

POTENTIAL OF PROCESSING BAGASSE AND BAGASSE PELLETS FROM WESTERN KENYA INTO CLEAN SUSTAINABLE TRANSPORT FUEL

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ABSTRACT

Human activity increases with population growth, causing severe negative environmental and food security impacts. Uncontrolled human activity has resulted in alarming pollution, climate change, global warming, waste disposal and resource depletion notably fossil fuel. Carbon dioxide emissions directly affects climate change and hence global warming. Renewable biomass energy will be critical in the transportation, industrial and domestic sectors to limit global average temperature rise to 1.5°C below pre-industrial levels, since biomass fuel burns with a net zero increase in atmospheric CO₂. The primary objective of this research was to investigate the combustion properties of sugarcane bagasse and bagasse pellets produced by the West Kenya Sugar Company and Power-spot Pellets Limited in western Kenya, as well as the feasibility of using the materials for the production of pyrolysis oil, a precursor raw material in the processing of clean green transport fuel. Sugarcane bagasse and bagasse pellets from West Kenya Sugar Company and Power-spot Pellets Limited were characterized for proximate, ultimate and calorific value properties using BS EN ISO/EN international standard methods. A fast pyrolysis experiment was also carried out using the two feed-stocks to determine their feasibility for generation of bio-oil. The results reveal that the biomasses may be utilized as solid fuel based on their heating properties and to produce bio-oil for clean green transport fuel through fast pyrolysis, with an experimental bio-oil yield of approximately 42 - 46%, hence a potential for minimizing global climate challenges. FT-IR analysis also indicates that bagasse pyrolysis oil contains chemicals which may be converted to clean green transport fuel or used to

manufacture specialized chemical compounds.

Keywords: Biomass, Sugarcane bagasse, Fast Pyrolysis, Bio-oil, Clean Green Transport Fuel.

INTRODUCTION

According to current demographic statistics, the world's population as of June 2021 was 7.9 billion, with a predicted increase to 9 billion in 2037 and 10 billion in 2057 (United Nations, 2021). The rapid yearly growth rates of the world's population have a detrimental effect on environmental and food security issues. Uncontrolled human activities have resulted in alarming levels of pollution, climate change, global warming, waste disposal and natural resource depletion (Hoorweg *et al.*, 2013). As a consequence, these global issues need a solution that involves the circular bio-economy playing a key role in reducing future global warming to 1.5°C as stated in the Paris Agreement (Carus and Dammer, 2018; United Nations, 2020; United Nations Foundation, 2020). In the context of contemporary energy situations, biomass is a potential eco-friendly alternative source of renewable energy (Cheng *et al.*, 2016; Jahirul *et al.*, 2012). According to the U.S. Department of Agriculture and Energy, the U.S. had a capacity to generate one billion tonnes of dry biomass each year by 2009 (Marinangelli *et al.*, 2009). When commercial conversion techniques are developed, lignocellulosic biomass may play a key role in future liquid transportation fuels. (Figure 1)

Biomass is a rich and abundant natural resource that may be exploited to produce renewable fuel, reducing the dependency on finite fossil fuel resources and helping to mitigate the effects of climate change. It refers to

organic materials from living plants and animals or recent past living organisms with the exception of substances incorporated into and/or fossilised into

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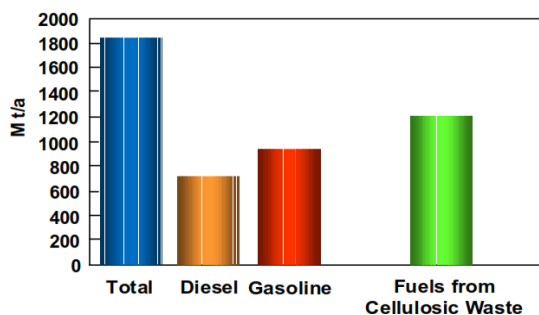


Figure 1: Global transport fuel potential. Source: Marinangelli *et al.* (2009).

geological formations (Basu, 2018b, 2018a; International Organization for Standardization, 2014). Biomass can be obtained from animal waste, plants, or a mix of the two, with plant biomass formed through photosynthesis by absorbing carbon dioxide and water from the soil (Basu, 2018b). Biomass is a carbon-neutral energy source since the CO_2 produced during its usage is equivalent to the CO_2 absorbed from the atmosphere during photosynthesis. It also contains less sulphur, nitrogen and heavy metals than coal (Cheng *et al.*, 2016; Masnadi *et al.*, 2015). The process of photosynthesis is shown by Figure 2.

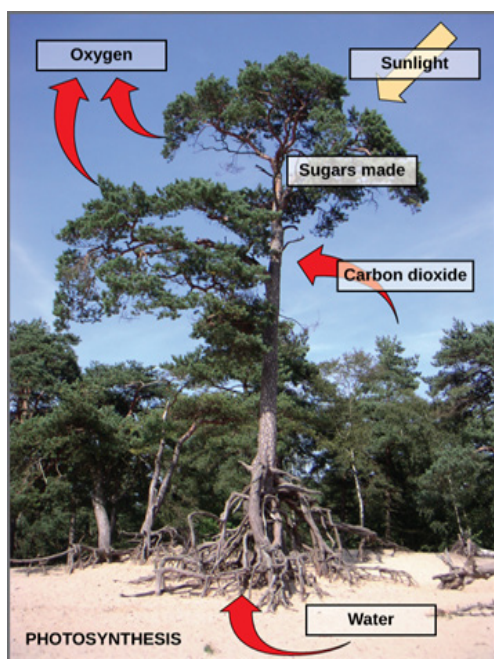


Figure 2: Natural process of biomass synthesis. Source: Basu (2018b).

