

## Thermochemical Conversion of Sugarcane Bagasse into Bio-Crude Oils by Fluidized-Bed Pyrolysis Technology\*

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### Abstract

Thermochemical conversion of sugarcane bagasse into bio-crude oils by fluidized-bed reactor has been taken into consideration in this study. The bagasse in particle form was pyrolyzed in an externally heated 7cm diameter and 37.5cm high fluidized-bed reactor with nitrogen as a carrier gas. The reactor chamber and gas-preheater were heated by means of a renewable energy biomass source cylindrical heater. At a reactor bed temperature of 450°C for a feed particle size of 420-600µm and at a gas flow rate of 30 l/min, an oil yield of 48wt% of dry feed was obtained. The pyrolysis process temperature was found to have influenced on the product yields. Characterization of the whole pyrolysis liquids obtained at optimum operating conditions has been carried out including physical properties, elemental analyses, GCV, FT-IR, and <sup>1</sup>H NMR analysis. The results show that pyrolysis of sugarcane bagasse waste is a good option for producing bio-crude oils to be used as alternative to petroleum fuels and valuable chemical feedstocks.

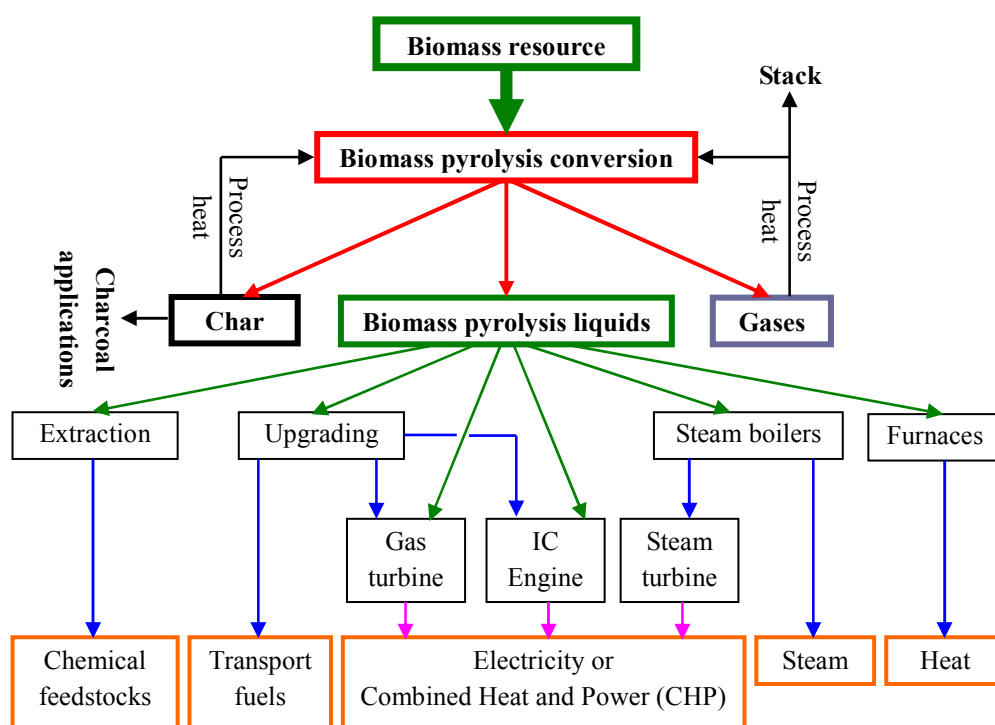
**Key words:** Fluidized-Bed, Sugarcane Bagasse, Alternative Bio-Crude Oils

### 1. Introduction

Amongst the thermochemical conversion processes for biomass, pyrolysis has received increasing attention since the process conditions may be optimized to produce high energy density pyrolytic oil in addition to the derived char and gas. Pyrolysis for energy conversion from carbonaceous wastes is defined as the thermal degradation of organic matter either in total absence of air or with a lack of a stoichiometrically needed amount of oxygen to the extent where gasification does not occur. Pyrolysis processes are usually conducted in a reactor where heat is applied to the feedstock either externally or by the partial combustion of the feedstock. Pyrolysis always produces gas, vapour that can be collected as liquid and solid char, yields of each depending on the process conditions [1-3]. The solid char has a good gross calorific value (GCV) of 17-36 MJ/kg [4-7] may be used internally to provide heat for the pyrolysis process itself. Solid char can also be used as a fuel either directly as briquettes or as char-oil or char-water slurries or it can be used as feedstocks to prepare activated carbons [8-9]. Some of the previous research groups [4, 7] studied the composition of evolved pyrolysis gas fraction and reported that it contains high concentration of CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and other hydrocarbons with a GCV of 6.4-9.8 MJ/kg and can be used internally to provide process heat, re-circulated as an inert carrier gas or exported for example for feed drying. The usages of char and gases products

in the pyrolysis process itself reduce the production cost for heating system.

