysis of sugarcane bagasse, Varma and Mondal (2017) examined the impact of operational conditions on yield and product qualities. The highest yield (45.2%) of bio-oil was found at 723 K at a heating rate of 323 K/min. The bio-oil produced contained a complex variety of components including alcohols, acids, aldehydes, furan, phenols, and aromatics. Sohaib et al. (2017) studied the impact of pyrolysis parameters on the output and product characterisation. It has been demonstrated that the highest bio-oil output (60.4%) can be produced at 500°C. At 600 °C, the maximum calorific values for both biochar and bio-oil were 27.8 MJ/kg and 24.7 MJ/kg respectively. Moreover, several laboratory-scale investigations on the liquefaction of sugar cane bagasse (SCB) have been carried out. The HTL of SCB in the presence of supercritical ethanol solvent was carried out utilizing FeS, Fe\textsubscript{2}S\textsubscript{3}/AC, and FeSO\textsubscript{4} catalysts at temperatures ranging from 522 to 603 K (Chumpoo and
By using a FeSO$_4$ catalyst, the highest bio-oil output of 60% and biomass transformation of 90% were recorded with pure ethanol, 603 K, and 49.3 bar of H$_2$, which raised to 74% and 100%, accordingly, when the FeSO$_4$ catalyst was used. This show that the introduction of catalyst tends to facilitate the biomass degradation process for an increased yield. The catalytic HTL of SCB was described in another study, which used twelve (12) solid catalysts. Among the catalyst investigated, Fe-CoO produced the maximum yield of bio-oil (58%) while emitting the least amount of oxygen (11%) (Govindasamy et al. 2019).

Zeolite catalyst has been recognized as a desirable catalyst for biomass transformation due to its tunable acidity, shape-selective microporous structure, and large surface area, all of which make it an excellent choice. The introduction of a zeolite catalyst in the pyrolysis process has been shown to lower the quantity of O$_2$ in the bio-oil while increasing yield (Balan 2014; Bridgwater 2003). Yan et al. (2018) studied the effects of incorporating ZSM-5 into sugarcane HTL bagasse. The highest bio-oil output (35.40%) was produced at a temperature of 285.0°C without the use of a catalyst. However, with the use of catalyst ZSM-5, bio-crude synthesis was boosted while decreasing acidic components (Yan et al. 2018). Owing to the viability of SCB, this biomass type appears to be a viable feedstock alternative because of its current underutilization, availability, and properties (Miranda et al. 2021). However, sugarcane bagasse properties, operating conditions and type of conversion processes employed may influence the product yield, distribution and subsequent applications as fuels and chemicals. Hence, this study aims to employ different thermal conversion processes (Pyrolysis and HTL) for the synthesis of fuels and other chemical products from sugarcane bagasse. The effect of varying operating conditions and the use of catalyst on product yield and distribution for both pyrolysis and hydrothermal liquefaction process was studied.

2. Materials And Methods

2.1. Materials

Sugarcane bagasse (SCB) was collected from the South African Sugar Mill, KwaZulu Natal, South Africa. The SCB was dried at 45 °C until constant weight. Before its application in the thermochemical conversion processes, the air-dried bagasse was milled to reduce the size to 2.0 mm. The powdered form of ammonium ZSM-5 zeolite (Si/Al of 50:1) was obtained from Zeolyst International. Pure N$_2$ gas (99.99%) purchased from Afrox® was employed in this study. All chemicals utilized in this work were of analytical grade.

2.2. Characterization of Sugarcane bagasse

The Scanning Electron Microscope (SEM) using ZEISS Sigma 300 VP equipped with a field emission gun was employed to investigate the morphological framework of the SCB. The ultimate analysis (C, H, N, S, O) was conducted while proximate analysis was used to determine the composition of SCB such as moisture, ash, volatile matter and fixed carbon content.
2.3. Thermochemical Conversion of Bagasse