Lignocellulosic biomass is the most prevalent form of biomass for almost all plants and plant derivatives, ranging from wood waste and grasses to agricultural residues

and city/municipal solid wastes (Yang, 2007). This form of biomass, which is often composed of cellulose, hemicellulose and an aromatic polymer known as lignin, is a non-starchy, fibrous plant material that cannot be readily digested by humans (Zoghalmi and Paës, 2019). Figures 3 and 4 shows the structures of cellulose, hemicellulose and lignin constituents, respectively. Woody plants, agricultural or horticultural waste and crops produced for energy are examples of lignocellulosic biomass (Basu, 2018b, 2018a). Biomass is a vast and complex mixture of organic materials including carbohydrates, lipids and proteins, as well as trace quantities of minerals like phosphorus, calcium, sodium and iron (Zoghalmi and Paës, 2019). Plant biomass has three major structures: extractives, fibre/cell separation and ash (Khalil *et al.*, 2008). Cellulose $\{(\text{C}_6\text{H}_{10}\text{O}_5)_n\}$ is an abundantly available natural substance on the earth's crust and a major structural component of the lignocellulosic biomass cell wall (Credou and Berthelot, 2015). It is a long-chained polymer with a high molecular mass ($\leq 500,000$) and a crystalline-like structure of thousands of D-glucose units (Credou and Berthelot, 2015). It is highly insoluble and dominates wood cell wall components at about 40% - 44% by dry weight (Rowell *et al.*, 2012). Hemicellulose $\{\text{C}_5\text{H}_8\text{O}_4\}_n$ exhibits an amorphous, non-regular form of less strength. It is basically a grouping of sugars, i.e., carbohydrates, with quite an extended polymer chain structure and an average degree of polymerization of 100 - 200 (Credou and Berthelot, 2015; Rowell *et al.*, 2012). Hemicellulose, in general, yields more gases and less tar than cellulose, may be dissolved in weakly alkaline solutions and can be effectively hydrolyzed with moderate acids and bases (Basu, 2018b). Lignin is a 3D polymer of 4-propenyl-2-methoxy-phenol, 4-propenyl-2,5-dimethoxy-phenol and 4-propenyl-phenol. It is predominantly aromatic and constitutes a fundamental component of the auxiliary plant cell wall (Rowell *et al.*, 2012). Wood lignin is composed of three major components: *p*-hydroxyphenyl, syringyl and guaiacyl fractions. The lignin content of hardwoods ranges from 18 - 25%, while the lignin content of softwoods ranges from 25 - 35% (Basu, 2018b). It is lignin that plays an important role as an agent that cements the cellulose filaments.

Since plant composition differs in terms of cellulose, lignin and hemicellulose content, bio-oil synthesised from different plant biomass materials may vary in content characteristics (Khalil *et al.*, 2008). A high mineral or

high ash content affects the production of biomass oil via fast pyrolysis and inhibits the development of tar; in some circumstances, it may accelerate the production of an aqueous product (Khalil *et al.*, 2008).

a significant quantity of bagasse remains unutilized, presenting storage and disposal problems. According to Zhou *et al.* (2012), stacked sugarcane bagasse generates volatile organic compound fumes and leachate mostly

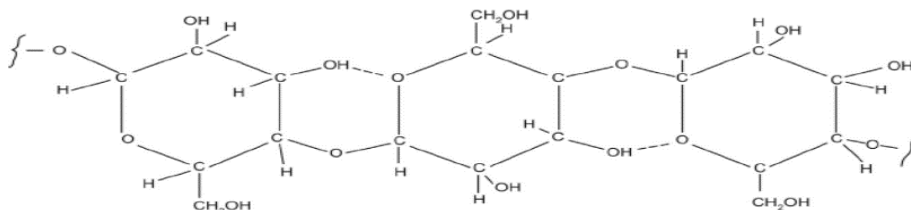


Figure 3: Typical chemical structure of cellulose. Source: Basu (2018b).

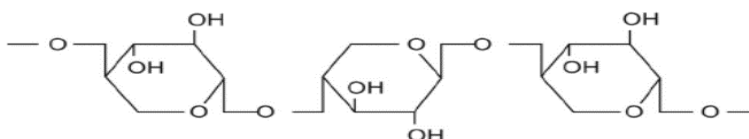


Figure 4: Molecular structure diagram hemicellulose / xylan. Source: Basu (2018b).

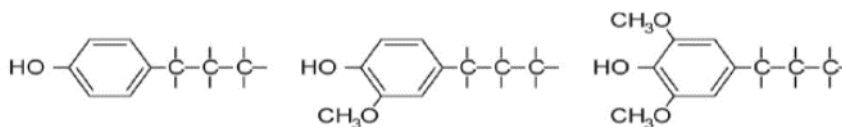


Figure 5: Some structural units / monomers of lignin; *p*-hydroxyphenyl, guaiacyl and syringyl respectively. Source: Basu (2018b).

Sugarcane bagasse and bagasse pellets were chosen as the biomass of interest in the study due to the sheer amount of the original waste left over from the Kenyan sugar industry, which often creates storage and disposal challenges. Sugarcane bagasse is a type of agro-industrial waste biomass that remains after milling and sucrose extraction from cane stalks (Martinez-Hernandez *et al.*, 2018). Sugarcane (*Saccharum officinarum* L.) is a valuable commercial field crop in the tropical regions, contributing to the economy as food, fodder, fibre, fuel and fertilizer (Heuzé *et al.*, 2018; OECD, 2016). In Kenya, sugar is produced mainly from sugarcane cultivated in the Nyanza (Migori, Nyando, and Kisumu Districts), Western Kenya (Mumias, Butere, Bungoma, Kakamega, and Busia areas) and Ramisi in Kwale County (Sugar Research Institute, 2021). This makes sugarcane one of the major crops grown within the country, generating over 2 million tons of bagasse from 2010 to 2016 and over 1.6 million tons from 2017 to 2019 (Agriculture and Food Authority, 2020). Despite being used in the sugar mills to produce heat for steam generation in boilers through direct burning,

comprising organic acid pollutants. Excess bagasse is therefore a potential resource for the region's renewable fuel development. Several technologies exist for turning bagasse into liquid, solid or gaseous biofuel. Nevertheless, pyrolysis appears as the most effective and promising approach for biofuel production (Charusiri and Vitidsant, 2017).

This study investigated the combustion properties of bagasse and bagasse pellets from Western Kenya, as well as the feasibility of the materials for the production of pyrolysis oil, which is a precursor potential raw material for the processing of clean transport fuel and other valuable chemicals.

MATERIALS AND METHODS

Sampling

Bagasse and bagasse pellets were sampled in compliance with the standard BS EN 14778:2011 (BSI, 2011a). West Kenya Sugar Factory provided fresh sugarcane bagasse, while Power-spot Pelletizers Limited provided bagasse

pellets. The factories are located in Kakamega County, western Kenya.

Samples of dewatered bagasse were collected using a fork / shovel, whereas bagasse pellets were collected with a scoop. To ensure sample representativeness, incremental sampling was performed to each bulk of product generated in the plant throughout the preceding week. All increments from a lot / sub-lot were merged and blended to generate one homogenous sample, which was then packed in airtight bags.

Sample Preparation

The samples were prepared using BS EN 14780:2011 protocol (BSI, 2011b). The fresh bagasse samples were naturally dried to a moisture content of $\leq 10\%$, whereas the bagasse pellets were not dried since the industrial processing of pellets requires a drying pre-treatment to a moisture content of $\leq 10\%$.



Figure 6: Sampling equipment; fork, shovel and scoop respectively .