Pyrolytic liquid (bio-crude oil) derived from biomass wastes has moderate GCV ranging from 15-38 MJ/kg with some advantages in transportation, storage, combustion, retrofitting and flexibility in production and marketing [4, 7, 10-12]. The liquid product, is useful as a fuel, may be added to petroleum refinery feedstocks or upgraded by catalysts to produce petroleum grade refined fuels. The bio-crude oil is a mixture of about 300 types of major and minor organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds [13]. The pyrolysis reaction pathways as well as its products potential applications are presented in Fig. 1. Bio-crude oil has several environmental advantages over fossil fuels as a clean fuel. It is CO<sub>2</sub>/GHG neutral. Therefore, bio-oil can generate carbon dioxide credits. No SO<sub>x</sub> emissions are generated, because plant biomass contains insignificant amounts of sulfur. Thus, bio-oil would not be subjected to SO<sub>x</sub> taxes. Bio-oil fuels generate more than 50% lower NO<sub>x</sub> emissions than diesel oil in a gas turbine [14-15].



**Figure 1.** Biomass pyrolysis conversion and applications of products

Sugarcane is the world's largest agricultural crop. Located in tropical and subtropical areas of the world, over 1200 sugarcane factories in 80 countries grind and process nearly 800Mt of sugarcane [16]. The composition of sugarcane bagasse is similar to that of other lignocellulosic materials, cellulose (40-50%), hemicellulose (20-30%), lignin (20-25%), and ash (1.5-3.0%), which possess a high-energy content [17]. Typically, one tones of crude sugarcane can produce 100 kg of sugar, 35 kg of molasses and approximately 270 kg of dry bagasse [4]. Some amount of the bagasse is used as fuel for boiler in the millhouse. Mostly, this by-product is either under-utilized or unutilized as a source of heat energy. It is creating waste management problem, especially in the sugar milling sites. Moreover, generating power by direct combustion of sugarcane bagasse in boilers has a maximum efficiency of 26%. In populated areas, bagasse-fired boilers can be one of the major health hazards due to airborne fly ash. Bagasse transformation into high-density renewable fuels, like charcoal and bio-oil, can significantly increase the profitability of sugarcane plantations. Thus, an

endeavor from the point of view of the energy recovery from this sugarcane bagasse waste by pyrolysis technology may be worthwhile.

Although pyrolysis of biomass has achieved commercial status, there are still many aspects of the process which are largely empirical and require further study to improve reliability, performance, product consistency, product characteristics and scale-up. A quite number of the previous research groups worked for the potential recovery of fuels and chemicals from different agricultural residues and by-products including rice straw [5-6, 18-21], guayule bagasse [7], sesame stalk [11], hazelnut shells [12], olive husk, corncob and tea waste [15], rice husks [22-26], jute stick [27-28], sugarcane bagasse [4, 10, 17, 23, 29-30], olive bagasse [31], sweet sorghum bagasse [32], cotton stalk [33] via pyrolysis in relation to process conditions. Most of the works have been performed for the effect of reactor temperature on the product yields and product compositions but there have been very limited studies for the effect of feed size and vapor residence time. A variety of reactor configurations with electrical and/or microwave heater have been found in literature those have received considerable creativity and innovation in devising reactor systems while fluidized-bed with renewable biomass burning heating mode is still unstudied.

The objective of this study is to provide a new approach in heating system for pyrolysis technology to the recovery of liquid hydrocarbons from biomass solid wastes. A fluidized-bed pyrolysis reactor system with biomass burning heater has been designed and fabricated considering all of the process parameters and present engineers challenge. Sugarcane bagasse has been pyrolyzed in the reactor system under N<sub>2</sub> atmosphere. The effects of operating temperature, feed size and fluidizing gas flow rate on the yields and compositions of product liquids were investigated. Characterization of the whole pyrolysis liquids obtained at optimum operating conditions has been carried out including physical properties, elemental analyses, GCV, FT-IR, and <sup>1</sup>H NMR analysis.

## 2. Materials and methods

### 2.1 Biomass feedstock

Sugarcane bagasse was collected from Rajshahi Sugar Mills Limited, Rajshahi, Bangladesh. It was ground and sieved to the size ranges of 0-150, 150-300, 300-420, 420-600, 600-1180µm and finally dried for 3 hours at 110°C prior to pyrolysis. The gross calorific value of the solid sugarcane bagasse is 16.81 MJ/kg. The proximate and ultimate analysis of the solid biomass is presented in Table 1.