2.3.1 Pyrolysis of SCB

Pyrolysis of SCB in the presence and absence of HZSM-5 catalyst was conducted using a fixed bed reactor (Fig. 1). The pyrolysis experiments were carried out using a stainless-steel reactor of dimension length (L = 450 mm), inner diameter (ID = 10.6 mm) and outer diameter (OD = 12.7 mm). The heat source was provided by the electric furnace and K-type thermocouple was placed inside the reactor to measure the reactor temperature. Before pyrolysis runs, the biomass sample was dried overnight at 105 °C. For the non-catalytic pyrolysis tests, 1g each of the dried bagasse samples was charged into the reactor while for the catalytic tests, a mixture of the catalyst with bagasse sample (0.1:1 g/g) was used. The reactor was first purged with nitrogen at a flow rate of 30 ml min⁻¹ for 30 min to remove the air in the system and ensure an inert atmosphere. The pyrolysis tests were performed according to the method described by (Mustapha et al. 2021). The pyrolysis reactor was heated at a rate of 10 °C/min until the temperature attained the required temperature of 400°C, 450°C and 500°C to examine the influence of varying temperatures on product yield and composition. The effect of catalyst to biomass ratio (0.1:1 g/g), (0.25:1 g/g) and (0.5:1 g/g) on the product yield and composition was also investigated at 400°C.

The reactor temperature was held for 60 min while the sweeping gas was allowed to continue to flow. The vapour exiting from the reactor was condensed in the condenser and kept at 0 °C. After cooling, acetone was used to wash the flask and connectors, and then the remaining solids inside the reactor were collected and stored in an airtight container. Thereafter, acetone solvent was evaporated at 40 °C for 12 hrs to recover the bio-oil. The yield of bio-oil and biochar were estimated gravimetrically while the gas plus any other losses were determined by difference (“gas + losses” yield = 100 – (biochar yield + bio-oil yield)). All experiments were repeated twice and the average values were reported.

2.3.2. Liquefaction of SCB

The HTL of SCB experiment was performed using a 70 mL stainless steel bioreactor with approximately 60 mL working volume. The SCB used for this study was pulverized and 5 g of dried bagasse was weighed into the reactor followed by 50 mL of solvent (deionized water) which was fed into the reactor. The experiment was conducted with and without catalyst. The first batch was without catalyst while 0.4 g of HZSM-5 zeolite catalyst was used for the catalytic process while ensuring the reactor was well-sealed to avoid leakage. Then, the furnace was used for heating the reactor to the set temperatures (220, 300 and 373°C) while heating time was varied between 30–60 min to study the influence of varying process parameters on product distribution. At the end of each session, the reactor was cooled to room temperature before collecting the products. The liquid and solid products were recovered by filtering through Whatman filter paper. The solid residue was dried overnight in an oven at 80 °C. Subsequently, the analysis of reaction products was conducted.

2.4 Analysis of Bio-oil
The gas chromatography / mass spectrometer (Agilent 7890-5975C model) was used to analyse the main compounds in the HTL and pyrolytic bio-oils. The GC-MS was done using the procedure earlier reported in our previous study (Mustapha et al. 2021).

3. Results And Discussion

3.1. SCB Characterization

The results of the ultimate and proximate analysis of sugarcane bagasse are presented in Table 1. Figure 2a - c depicts the SEM images of SCB residual solid recovered after catalysed HTL. According to the HTL process, at 220°C, the structure displayed fissures and lignocellulosic portions were freed from the biomass (Fig. 2a) which showed a more intact structure with slight rigidity. When heated at 300°C, residual solid exhibited increased surface cracks and structural disruption (Fig. 2b). After being heated to 373°C, solid residues developed more particles on the surface with fragmented structure and agglomerates than they had been previously (Fig. 2c). However, the uncatalyzed SEM image of Fig. 2d show increased degradation but not to the extent of the catalysed process (Fig. 2c). This solid residue was produced most likely as a result of the minerals that were present during the thermal decomposition process. Temperature and catalyst affect the SCB decomposition as temperature increase results in increased surface degradation which is further enhanced by catalyst (Peng and Wu 2010; Bian et al. 2012).