Using rotary sample divider shown in Figure 7, laboratory samples were separated into sub-samples. The sub-samples for both the analytical and pyrolysis experiments were reduced to 1 mm in size using a cutting mill and then ground to a particle size of less than 500 microns (0.5 mm). The samples were held in closely sealed containers.

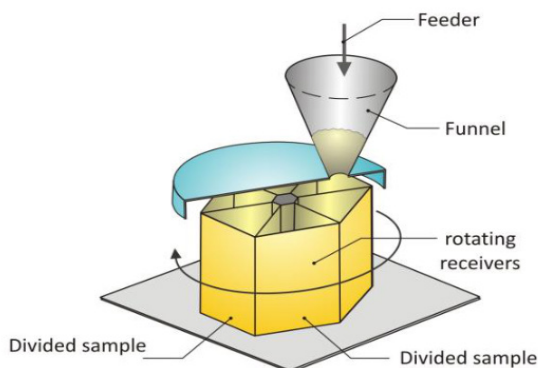


Figure 7: Rotary sample divider.

Characterization of Biomass / Feedstock Analysis

Proximate analysis of biomass

Bagasse and bagasse pellets biomass samples were analyzed for moisture, ash and volatile matter in conformity with the BS EN ISO standards 18134-1:20 (BSI, 2015b), 18122:2015 (BSI, 2017b) and 18123:2015 (BSI, 2017c). Analyses of ash and volatile matter were performed in a nabertherm and a carbolite furnace, respectively.

Moisture content: The oven dry technique defined in BS EN ISO 18134-1:2015 (BSI, 2015b) was used to determine the total moisture amount of the samples. The moisture content was evaluated by drying 200 g of the sample at $105 \pm 2^\circ\text{C}$ to a constant weight (4 hours) in the Memmert oven UF55plus. A reference tray similar to the tray used for sample analysis was used to correct buoyancy.

Ash content: Prior to sample analysis, porcelain dishes were first conditioned by heating and then cooling. Final ash content analysis was carried out at $550 \pm 10^\circ\text{C}$. A sample of 5.0 g of the general analysis sample was put in a porcelain dish and dried at 105°C . The dish and sample were then weighed. The dish and the sample were placed in a cold furnace and the furnace temperature gradually raised to 250°C over a period of 30 - 50 minutes (i.e., a heating rate of $4.5 - 7.5^\circ\text{C}/\text{min}$). The temperature was kept at that level for 60 minutes to let the volatiles leave the sample before it was ignited. A heating rate of $10^\circ\text{C}/\text{min}$ was used to raise the temperature of the furnace to $550 \pm 10^\circ\text{C}$ in 30 minutes. The temperature was then kept at that level for 125 minutes. The dishes and their contents were removed from the furnace, put on a heat-resistant plate and cooled for 5 to 10 minutes before being placed in a desiccator to cool to room temperature. After reaching room temperature, the dish and ash were weighed to 0.1 mg accuracy and the ash content on dry basis determined by the formula in BS EN ISO 18122:2015.

Volatile matter: The amount of volatile matter was assessed in a carbolite furnace at $900 \pm 10^\circ\text{C}$ (without air contact) for 7 minutes. To measure the quantity of volatile matter in the samples, cylindrical fused silica containers with well-fitting lids were first conditioned for 7 minutes at $900 \pm 10^\circ\text{C}$ and then cooled to ambient temperature in a desiccator. Pre-weighed empty crucibles with lids were filled with 1.0 ± 1.0

g of biomass material from the general analysis sample, lids were restored and the sample was evenly spread at the bottom before being put in a pre-heated furnace set to $900 \pm 10^\circ\text{C}$. The furnace door was closed and the samples were left inside for $7 \text{ min} \pm 5 \text{ s}$ before being taken out. The crucibles were cooled for 10 minutes on a heat-resistant surface before being cooled in a desiccator to ambient temperature and weighed to the nearest 0.1 mg. The formula contained in BS EN ISO 18123:2015 was used to determine the amount of volatile matter, V_p , in the test portion, in terms of mass on a dry basis.

Fixed carbon: The solid combustible residue that remains after heating a sample at $900 \pm 10^\circ\text{C}$ for 7 minutes and removing the volatile components is known as fixed carbon. In Equation 1, fixed carbon is represented as a calculated value that was determined empirically by subtracting the sum of the experimentally determined moisture, ash and volatile matter contents from 100 (% wt.) to arrive at a calculated value (% wt.). All proportions were computed using the same moisture reference basis.

$$\% \text{ FC} = 100 - (\% \text{ M} + \% \text{ A} + \% \text{ VM}) \dots\dots (\text{Equation 1});$$

where: M = Moisture content;
A = Ash content;
VM = Volatile matter;
FC = Fixed carbon.

Ultimate (elemental) analysis

The ultimate analysis is the quantification of hydrogen and carbon in organic wastes, as well as the estimation of sulphur, nitrogen and ash in the overall material, and the computation of oxygen by difference (ASTM, 2011). BS EN ISO 16948 and BS EN ISO 16994:2016 procedures were adopted for CHNS/O analysis (BSI, 2015a, 2016). CHNS analysis was done using the Elementar MACRO cube elemental analyser, which employs the modified Dumas Method for analysis as displayed in Figure 8.

In this procedure, 200 mg of a finely milled sample was accurately weighed to the nearest 0.1% (relative) for an analysis. The system was calibrated with three certified / standard reference materials and then examined for daily instrument drift correction factor by a separate certified reference material or standard reference material (CRM or SRM). The average peak area of blank sample analyses was subtracted from the elemental peak areas of the samples of interest. The moisture content, as-analysed, of the same samples was also determined at the same time, using a method described in BS EN ISO 18134-3 (BSI, 2015c). A different portion of the test samples was used for this purpose. The amount of carbon, nitrogen, hydrogen and sulphur of the biofuel samples as-analysed (Ad), were recorded as a percentage by mass and the results reported on dry basis, as mean duplicate determinations. The dry basis calculations of C, N, H and S were performed using the formulas shown in Equations 2 - 5.