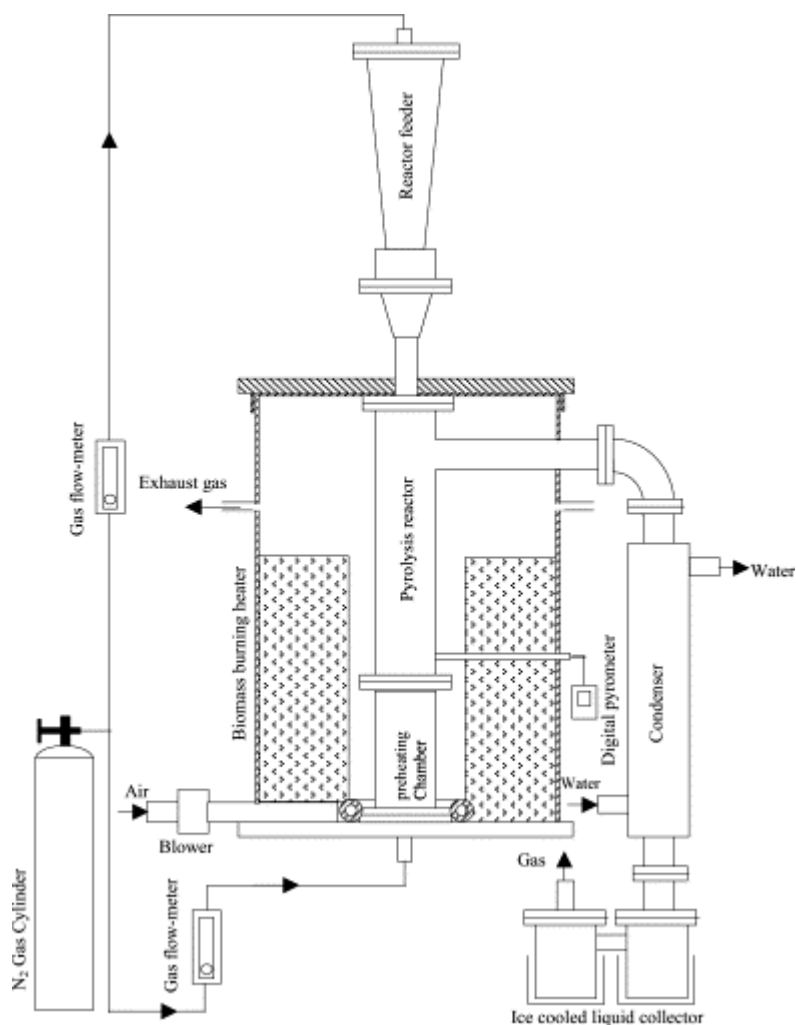
**Table 1.** Proximate and ultimate analysis of solid sugarcane bagasse

| Proximate analysis (Bagasse anhydrous basis) |       | Ultimate analysis (Ash-free basis) |       |
|--|-------|------------------------------------|-------|
| Contents                                     | Wt%   | Elements                           | Wt%   |
| Volatile                                     | 75.85 | C                                  | 48.67 |
| Fixed carbon                                 | 20.01 | H                                  | 6.70  |
| Ash  | 4.14  | N                                  | 0.45  |
|  |       | O                                  | 44.10 |
|  |       | S                                  | 0.08  |

### 2.2 Experimental system and procedure

The experimental system was a fluidized bed pyrolysis unit. Nitrogen gas was used as fluidizing gas to make the system inert and dry silica sand was used as bed material. The sand in the fluidized bed was of mean size 181µm diameter with static bed height of 5cm.

The schematic diagram of the experimental system are presented in Figure 2. The reactor was 7 cm (diameter), 37.5 cm (height), constructed of stainless steel with full gas flow and temperature control. The reactor was heated externally. The incoming fluidizing nitrogen gas was pre-heated before entering into the reactor in a pre-heating chamber. The fluidizing gas flow rate was measured and controlled by nitrogen gas flow meter and flow control valve, respectively. The reactor bed and gas pre-heating chamber were heated by means of renewable energy biomass burning cylindrical heater. A blower supplied air required for burning biomass in the heater. By varying the air supply that was directly related to the blower speed, the temperature of the reactor was controlled. The temperature in the fluidized bed reactor was measured by a digital pyrometer. The gravity feed type heater