Table 1
Proximate Analysis (%)

<table>
<thead>
<tr>
<th>Moisture</th>
<th>Ash</th>
<th>Volatile Matter</th>
<th>Fixed Carbon (by difference) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.51</td>
<td>6.79</td>
<td>58.95</td>
<td>14.75</td>
</tr>
</tbody>
</table>

aFixed carbon content (%) = 100% = (%Moisture content + %Ash + %Volatile matter)

Table 2
Ultimate Analysis (%)

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O (by difference) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.07</td>
<td>4.56</td>
<td>1.05</td>
<td>0.00</td>
<td>60.33</td>
</tr>
</tbody>
</table>

bO composition (%) = 100% - (%C + %H + %N + %S)

3.2. Pyrolysis - Results and Discussion

The product yields and conversion from the pyrolysis of sugarcane bagasse are presented in Figs. 3a and 3b respectively. The effect of the addition of HZSM-5 catalyst on the product yield and conversion was investigated at a temperature of 400°C, 450°C and 500°C using 0.1g:1g (catalyst: biomass ratio). Figure 3a shows that pyrolytic bio-oil increased with an increase in temperature from 400°C to 450°C with
or without the addition of the HZSM-5 catalyst. For the non-catalytic process, the bio-oil yield increased from 4.95 wt% to 11.07 wt% as the temperature increased from 400°C to 450 °. However, a further increase in the temperature to 500°C did not result in any significant change in the bio-oil yield. A similar trend was observed with the conversion of sugarcane to bio-oil without the use of HZSM as shown in Fig. 3b. The conversion of sugarcane bagasse increased from 57.9 wt% to 67.6 wt% as the temperature increased from 400°C to 450°C. With a further increase in the temperature to 500°C, the conversion of sugarcane bagasse was slightly increased to 72.3 wt%. On the other hand, the maximum bio-oil yield (14.44 wt%) from the catalytic pyrolysis of sugarcane bagasse was produced at a temperature of 450°C and the highest conversion (79.45 wt%) was achieved at a temperature of 500°C.

For all the temperatures considered in this study, a higher yield of pyrolytic bio-oil and higher conversion of sugarcane bagasse was obtained with the addition of HZSM-5 catalyst when compared to the non-catalytic pyrolysis process. The cracking activity of the HZSM-5 catalyst is attributed to the bio-oil yield improvement. The activation energy can be reduced by the presence of catalyst during pyrolysis thereby enhancing bio-oil or gaseous product yield (Gong et al. 2020). A previous study by Stegen and Kaparaju (2020) investigated the effect of temperature (300–650°C) on the yields and quality of bio-oil obtained from SCB pyrolysis. The authors observed temperature had a significant influence on the pyrolysis product yields as well as on the quality of bio-oils produced. Also, the yields of bio-oil were found to improve and reduce with an increase in temperature. Similar to findings from the non-catalytic pyrolysis process in this study, their maximum yield of bio-oil (56.6 wt%) was obtained at 500 °C. Past studies have also shown that the presence of catalysts during pyrolysis could either favour the yield of bio-oil or gaseous products depending on the performance of the catalyst. For instance, Balasundram et al. (2018) found that the use of Ce/HZSM-5 during the catalytic pyrolysis of sugarcane bagasse enhanced the bio-oil yield produced at various catalysts to biomass ratio when compared to HZSM-5 catalyst and also higher yield of pyrolysis bio-oil was obtained when compared to the non-catalytic process.

Contrary, Mendes et al. (2016) reported the catalytic pyrolysis of sugarcane bagasse but found gaseous products yield increased with an increase in temperature and the addition of ZSM-5 catalyst could favour the generation of more gaseous deoxygenated products during pyrolysis. They also found maximum liquid yield at 500°C. Iftikhar et al. (2019) investigated the co-pyrolysis of sugarcane bagasse and polystyrene and found that the addition of catalysts (HZSM-5, MgO and CaO) decreased the liquid yield but with improved quality. Kuan et al. (2013) reported the catalytic pyrolysis of sugarcane bagasse using microwave heating and found that the addition of either CaO or MgO catalyst enhanced the gaseous production while the presence of either NiO or CuO catalyst enhanced the liquid production. A series of reactions such as dehydration, decarboxylation, decarbonylation and several secondary reactions occurred during pyrolysis that’s could alter the product yield and composition.