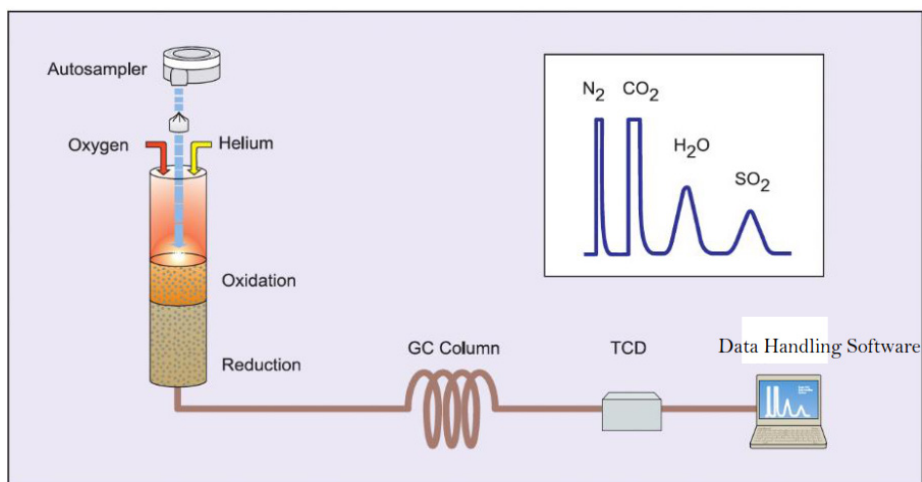


Figure 8: CHNS Elementar MACRO cube analyser setup. Source: Krotz and Giazzi (2014).

$$\text{Carbon content: } C_d = C_{ad} \times \frac{100}{100 - M_{ad}} \dots\dots\dots (\text{Equation 2});$$

$$\text{Nitrogen content: } N_d = N_{ad} \times \frac{100}{100 - M_{ad}} \dots\dots\dots (\text{Equation 3});$$

$$\text{Hydrogen content: } H_d = \left[H_{ad} - \frac{M_{ad}}{8.937} \right] \times \frac{100}{100 - M_{ad}} \dots\dots\dots (\text{Equation 4});$$

$$\text{Sulphur content: } S_d = S_{ad} \times \frac{100}{100 - M_{ad}} \dots\dots\dots (\text{Equation 5});$$

where: d = Dry basis;

ad = As-determined;

M_{ad} = Moisture content of the general analysis sample when analysed.

Oxygen was quantified by difference according to Equation 6.

$$\% O = 100 - \% C - \% H - \% N - \% S - \% A \dots\dots\dots (\text{Equation 6});$$

where: O = Oxygen percent of the biomass (% dry basis);

C = Carbon content of the biomass (% dry basis);

H = Hydrogen content of the biomass (% dry basis);

N = Nitrogen content of the biomass (% dry basis);

S = Sulphur content of the biomass (% dry basis);

A = Ash content of the biomass (% dry basis).

Calorific value / heating value

The heat generated by burning a unit amount of a material under specified conditions is known as its calorific value or heating value (ASTM, 2019). The calorific value of bagasse and bagasse pellets were evaluated using the established protocol in BS EN ISO 18125:2017 (BSI, 2017a).

Prior to determination of the calorific value, a general analysis sample was prepared to pass through a test sieve with a mesh size of 1.0 mm in compliance with EN ISO 14780:2011. Due to the low density of solid biofuel samples, bagasse pellets and bagasse samples were analysed in pellet form. The test component consisted of a pellet of mass 1.0 ± 0.2 g that was compressed with sufficient force to generate a compact, unbreakable test piece. The test portion may also be in powder form closed in a combustion bag or capsule. To allow for proper moisture adjustment in the analysis sample, the moisture content, M_{ad} , of the test sample was measured concurrently with the calorific value test, using the protocol outlined in BS EN ISO 18134-3. For the calorimetric combustion tests, the procedure indicated in 8.2.1 - 8.6 of the BS EN

ISO 18125:2017 standard was applied, with the same calorimetric conditions as in the calibration process stated in 9.2.2 of the same document. There are two different experiments that make up the calorimetric measurements: the burning of the calibrant (benzoic acid), followed by the combustion of the biofuel sample, both of which are performed under the same set of conditions. To determine the energy necessary to burn the biofuel sample, all secondary reactions' energy inputs are subtracted from the quantity $(\epsilon \times \theta)$, which reflects the total energy change for the bomb process. θ is the adjusted temperature increase, while ϵ is the effective heat capacity. Procedure steps 9.6 to 9.8 in BS EN ISO 18125:2017 was used to determine the value of effective heat capacity (ϵ). The formula in Equation 7 was applied to calculate the gross calorific value at constant volume.

$$q_{V,gr} = \frac{\epsilon_{(n)} \times \theta - Q_{fuse} - Q_{ign} - Q_N - m_2 \cdot q_{V,2} - \frac{Q_s}{m_1}}{m_1} \dots\dots\dots (\text{Equation 7});$$

where: $q_{V,gr}$ = Gross calorific value at constant volume of the fuel as analysed, in J/g;

$\epsilon_{(n)}$ = Mean value of the effective heat capacity of the calorimeter in J/K, or, J per some arbitrary unit;

Q_s = Correction for formation of sulphur dioxide from aqueous H_2SO_4 , in J;

m_1 = Mass (g) of the sample fuel;

m_2 = Mass (g) of the combustion aid (if relevant);

$q_{V,2}$ = Gross calorific value at constant volume of the combustion aid (if relevant), in J/g;

Q_{fuse} = Contribution from combustion of the fuse, in J;

Q_{ign} = Contribution from oxidation of the ignition wire, in J;

Q_N = Contribution from formation of nitric acid, in J;

θ = Corrected temperature rise, in K or in an arbitrary unit.

The gross calorific value at a constant volume of fuel as analysed was converted to a dry basis by correcting for the moisture content of the actual analysis sample, M_{ad} , by multiplying by a factor prescribed in EN 15296:2011 (BSI, 2011c), as indicated in Equation 8.

$$q_{V,gr,d} = q_{V,gr} \times \frac{100}{100 - M_{ad}} \dots\dots\dots (\text{Equation 8});$$

where: $q_{V,gr,d}$ = Gross calorific value at constant volume on dry basis, in J/g;

M_{ad} = Moisture content in the analysis sample, in % mass;

$q_{V,gr}$ = Gross calorific value at constant volume of the fuel as analysed, in J/g.

The net calorific value at constant pressure which is most cited for practical purposes was computed from the value of the gross calorific value (dry basis) as shown in the Equation 9. In this case, the elemental composition, i.e., nitrogen, hydrogen and oxygen of the fuel under test had to be known.

$$q_{p,net,d} = q_{V,gr,d} + 6.15 \times w(H)_d - 0.8 \times [w(O)_d + w(N)_d] - 218.3 \times w(H)_d \\ = q_{V,gr,d} - 212.2 \times w(H)_d - 0.8 \times [w(O)_d + w(N)_d]; \dots (Equation 9);$$

where: $q_{V,gr,d}$ = Gross calorific value at constant volume, in J/g, of the dry fuel;

$w(H)_d$ = Hydrogen content, in % wt., of the dry biofuel;

$w(O)_d$ = Oxygen content, in % wt., of the dry biofuel;

$w(N)_d$ = Nitrogen content, in % wt., of the dry biofuel.