**Figure 2.** Schematic diagram of fluidized-bed pyrolysis system

feeder supplied the heater biomass required for continuous heating of the reactor. The ash of burned biomass in the heater was disposed through the ash disposal system at the bottom of the heater due to gravitational force only. Exhaust gas due to burning of heater biomass was exhausted into the atmosphere through a pipeline at the top of the heater. The biomass solid waste particles were fed into the reactor by a gravity feed type reactor feeder. The feed rate was maintained near about constant by a feed control valve at the bottom of the reactor feeder. Gravitational force was the main agent for feeding the reactor. The system was

maintained at a pressure slightly above atmospheric by a nitrogen gas pressure regulator. The char was collected from the reactor after completing a run. The vapors and gases were passed through a water-cooled condenser to a series of two ice-cooled collectors to trap the derived liquid product. The fluidizing gas and noncondensable vapor were flared into the atmosphere. The reactor bed temperature was varied between 400°C to 500°C at an interval of 25°C while the fluidizing gas flow rate was varied between 22 to 38 l/min at an interval of 4 l/min. To enhance the liquid yields as well as its quality from fast pyrolysis of biomass, several research groups worked with different heating rates including 5°C/min [21], 7°C/min [12], 10°C/min [31], 100-500°C/min [23], 500°C/min [11] and even of 1000°C/sec [17]. However, the presented experiment has been carried out with a heating rate of 100±5°C/min.

### 2.3 Physical and chemical property analysis of the derived oils

Pyrolytic liquids obtained under the maximum liquid yield conditions were well mixed and homogenized prior to analysis being made. Some physical properties of pyrolytic liquids including density, viscosity, flash point, pour point and GCV were determined by using the standard methods ASTM D189, ASTM D445, ASTM D92, ASTM D97, and ASTM D240, respectively. Water content of the liquids was determined by Karl-Fischer titration. Elemental analysis (C, H, N and S) of liquids was determined with an elemental analyzer of model EA 1108, which followed the quantitative "dynamic flash combustion" method. The functional group compositions of the product liquids were analyzed by Fourier Transform InfraRed (FT-IR) spectroscopy. The FT-IR instrument of model PERKIN ELMER FTIR 2000 was used to produce the ir-spectra of the derived liquids. The <sup>1</sup>H NMR analyses of pyrolytic liquids were recorded at a frequency of 500 MHz with an instrument of model JEOL A-500 using CDCl<sub>3</sub> as solvent.

## 3. Results and discussions

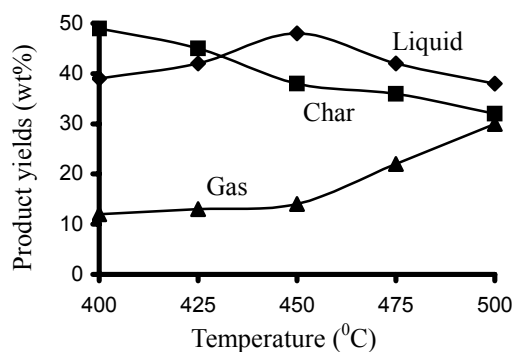
### 3.1 Product yields

Three common products: oil, char and gas were recovered after each run of sugarcane bagasse pyrolysis. Higher percentage of liquid collection makes this biomass potential for liquid fuel extraction. The liquid appeared brownish dark with a strong acrid smell. Careful handling of the liquid was required since the liquid reacted easily with human skins, leaving permanent yellowish brown marks and an acrid smell for a few days, which cannot be removed by detergent. No phase separation was found to take place. The liquid product was collected in two ice-cooled liquid collectors in series. The char was collected from the reactor. This char were expected to be very reactive, and precautions were required to ensure that it would not be exposed to air when still hot. The gas was diluted by the large flow of nitrogen gas and flared into the atmosphere.

### 3.2 Effect of reactor temperature

Figure 3 shows the variation of percentage mass of liquid, char and gaseous products at different reactor bed temperature for bagasse pyrolysis with particle size 420-600µm, fluidizing gas flow rate of 30 l/min. From this figure it is found that the maximum liquid product yield was obtained at a reactor bed temperature of 450°C and this was 48wt% of total biomass fed. With the decrease of bed temperature at 400°C, the liquid product yield was decreasing (39wt% of biomass fed) while with the increase of bed temperature at 500°C the liquid product yield was again decreasing (38wt% of biomass fed). With the increase of reactor bed temperature, the solid char yield was decreasing for the temperature