The bio-oil compositional analysis was done using GC-MS and the main compounds identified are presented in Fig. 4, respectively. The major compounds identified were classified into aliphatic hydrocarbon, aromatic hydrocarbon, and acids among others. As shown in Fig. 4, the use of catalyst promotes the production of higher aromatic and aliphatic hydrocarbons when compared to the non-
catalytic bio-oil. The proportion of aromatic hydrocarbon was increased from 16.37 wt% (without HZSM-5 catalyst) to 28.66 wt% (with HZSM-5 catalyst). Also, the proportion of aliphatic hydrocarbon was increased from 67.03 wt% (without HZSM-5 catalyst) to 79.96 wt% (with HZSM-5 catalyst). The increment in aromatics with the use of a catalyst is more likely due to secondary reactions taking place and the deoxygenation of oxygenated aromatic compounds (Mustapha et al. 2021).

As shown in Fig. 5, the catalytic pyrolysis of sugarcane bagasse was found to produce a greater amount of valuable aromatic compounds such as benzene which is a high-value petrochemical intermediate. The highest benzene production (2.85g / 100g) was obtained at a temperature of 450°C. Past work of Iftikhar et al. (2019) also showed that the addition of HZSM-5 catalyst during the co-pyrolysis of sugarcane bagasse and polystyrene resulted in maximum conversion efficiency of hydrocarbon (phenols, acids and other hydrocarbon sources) for aromatic production.

### 3.2.1 Influence of catalyst-to-biomass ratio (C:B)

The effect of C:B (0.1g:1g, 0.25g:1g and 0.5g:1g) on the yield and product distribution during the pyrolysis of SCB at 400°C is shown in Fig. 6. The yield of bio-oil for non-catalytic pyrolysis test (4.95 wt%) was found to increase significantly with the addition of catalyst (7.32 wt% to 10.73 wt%) at varying catalyst to biomass ratios. The maximum bio-oil yield (10.73 wt%) was observed using C:B of 0.1g:1g. As shown in Fig. 6a, the bio-oil yield was found to reduce in favour of gas yield as the catalyst to biomass was increased. The decline in the yield of bio-oil bio-oil observed as C:B was increased may be a result of excessive cracking reactions due to the availability of more catalyst active sites favouring the production of more gaseous products with a reduction of bio-oil yield (Hernando et al. 2016). A series of secondary reactions can cause the release of oxygen when the bio-oil vapours undergo catalytic deoxygenation. This can also favour the generation of more gaseous (light hydrocarbons, CO₂, or H₂O) with a reduction of bio-oil yield (Mustapha et al. 2021). Ghorbannezhad et al. (2018) studied catalytic pyrolysis of sugarcane bagasse for aromatics (benzene, toluene and xylene) production. The authors also found the bio-oil yield was significantly influenced by pyrolysis temperature and catalyst to biomass ratio.

The effect of catalyst to biomass ratio on the chemical composition of the bio-oils obtained from the pyrolysis of SCB at 400°C was analyzed using GC-MS and the main compounds identified are presented in Fig. 6. As shown in Fig. 6, it is evident that the presence of more catalysts during pyrolysis of the sugarcane bagasse promotes the aromatization of the bio-oil produced. The proportion of aromatic compounds in the pyrolysis bio-oil increased from 14.46–31.93% as the catalyst to biomass ratio was changed from 0.1g:1g to 0.5g:1g.

### 3.3. HTL – Result and Discussion

To study the influence of reaction parameters (temperature, time, and ZSM-5) on product yields, a total of 27 runs were conducted for the HTL of SCB. The product of the SCB HTL process, bio-oil is a complex mixture that was analyzed using gas chromatography-mass spectrometry (GC-MS). A summary of the findings can be found in Figs. 7, 8 and 9 which provide detailed information on the conditions that were
used during the HTL of sugarcane bagasse. The analysis shows that the bio-oil produced contained products of aromatics and heterocyclics, hydrocarbons and oxygenation (esters, acids, phenols, ketones, and aldehydes) under a range of reaction parameters, and the cellulose contained an appreciable concentration of hydroxyl groups.