In contrast, the net calorific value at constant volume was determined using solely the elemental value of hydrogen, as shown in Equation 10. In this case, the oxygen and nitrogen contents were irrelevant.

$$q_{V,net,d} = q_{V,gr,d} - 0.2122[w(H)_d] \dots (Equation 10)$$

NB: All the abbreviations are the same as before, except for the energy values that are expressed in MJ/kg.

Pyrolysis of bagasse and bagasse pellets

In a batch reactor, fast pyrolysis of bagasse and bagasse pellets were carried by heating the feed materials to 500°C and holding the temperature at 500°C. A heating rate of 50°C/min, particle size of 0.5 - 0.6 mm and 1 - 10 s of hot vapour residence time conditions applied. In separate batches, 800 g of air-dried bagasse and 1500 g of bagasse pellets were utilized as feedstocks for the fast pyrolysis experiment. Before heating, the reactor was purged for 20 minutes with an inert gas (helium/nitrogen) to remove air. The yields of bio-oil, char and combustible gases were determined. Figure 9 shows the experimental setup for the fast pyrolysis experiment, with pyrolysis oil as a main product.

The yields of bio-oil, char and permanent gases were calculated using the following equations (Equation 11–

Equation 13).

$$q_{V,net,d} = q_{V,gr,d} - 0.2122[w(H)_d] \dots (Equation 11);$$

$$\% \text{ Bio-oil yield} = \frac{\text{grams of bio-oil}}{\text{grams of bagasse/pellets}} \dots (Equation 12);$$

$$\% \text{ Char yield} = \frac{\text{grams of char}}{\text{grams of bagasse/pellets}} \times \dots (Equation 13).$$

Analysis of Pyrolysis Bio-oil

Water content

The water content of raw pyrolysis bio-oil was determined using the volumetric Karl Fischer titrimetric technique. The approach in ASTM E 203-01 was used because of its appropriateness for measuring water content across a wide concentration range, i.e., parts per million to pure water. A sample containing no more than 100 mg of water ought to be dissolved or dispersed in a suitable liquid and titrated with the KF reagent, which is composed of iodine, sulphur dioxide, an organic base and a solvent, often an alcohol such as methanol, ethylene glycol, or 2-methoxyethanol. Platinum electrodes register a sharp change in cell resistance when iodine is reduced by sulphur dioxide in the presence of moisture, which is applied to calculate the end point of the titration as shown in the general equation below (Equation 14):



where: RN = An organic base such as pyridine, and; R'OH = Alcohol.

The method comprises standardising the Karl Fischer reagent by employing methanol as a solvent, a water in methanol standard, a sodium tartrate dihydrate standard or a water standard to determine the water equivalent, F, of the KF reagent in mg/ml and then titrating the sample using the KF reagent. Calculation of the water content of the sample was done as per Equation 15.

$$\text{Water (\% wt.)} = ((A - B) \times F \times 0.001 \times 100)/W \dots (Equation 15);$$

where:

A = Millilitres of reagent required for titration of the sample;

B = Millilitres of reagent required to titrate solvent blank;

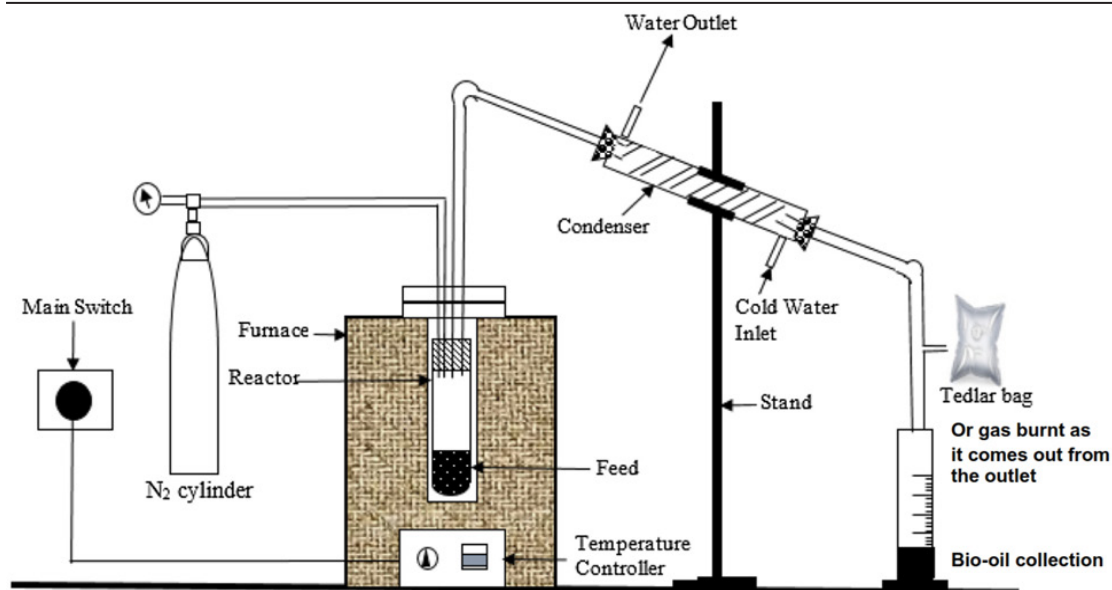


Figure 9: Fast pyrolysis of bagasse and bagasse pellets. Source: Varma & Mondal (2017).

F = Water equivalent, in milligrams of water per millilitre of KF reagent, and
W = Sample weight in grams.

pH

After a two-point calibration with buffer tablets of pH 4 and 7, the pH was measured directly using a Mettler Toledo pH metre model 1120-X by inserting the probe into the bio-oil contained in a vial and obtaining steady readings.

Density

Using a digital density metre, the density was measured according to the method specified in BS EN ISO 12185:1996/BS 2000 part 365:1996/ISO 12185:1996 (BSI, 1996). A small amount of the test sample, about 2 ml, was

placed in a temperature-controlled oscillating sample tube and the change in oscillation frequency caused by the tube mass change was utilised in conjunction with calibration data to determine the sample density. The sample injection was carried out manually. The density meter's calibration was validated by utilizing two different fluids of known density and noting the cell constants before inserting the sample test part into the cell using a syringe. The density meter displayed readings expressed to the nearest 0.1 kg/L, at a reference temperature of 20°C.