range of 400°C to 500°C. For feed particles of size 420-600µm, a bed temperature of 400°C yielded the maximum percentage mass of char, 49wt% of biomass fed. At a higher temperature of 500°C, the solid char production was lower, it was found to be 32wt% of biomass fed. Figure 3 also shows that as the reactor bed temperature was increased the gaseous product yield was increasing. A fluidized bed temperature of 500°C yielded the maximum percentage mass of gas yield of 30wt% of biomass fed. The gas yields were near to minimum at the condition of maximum oil production. This is supported by the thermogravimetric (TG) study of solid sugarcane bagasse, where the complete devolatilization of volatile in bagasse was found to take place at around 450°C. The reason for lower liquid product yield at lower bed temperature may be due to the fact that the temperature rise was not sufficient enough for complete pyrolysis to take place yielding less liquid product and higher char production. On the other hand at higher reactor bed temperature there was a possibility of secondary decomposition reactions to take place in the reactor rendering lower liquid and higher amount gas.

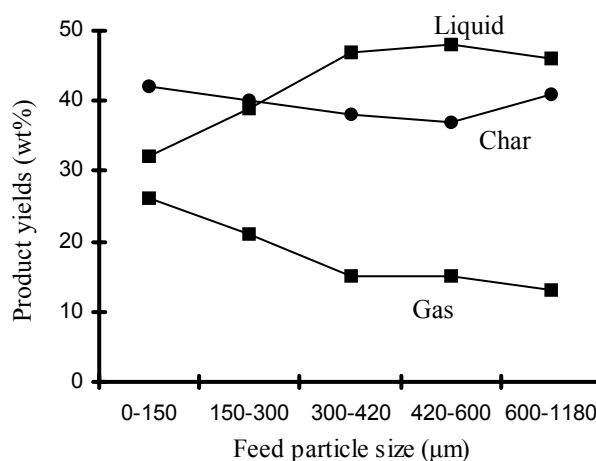


**Figure 3.** Effect of reactor bed temperature on product yields for feed size of 420-600 µm and gas flow rate of 30 l/min.

The liquid yields obtained in the presented study are slightly lower and char yields are higher compared to those of the previous studies [4-5, 10-11, 28]. These variations in the product yields are due to mainly the compositional differences (moisture, volatile, fixed carbon and ash content) in biomass feeds and quality of pyrolytic product liquids. Higher volatile content of feedstock with lower amount of fixed carbon and ash is desirable for higher percentage of liquid yields in pyrolysis process. Higher amount of fixed carbon and ash content of a feedstock contribute to char formation. Moreover, water in bio-oils results from the original moisture in the feedstocks and dehydration reactions occurring during pyrolysis [34-35]. Feedstock used (Table 1) in the presented study was of lower amount of volatile and moisture content with higher amount of fixed carbon and ash content compared to those of the quoted previous studies. The former research groups [4-5, 10, 28] used an additional cooling solvent to quench pyrolytic vapours in subzero range, while the product liquids contained quite amount of water. In the presented study, liquid yields are somewhat higher and char yields are somewhat lower compared to those of the previous studies [12, 18, 21, 29-31, 33] due to mainly variations in the design of reactors and operating conditions used.

### 3.3 Effect of feed particle size

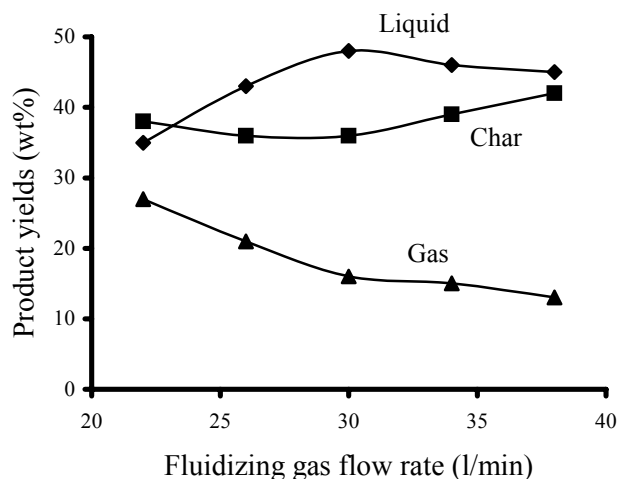
Figure 4 represents the percentage yield of liquid and solid char products for different particle size of bagasse at a fluidized bed temperature of 450°C and fluidizing gas flow rate of 30 l/min. It was observed that at a fluidization gas flow rate of 30 l/min, the percentage yield of liquid product was maximum, 48wt% of total biomass fed for particle size of 420-600 $\mu\text{m}$  with a solid char product of 37wt% of dry biomass fed. The particle of size less than 150 $\mu\text{m}$  produced a percentage yield of liquid product of 32wt% of dry biomass fed with a solid char product of 42wt% of biomass fed. The large particle of size 600-1180 $\mu\text{m}$  produced percentage yield of liquid and char products of 46 and 41wt% of biomass fed, respectively. This may be due to the fact that the smaller size particles were overheated while too quickly devolatilization occurred also and might blown out before commencing pyrolysis completely producing more char and gases, on the other hand, the larger size particles were not adequately heated up so rapidly causing incomplete pyrolysis rendering reduced liquid product yield. With the increase of feed particle size, gas yield was decreasing from 26 to 13wt% of biomass fed.