3.3.1. Effect of reaction temperature on production distribution of bio-oil

Experimental studies for the HTL of SCB were conducted in 30, 45 and 60 min to investigate the effect of varying heating times at constant temperatures (220, 300 and 373°C). The product distribution from the HTL of SCB using an SCB/water ratio of 1:10 comprises mainly aromatics and heterocyclics, oxygenation products. Figure 7 shows that at 220°C, esters, aromatics and heterocyclic compounds dominate the bio-oil component for non-catalytic and catalytic HTL of SCB. However, the introduction of the ZSM-5 catalyst shows a similar trend with a reduction in the amount of acid produced at 220°C when compared to uncatalysed HTL (Fig. 7). The increase in reaction temperature to 300°C increased the production of aldehyde and other compounds. The catalytic HTL at 300°C recorded the highest amount of hydrocarbon compound in the bio-oil of approximately 6% at 45 mins heating time with an appreciable amount of aromatics and esters as shown in Fig. 8. Initially, at a reduced temperature, the biomass was degraded and depolymerized into tiny compounds, and as the temperature increased, the molecules may have reorganized by condensation, cyclization, or polymerization processes to generate new compounds which are evident in the product distribution. This indicated that various reactions were prevalent at different stages of the experiment which influences bio-oil yield and components (Yan et al. 2018; Beauchet et al. 2011).

However, a further increase of reaction temperature to 373°C experienced a reduction in the hydrocarbons, aromatics and heterocyclic compounds of the bio-oil of catalytic HTL while a similar trend was observed in non-catalytic treatment but with a little increase in hydrocarbon content compared to catalytic HTL (Fig. 9). Other oxygenated compounds (phenols, aldehyde, and ketones) show no significant changes with an increase in reaction temperature for the two HTL processes. The influence of temperature on liquefaction products yield and distribution appeared to occur in a particular sequence. Initially, the production of bio-oil was enhanced with an increase in temperature. After attaining a maximum yield, any further rise in temperature prevented the liquefaction of the biomass produced. In general, extremely high temperatures > 300°C were not suited for the synthesis of liquid oils, both because of the high operational costs and the low yield of liquid oil produced as a result (Tran 2016). Interestingly, this is consistent with the findings of Gai et al (2015), who discovered that the yields of bio-oil fell when the temperature exceeded a particular point (300°C). Using the experimental parameters described in this study, the maximum total hydrocarbon yield (6 wt%) was obtained at 300°C also in conformity with the study by Kosinkova et al. (2015). The overall bio-oil output also suggests water as a viable and cost-effective HTL solvent in this experiment (Li, Cao, et al. 2015).
The relative proportions of phenols, ketones, aromatic and heterocyclic, acids, and aldehydes in the bio-oil altered in proportion with the increase in temperature. The temperature of the reaction had a significant impact on the relative abundance of aromatic and heterocyclic compounds. A reduction in relative abundance was observed with an increase in temperature. In response to a rise in reaction temperature, the relative abundances of the ketone and phenol compounds grew consistently more with catalysts from 300 to 373°C which was recorded without catalyst, 0wt.% to 5.21wt.% for phenols, and 0.48wt.% to 2.46wt.% for ketones and with catalysts, 0wt.% to 1.43wt.% for phenols and 0.47 to 0.72wt.% for ketones and respectively (Figs. 8 and 9). Following the hydrothermal breakdown routes of cellulose and hemicellulose, it was clear that a significant amount of aromatic and heterocyclics may be produced at the relatively low temperature of 220°C. As the temperature of the reaction increased, the aromatic and heterocyclic compounds reduced, which suggests subsequently decomposition into ketones, phenols, and acids (Yu and Lou 2008). In general, phenols are produced primarily by lignin hydrothermal degradation, which was ineffective at 220°C., resulting in the production of little or no phenol components at low temperatures. It was discovered that increasing the temperature to 373°C enhanced the efficiency of delignification and the relative abundance of phenols (Yan et al. 2018).