Elemental analysis (C, H, N, S and O)

For CHN analysis, the ASTM D 5291-16 (ASTM, 2016) procedure was used, and for sulphur analysis, the wavelength dispersive X-ray fluorescence (WDXRF) spectrometry described in BS EN ISO 20884:2019/

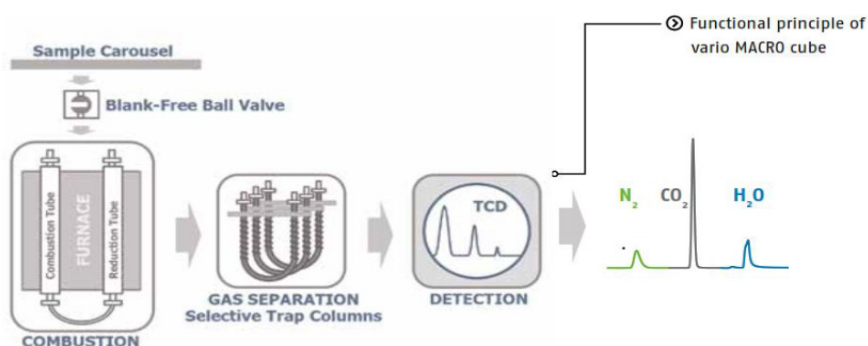


Figure 10: Vario MACRO Cube CHN Analysis Configuration for Bio-oil. Source: Elementar (2019).

ISO 20884:2019 (BSI, 2019) was applied. The carbon, hydrogen and nitrogen contents were determined using the Elementar Vario MACRO Cube CHNS elemental analyser configured to the conventional CHN mode as demonstrated in Figure 10. The basic premise of this kind of analysis is the same as that described here for solid materials.

For CHN analysis, the test protocol, test method C, in ASTM D 5291-16, section 9.3 (9.3.1 to 9.3.6), was used. The analytical procedure employed 5 mg of homogenous test material sealed in a tin capsule with forceps. Calibration was carried out with the use of a CHN standard / reference material (acetanilide) and the K factor as the calibration method. Three runs of a different reference material, CEDFNI (cyclohexanone 2,4-dinitrophenylhydrazone), were performed as unknown to verify the calibration. The concentrations of carbon, hydrogen, nitrogen and sulphur were calculated on an appropriate sample basis using Equation 16.

$$A = \frac{B \times E \times F}{C \times D} \dots\dots\dots \text{(Equation 16);}$$

where:

A = C, H, or N in the sample, expressed as a % mass;

B = Sample detector response for C, H, or N minus the blank detector response;

C = C, H, and N detector responses minus the blank response;

D = Sample's mass, in mg;

E = Mass of the standard, in mg, and

F = Mass % of C, H, or N in the standard.

The sulphur content of raw bio-oil was determined by exposing the sample to primary radiation from an X-ray tube in a sample cell. The count rates of S K-L_{2,3} X-ray fluorescence and, if necessary, the count rates of background radiation were measured. The sulphur content of the sample was then estimated using a calibration curve designed for the suitable measurement range.

To facilitate in the estimation of the oxygen content, the oil's ash content was also evaluated using BS EN ISO 6245:2002/BS 2000-4:2002 (BSI, 2002). The oxygen content was determined using the values of carbon, hydrogen, nitrogen, sulphur and ash content as indicated in Equation 6.

Calorific value / heating value

The calorific value of the raw bio-oil sample was calculated using the results of the CHNS/O analysis. The Vandralk formula (Nzihou *et al.*, 2014) shown in Equation 17 was used to estimate the higher heating value of the raw pyrolysis bio-oil. In order to get the lower heating value, a direct formula (Nzihou *et al.*, 2014) was used, which is shown in Equation 18.

$$\text{HCV (KJ/kg)} = 4.18 \times (85C + 270 \times H + 26 \times (S - O)) \dots\dots\dots \text{(Equation 17);}$$

$$\text{LCV (KJ/kg)} = 4.18 \times (94.19C - 0.5501 - 52.14 \times H) \dots\dots\dots \text{(Equation 18).}$$

The conversion from wet basis to dry basis was accomplished using the formulas presented in EN 15296:2011 standard (BSI, 2011c).

FT-IR analysis

The IR spectrum from the material was collected using a Shimadzu IRAffinity-1S ATR FT-IR spectrometer without further sample preparation. The bio-oil sample was placed on the ATR crystal for infrared spectral data acquisition. In terms of acquisition parameters, the wavelength range was 4000 - 400 cm⁻¹, a resolution of 4 cm⁻¹ and 50 scans for spectra averaging. LabSolutions IR software was used to manipulate the results originating from a highly-sensitive DLATGS (deuterated L-alanine doped triglycine sulphate) IR detector, i.e., spectra processing for baseline correction and smoothening of peaks.

RESULTS AND DISCUSSIONS

Biomass Characterization / Feedstock Analysis

Proximate analysis of biomass and calorific value

Figures 11-16 illustrate the results of proximate and calorific analyses of sugarcane bagasse and bagasse pellet biomass samples.

The dry ash free and dry mass base proximate analysis results and calorific values were higher than the received basis (% wet mass). The findings indicate that wet biomass fuel is characterized by a lower volatile matter content, a lower fixed carbon content and a lower calorific value than dry biomass fuel. Moisture content is determined on the sample as received; on a dry basis, the moisture content is presumed to be zero. Bagasse had a higher moisture percent than bagasse pellets with 6.94 ± 0.01% and 5.79 ± 0.05%. respectively. Despite this fact, bagasse still had

better combustion properties than the pellets. Generally, in terms of volatile matter, fixed carbon and heating value, air-dried fresh bagasse from the sugar mill outperformed bagasse pellets, although the variations in fixed carbon content were insignificant at 95% confidence level.

Proximate analysis data on a dry matter basis (% dry mass) and as received basis (% wet mass) indicate that fresh dried bagasse from the sugar factory has less ash content

and more volatile matter than bagasse pellets from the pelleting plant. As a result, bagasse from the sugar plant is more suited for both combustion and pyrolysis operations than bagasse pellets. The bagasse pellets have high ash content but favourable amount of volatile matter and fixed carbon. Bagasse and bagasse pellets are both suitable for combustion and pyrolysis operations (production of pyrolysis bio-oil), but bagasse may perform better than