**Figure 4.** Effect of feed particle size on product yields for bed temperature 450°C and gas flow rate of 30 l/min

### 3.4 Effect of fluidizing gas flow rate

Figure 5 shows the variation of percentage yield of liquid, solid char and gas product at a reactor bed temperature of 450°C for feed particle of size 420-600 $\mu\text{m}$ . The maximum liquid product was 48 wt% of biomass fed while the solid char product was 36wt% of dry fed at a fluidization gas flow rate of 30 l/min. It was observed that at the beginning with lower fluidization gas flow rate at 22 l/min, the liquid product was 35wt% of biomass fed with a char product of 38wt% of biomass fed and a gas yield of 27wt%. With the increase of fluidization gas flow rate up to 30 l/min, the liquid product was increasing with a decreasing trend of gas yield. The char yield appeared to be more or less constant. This may be due to the fact that at lower fluidization gas flow rate the fluidization was not achieved completely and hence, the fast pyrolysis reaction could not take place properly. At higher gas flow rate, the fluidization was good enough for high heating rate causing fast pyrolysis for maximum liquid yield and the vapor residence time was quite low which was not enough for secondary reaction to take place yielding less gas and more liquid product. When the fluidization gas flow rate was increased to values higher than 30 l/min, char particles of 420-600 $\mu\text{m}$  size feed particles were found to be elutriated significantly into liquid collector, thus disturbing the system as a whole.



**Figure 5.** Effect of fluidizing gas flow rate on product yields for particle size of 420-600  $\mu\text{m}$  and bed temperature of 450°C.

### 3.5 Product oil characteristics

#### 3.5.1 Physical and chemical characteristics

The elemental composition and the physical characteristics of the bagasse pyrolysis oil obtained at the maximum yield temperature of 450°C are shown in Table 2. The average chemical composition of the pyrolytic liquids obtained from sugarcane bagasse has been analyzed as  $\text{CH}_{1.56}\text{O}_{0.634}\text{N}_{0.014}$ . Water is the most abundant single component in bio-crude oils. It results from original moisture in feedstocks and dehydration reactions during pyrolysis process. Water content of the pyrolytic liquids derived from sugarcane bagasse was 12.10 wt% while literature reports that it contents of bio-oils usually vary in the range of 15–30 wt%, depending on the initial moisture in feedstocks and pyrolysis conditions. The energy content of the oil was 21.85 MJ/kg, due to the presence of water and oxygenated compounds. However, it was significantly higher than that of raw bagasse. The oil was heavier than water with density at 30°C is 1160  $\text{kg}/\text{m}^3$  and hence, results higher volumetric energy content. The flash point of the oil was 103°C hence, precautions are not required in handling and storage at normal atmosphere. The oil was easily pourable and the pour point was low, less than -16°C. The viscosity of liquid products from bagasse sample was higher than that of diesel but too much lower than that of heavy fuel oil (200 cSt at 50°C). Low viscosity of the liquids of 18.80 cSt at 30°C is a favorable feature in the handling and transporting of the liquid. The viscosity of bio-oils usually vary over a wide range (35-1000 cP at 40 °C) depending on the feedstock and process conditions, and especially on the efficiency of collection of low boiling components. It decreases at higher temperatures much faster than for petroleum-derived oils, so that even very viscous bio-crude oils can be easily pumped after a moderate preheating. A significant reduction in viscosity can also be achieved by addition of polar solvents such as methanol or acetone. The liquid was acidic with low pH value of 2.98 suggesting its corrosive in nature. Bio-oils usually contain about 7-12 wt% acids, and have a pH of 2-4. It has been reported that bio-oils are very corrosive to aluminum, mild steel and nickel based materials. The corrosion-resistant materials include stainless steel, cobalt materials, glass, PET plastic and/or other various polymers such as polyethylene, polypropylene and polyester resins. The pH value of soft drinks like Cola and Pepsi of Coca Cola company is 2.5 and they use PET plastic bottles for its storage and handlings. Thus, storage and handling of the liquids are little problematic in industrial usage in this regard.