It was discovered that numerous types of heterocyclics, including hydroxymethylfurfural (HMF), methyl furfural, and furfural (2-furaldehyde), were produced. In addition, 5-HMF was discovered to be a transformation product of D-fructose. MF and furfural were both produced as a result of the hydrothermolysis of 5-HMF (Thananatthanachon and Rauchfuss 2010). An increased reaction temperature was shown to be detrimental to the formation of aromatics and heterocyclics. The relative abundance of aromatics and heterocyclics declined dramatically from 84.41wt.% at 220°C to 38.18wt.% at 373°C and 76.03wt.% at 220°C to 19.76wt.% at 373°C (Figs. 7 and 9). The introduction of ZSM-5 resulted in the production of fewer aromatics and heterocyclics as well (Figs. 7, 8 and 9). However, ZSM-5 appeared to stimulate further decarburization and other chemical processes of aromatics and heterocyclic compounds, resulting in the synthesis of phenolic and other oxygenated compounds, as demonstrated by the results (Li et al. 2013). Therefore, they were not conducive to the production of aromatics and heterocyclics.

3.3.2. Effect of reaction time on product distribution of bio-oil

The effects of the reaction time (30, 45 and 60 mins) on bio-oil yield were studied at different temperatures using a sugarcane bagasse to water ratio of 1:10. The effect of reaction time on the relative abundance of the various compounds in the bio-oil was similar to the effect of process temperature on the relative abundance of the different compounds in bio-oil. Figure 10 (a, b & c) shows that product distribution is dependent on reaction time. The amount of ester component of the bio-oil decreased as reaction time was increased from 30–60 mins for both catalytic and non-catalytic treatment while a similar trend was observed for aromatics and heterocyclics. This can be attributed to the condensation and repolymerization of intermediates that generated residues, and subsequent decomposition processes
that released gaseous products after the reaction period was extended (Yin and Tan 2012). It is believed that acids, ketones, esters, and aldehydes are obtained from cellulose and hemicellulose liquefied products, while the secondary products, phenols and aromatic compounds, are generated from lignin decomposition (Cheng et al. 2010; Meryemoğlu et al. 2014). Contrary to non-catalytic treatment, the introduction of ZSM-5 recorded a decline in the production of acid compounds from 30 to 45mins but a slight increase was observed at 60 mins heating time. Hydrocarbon compounds increases from 30 mins to 45 mins and experienced a decline at 60 mins heating time for both treatments. Other compounds including phenols, aldehydes, and ketones show no significant changes as the reaction time increases, however non-catalytic recorded slightly more oxygenated products than catalysed HTL. It can be noted that when ZSM-5 was utilized as a catalyst, ester compounds were significantly detected, and the amount of acids was decreased (Figs. 10a, b and c). This demonstrated that, given the catalytic conditions of ZSM-5, most of the acids were mostly probably transformed into esters (Veses et al. 2015).

In contrast to the phenols where reaction time was shown to be positively connected with peak area ratio, a prolonged reaction time was found to be inversely correlated with the relative abundance of the esters, aromatics and heterocyclics. However, with the addition of catalyst, the proportion of esters grew dramatically, rising from 19.76–80.21% in a short period (30–45 mins) before declining (Figs. 10a and b). The acid generation, on the other hand, followed the reverse pattern. Initially, it dropped from 0.53–0%, but then it rose to 1.65% afterwards (Fig. 10). In most cases, few molecular carboxylic acids were generated by the breakdown of polysaccharides and cellulose, and these acid molecules were then degraded via condensation, and polymerization reactions, resulting in the formation of new compounds as the reaction time was prolonged (Srokol et al. 2004). The amount of phenols, aromatic and heterocyclics in the solution reduced as with ZSM-5 and increase in reaction time. The reduction in oxygenated components is caused by dehydration and decarboxylation processes where the oxygen is eliminated in the form of water vapour, carbon dioxide, and carbon monoxide (Thring et al. 2000). According to Barbier et al. (2012), lignin is hydrolyzed into methoxylated benzenes first and then disintegrates into oxygenated hydrocarbons. It is possible that the oxygenated hydrocarbons were reorganized via condensation, cyclization, or polymerization processes to produce some aromatics (hydroxylated and methoxylated benzenes).