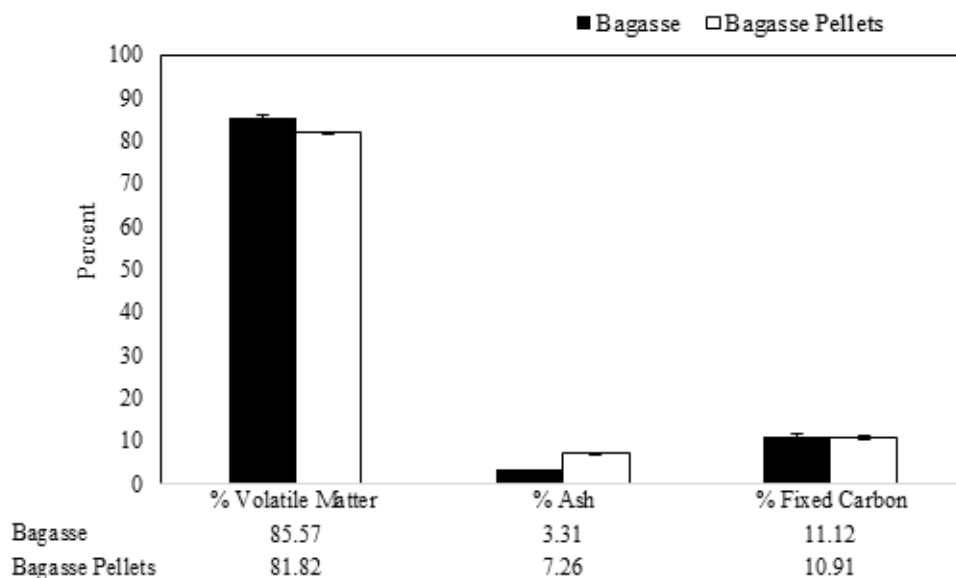


Figure 11: Proximate analysis of bagasse and bagasse pellets (% dry mass).

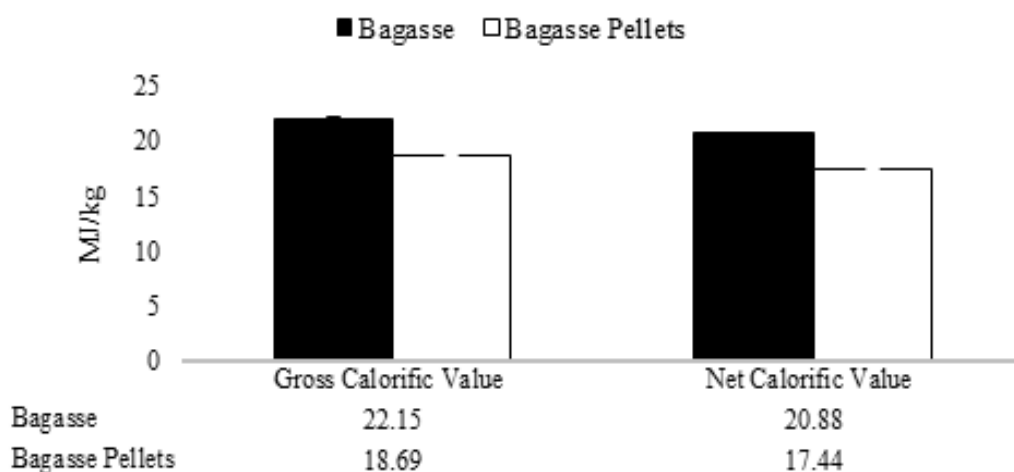


Figure 12: Calorific value of bagasse and bagasse pellets (% dry mass).

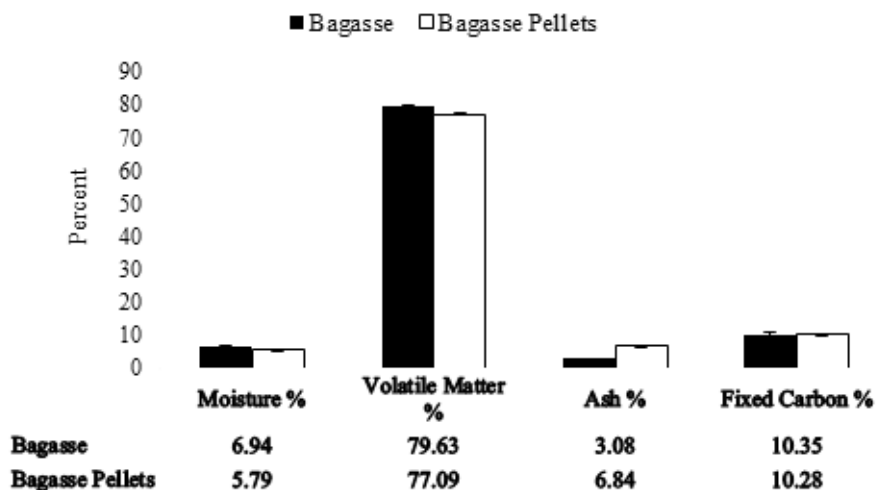


Figure 13: Proximate analysis of bagasse and bagasse pellets (% wet mass).

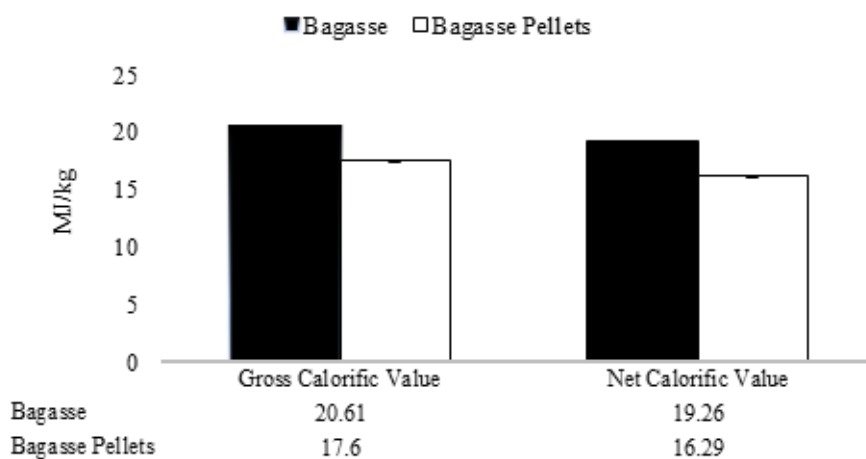


Figure 14: Calorific value of bagasse and bagasse pellets (% wet mass).