The elemental analysis of the oil is an important criterion for the design of a combustion plant utilising the oil with the help of the elemental analysis, the combustion calculation can be carried out from which the quantities of combustion air and flue gas and also the composition of the flue gas can be determined. Bio-crude oils have some properties that are quite different from those of petroleum-driven oils. Biocrude oils contains a large amount of oxygen. The oxygen content of bio-oils (excluding water) is a function of the oxygenated feedstock from which they are made, as well as the residence time and temperature of the pyrolysis step. The oxygen content in the liquid was 42.31wt%, calculated by difference, was close to that of feedstock composition. The sulfur content of bio-oils is naturally low, due to the low sulfur content of biomass. This low sulfur content is one of the positive aspects of bio-oils. The amount of sulfur in the biomass derived oils will indicate the quantity of the hazardous SO<sub>2</sub> emission in combustion processes. The sulfur was found to be 0.08 wt% and ash content was also found to be low as 0.25wt% of the oil weight. One of the variables with bio-oils will be the nitrogen content of the oil, which will reflect the variable protein content possible with biomass. Biomass which has a significant content of green, living plant cells (e.g. green grasses) will have a higher nitrogen content than biomass having a large content of dead plant cells (e.g. straw and wood). The nitrogen content in the bio-oils will contribute to NO<sub>x</sub> emissions and it was detectable as 0.85wt% in the sugarcane bagasse pyrolytic liquids.

Table 2 shows that bio-crude oils obtained from the presented study have better physico-chemical properties than those of the previous works [18, 30]. Above discussions ensure that these better characteristics are due to mainly the presence of lower amount of water in the present bio oils, which proves the superiority of the system configuration.

**Table 2.** Physico-chemical characteristics of the pyrolysis oil and its comparison

| Analyses                     | Present oil | Islam et al. [18] | Islam et al. [30] | Diesel  |
|------------------------------|-------------|-------------------|-------------------|---------|
| Elemental (wt%)              |             |                   |                   |         |
| C                            | 50.01       | 42.30             | 45.01             | 86.10   |
| H                            | 6.50        | 6.53              | 6.00              | 12.80   |
| N                            | 0.85        | 0.60              | 0.30              | <0.30   |
| S                            | 0.08        | N/D               | 0.04              | <0.70   |
| Ash                          | 0.25        | 0.21              | 0.25              | 0.01    |
| O                            | 42.31       | 50.36             | 48.40             | 0.00    |
| Viscosity @ 30°C (cSt)       | 18.80       | 10.81             | 13.80             | 2.0-4.5 |
| Density (kg/m <sup>3</sup> ) | 1160        | 1153              | 1180              | 860     |
| pH value                     | 2.98        | 3.21              | 3.00              | --      |
| Water content (wt%)          | 12.10       | 16.01             | 14.21             | 80ppm   |
| Flash point (°C)             | 103         | 103               | 102               | >55     |
| Pour point (°C)              | -16         | -8                | -10               | -40--30 |
| GCV (MJ/kg)                  | 21.85       | 18.34             | 19.18             | 45.00   |

### 3.5.2 Compositional analysis

#### 3.5.2.1 FT-IR analysis

From the Fourier transform infra-red spectroscopy of the derived pyrolytic oil, the FT-IR functional groups and the indicated compositions of the liquid product were presented in Table 3. The presence of water impurities and other polymeric O-H in the oil are indicated by the broad absorbance peak of O-H stretching vibration between 3600 and 3200 cm<sup>-1</sup>. The presence of alkenes were indicated by the strong absorbance peak of C-H vibrations between 3050 and 2800 cm<sup>-1</sup> and the C-H of deformation vibrations between 1490 and 1325cm<sup>-1</sup>. The absorbance peaks between 1775 and 1650 cm<sup>-1</sup> represented the

C=O stretching vibration, indicating the presence of ketones, aldehydes and carboxylic acids. The possible presence of alkenes were indicated by the absorbance peaks between 1680 and 1575  $\text{cm}^{-1}$  representing C=C stretching vibrations. The sharp but less prominent absorbance peaks between 1550 and 1475  $\text{cm}^{-1}$  represented  $-\text{NO}_2$  stretching vibration indicated the presence of small nitrogenous compounds. The overlapping peaks between 1300 and 950  $\text{cm}^{-1}$  were suggested due to the presence of primary, secondary and tertiary alcohols, ethers and esters due to the C-O stretching and O-H deformation vibration of these functional groups. Absorbance peaks between 900 and 650  $\text{cm}^{-1}$  indicated the possible presence of single, polycyclic and substituted aromatics groups. These functional groups and indicated compounds have also been identified in the pyrolytic oils derived from agricultural wastes by the previous studies [18, 24, 27, 30]. The pronounced oxygenated functional groups of O-H; C=O; C-O and aromatic compounds showed that the oil was highly oxygenated and therefore very acidic, as have also been indicated by the elemental composition and the pH value. The high fraction of oxygenated compounds reduce the calorific value of the oil since C=O bonds do not release energy during combustion. The presence of hydrocarbon groups C-H; C=C; and alcohols indicate that the liquid has a potential to be used as fuel.