Higher reaction temperatures and longer reaction times were shown to be unfavourable for the production of aromatics and heterocyclics. Yang et al. (2014) believed that aromatics and heterocyclics, such as 5-HMF, may easily be converted into acetic acid by an oxidation reaction. This may be the logical explanation for why the acid production surged when the reaction time was more than 30 minutes in the present study. The result demonstrates that there were some changes in the amount of acids present in the solution. However, when the acids and esters were subjected to different reaction times and temperatures, it was feasible that they were interconverted which generally reduced the amount of acid in the bio-oil produced. The acidity, corrosiveness, and stability of bio-oils can all be weakened by ester species (Li et al. 2016). Under comparable parameters, the decreased acid concentration of the bio-oil produced proved to be beneficial, as high levels of acid not only expedited bio-oil breakdown but also rendered the oil more susceptible to corrosion during internal combustion.
4. Conclusion

The synthesis of bio-oil from the pyrolysis and hydrothermal liquefaction conversion of SCB is dependent on the operating conditions. The two conversion processes recorded significant quantities of aromatic and aliphatic compounds in the product distribution. The catalysed pyrolysis operation (with HZSM-5 catalyst) resulted in a larger production of pyrolytic bio-oil and a greater transformation of sugarcane bagasse when compared to the non-catalytic operation. This was valid irrespective of the temperature at which the experiment was conducted. The cracking efficiency of the surface active sites of the HZSM-5 catalyst may be responsible for the increase observed in bio-oil production during the catalytic pyrolysis of sugarcane bagasse. The maximum pyrolytic bio-yield of 14.44 wt% was recorded at 450 °C with the use of catalyst. Also, higher aromatic and aliphatic hydrocarbons production was favoured with the use of catalysts. From the HTL process, the reaction temperature of 300°C showed appreciable bio-oil components and distribution of product with 6wt% of hydrocarbons produced at 45 mins heating time under catalytic hydrothermal liquefaction of SCB. This once again validates the effect of the HZSM-5 catalyst employed for this study which effectively decrease the acidic compounds and improved the liquid properties during HTL. Additionally, the HZSM-5 catalyst used for the HTL process improved the quality of the bio-oil with lower oxygen content when compared to the non-catalytic process. Moreover, the effect of the reaction temperature depends on reaction time as increased reaction temperature and time reduced the production of dominant compounds. The study shows that the pyrolysis and HTL processes are viable for SCB conversion for bio-oil production.

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Declarations

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All authors have given consent for the work to be published

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Yusuf Makarfi Isa : Conceptualization, Resources, Supervision and Methodology, review and

References


Figures

Figure 1

Schematic diagram of the experimental pyrolysis set-up: (1) Nitrogen cylinder, (2) Nitrogen controller valve (3) Rotameter (4) Reactor (5) Furnace (6) Biomass or a mixture of biomass and catalyst (7) Furnace temperature controller (8) Condenser (9) Bio-oil storage (10) Gasbag
Figure 2

Image analysed by SEM of residual solid after HTL hydrolysis at 30 minutes heating time and different temperatures: (a) At 220°C catalysed (b) At 300°C – catalysed (c) At 373°C – catalysed (d) At 373°C - uncatalyzed
Figure 3

Effect of temperature on (a) product yield and (b) conversion obtained from non-catalytic and catalytic pyrolysis of sugarcane bagasse (catalyst to biomass ratio of 0.1g:1g).
Figure 4

Main compounds distribution obtained from pyrolysis of sugarcane bagasse with and without catalyst at 450 °C using catalyst: biomass of 0.1g:1g.

Figure 5

Effect of temperature on production of benzene from pyrolysis of sugarcane bagasse (catalyst to biomass ratio of 0.1g:1g)
**Figure 6**

Effect of catalyst to biomass ratio on (a) products yields (b) Distribution of main compounds obtained from catalytic pyrolysis of sugarcane bagasse (temperature = 400 °C)
Figure 7

Catalytic and Non-Catalytic HTL Products at 220°C
Figure 8

Catalytic and Non-Catalytic HTL Products at 300°C

Non-Catalytic and Catalytic HTL @300°C

Non-Catalytic and Catalytic HTL @373°C
Figure 9

Catalytic and Non-Catalytic HTL Products at 373°C

Figure 10

Product Distribution at (a) 30, (b) 45 and (c) 60 minutes heating time for Catalytic (C) and non-catalytic (NC) HTL of SCB