**Table 3.** FT-IR functional groups and the indicated compounds of the pyrolysis oil

| Frequency range ( $\text{cm}^{-1}$ ) | Groups                    | Class of compounds  |
|--------------------------------------|---------------------------|---|
| 3600-3200                            | O-H stretching            | Polymeric O-H, water impurities                                 |
| 3050-2800                            | C-H stretching            | Alkanes   |
| 1775-1650                            | C=O stretching            | Ketones, Aldehydes, Carboxylic acids                            |
| 1680-1575                            | C=C stretching            | Alkenes   |
| 1550-1475                            | $-\text{NO}_2$ stretching | Nitrogenous compounds   |
| 1490-1325                            | C-H bending               | Alkanes   |
| 1300-950                             | C-O stretching            | Primary, secondary and tertiary alcohols, phenol, esters, ether |
| 900-650                              | O-H bending               | Aromatic compounds  |

### 3.5.2.2 $^1\text{H}$ NMR analysis

The  $^1\text{H}$  NMR has been performed for the pyrolytic liquids and the hydrogen distributions obtained from the  $^1\text{H}$  NMR spectrums are given in Table 4. The  $^1\text{H}$  NMR spectra is divided into three main regions: aromatic, olefinic and aliphatic; indicating that olefinic proton is the lowest percentage (peaks in 4.5-6.5 ppm chemical shift range). The main structure of the liquids seems to be aliphatic adjacent to aromatic/alkene group and aliphatic bonded to aliphatic only (3.3-1.8 and 0.4-1.8 ppm chemical shift range, respectively), and as a result the carbon aromaticity of the liquids is comparatively low. The alkanes and long alkyl spectrums are probably largely derived from solid sugarcane bagasse.

**Table 4.**  $^1\text{H}$  NMR results for the product liquids

| Type of hydrogen                            | Chemical shift (ppm) | Mol% (% of total hydrogen) |
|---|----------------------|----------------------------|
| Aromatic                                    | 9.0-6.5              | 9.60                       |
| Phenolic (OH) or olefinic proton            | 6.5-4.5              | 5.55                       |
| Aliphatic adjacent to oxygen/hydroxyl group | 4.5-3.3              | 8.40                       |
| Aliphatic adjacent to aromatic/alkene group | 3.3-1.8              | 40.65                      |
| Other aliphatic (bonded to aliphatic only)  | 1.8-0.4              | 33.82                      |

#### 4. Conclusions

Fluidized-bed pyrolysis of solid sugarcane bagasse had given maximum oil yield that was 48wt% of biomass fed at a reactor bed temperature of 450°C and at a fluidizing gas flow rate of 30 l/min.

- ① The main effects of operating conditions on the product distributions are that: (i) the lower temperature and larger feed size favor incomplete decomposition, which increase in char yields and decrease in the liquid and gas yields, (ii) the higher temperature and longer residence time contributes to secondary reactions results in more gaseous products with the expense of liquids while char yields remain almost constant.
- ② The physical properties analysis showed that the oil was heavy and acidic in nature with moderate viscosity. The pyrolytic oil was a single-phase liquid product. The oil possessed favorable pour and flash points.
- ③ The bio-oil was a mixture of aliphatic and aromatic hydrocarbons having an empirical formula of  $\text{CH}_{1.56}\text{O}_{0.534}\text{N}_{0.014}$ , H/C molar ratio 1.56, O/C molar ratio 0.634 and a heating value of 21.85 MJ/kg. Comparison of the H/C ratios with those of conventional fuels indicates that the bio-oils obtained in this work lay between light and heavy petroleum products.
- ④ FT-IR analysis showed that the bio-oil composition was dominated by oxygenated species. The high oxygen content is reflected by the presence of mostly oxygenated fractions such as carboxyl and carbonyl groups produced by pyrolysis of the cellulose and phenolic and methoxy groups produced by pyrolysis of the lignin. The  $^1\text{H}$  NMR results support well the FT-IR results.
- ⑤ However, further studies are necessary to utilize pyrolytic liquids as a liquid fuels or chemical feedstocks.

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