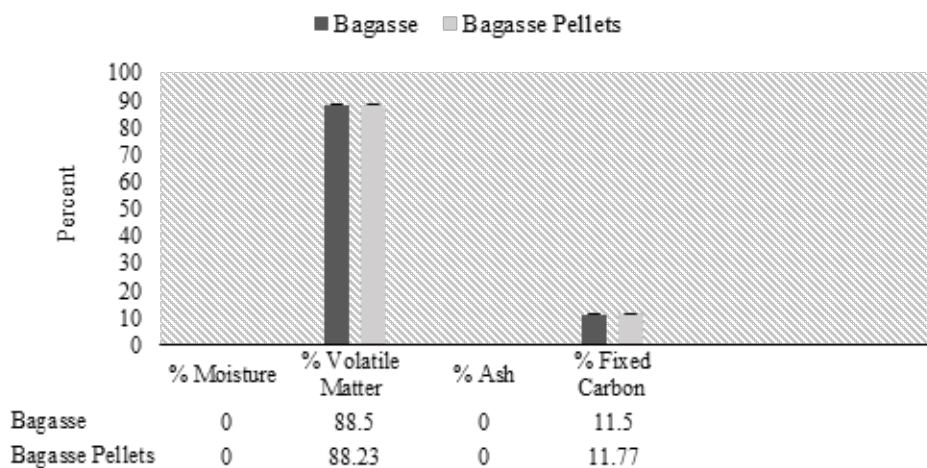


Figure 15: Proximate analysis of bagasse and bagasse pellets (% DAF).

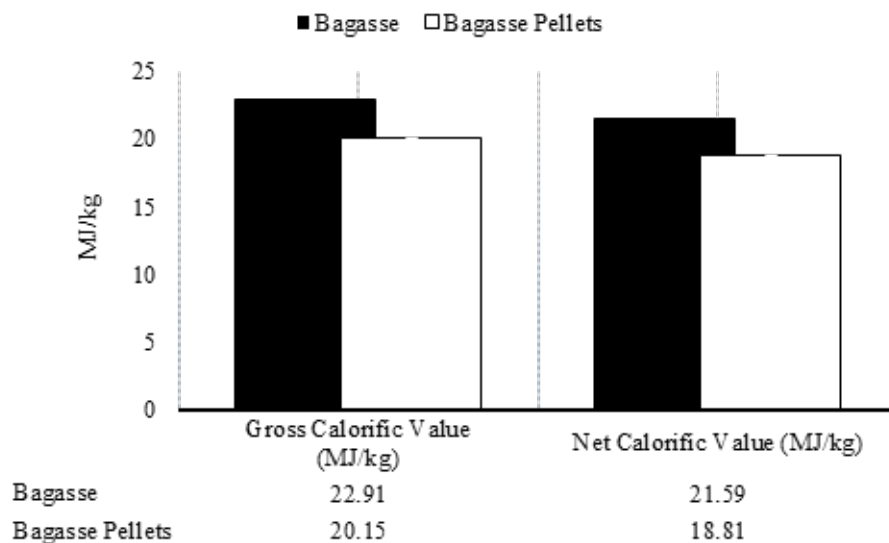


Figure 16: Calorific value of bagasse and bagasse pellets (% DAF).

bagasse pellets. Due to its high volatile matter content and low ash percentage, bagasse is expected to produce more pyrolysis oil and have a higher calorific value than bagasse pellets, as attested by this investigation.

A biomass with a high volatile matter proportion devolatilizes faster and is more reactive compared to one with a low volatile matter content, making it better suited for pyrolysis (Varma and Mondal, 2017). High ash in biomass complicates the thermochemical conversion process by lowering the rate of burning and raising the risk of fouling, slag formation and corrosion in pyrolysis reactors (Varma and Mondal, 2017). The results of this study support the aforementioned assertion.

It is widely accepted that the heating value of a fuel is one of the major criteria used to compare different kinds of fuels. While moisture in biomass typically lowers its heating value, ash and extractive content are two major characteristics that directly affect the heating value. A biomass fuel with a high ash percentage is not desirable, while the same kind of fuel with high extractive content is more attractive (Demirbas, 2002). As seen in this research, the high calorific value of fresh untreated dry bagasse compared to bagasse pellets is due to the higher fixed carbon, volatile matter and lower ash content.

Ultimate (elemental) analysis

The ultimate analysis data for bagasse and bagasse pellets is presented in Figures 17 - 19. The results are presented

in three different bases: dry matter basis (% dry mass), as-received basis (% wet mass) and dry ash-free basis (% DAF).

When ash and moisture are absent (dry ash-free basis), the level of elements in a sample remains the same but their concentration increases due to a decrease in the overall weight of the sample. Therefore, dry ash-free results ultimate analysis results are greater than as-received basis (% wet mass) and dry matter basis (% dry mass) results. As a result, removing moisture and ash from a biomass sample boosts its elemental content and calorific value. Note that when biomass is dried, its weight goes down, so the percent weight to weight (% w/w) elemental concentration goes up. The weight of the elements (C, H, N, S, O and Cl) in biomass does not change, but their concentrations do change as a result of the reduced weight of the dry biomass material compared to the wet material. Due to the fact that biomass ash is primarily inorganic, the dry ash-free assumption has no effect on the weight of the organic components, i.e., C, H, N, S, O and Cl, but the concentration of the organic components increases because the weight of the dry ash-free sample material is reduced in comparison to the weight of the wet and dry biomass material. The findings on a dry matter basis are likewise higher than the results on an as-received basis due to the absence of moisture. Bagasse and bagasse pellets have no substantial variations in their elemental composition when the results of similar elements are

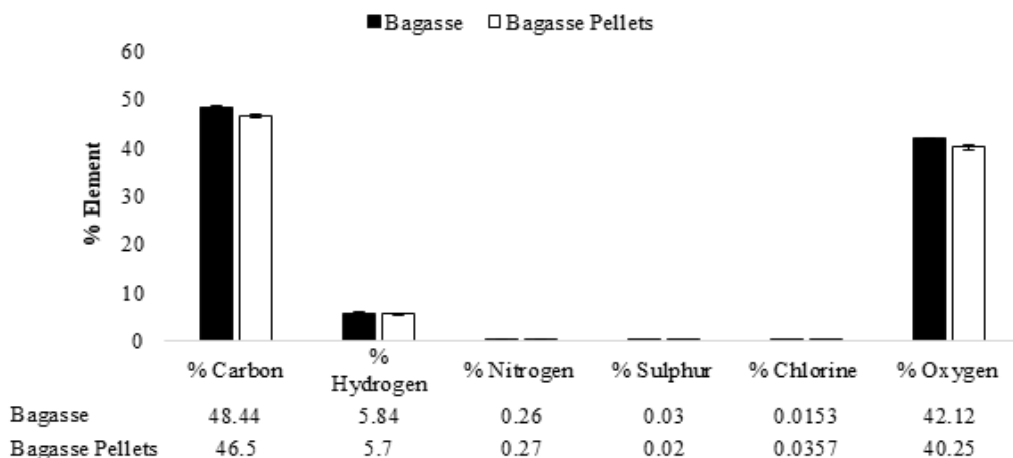


Figure 17: Ultimate analysis results for bagasse and bagasse pellets (% dry mass).

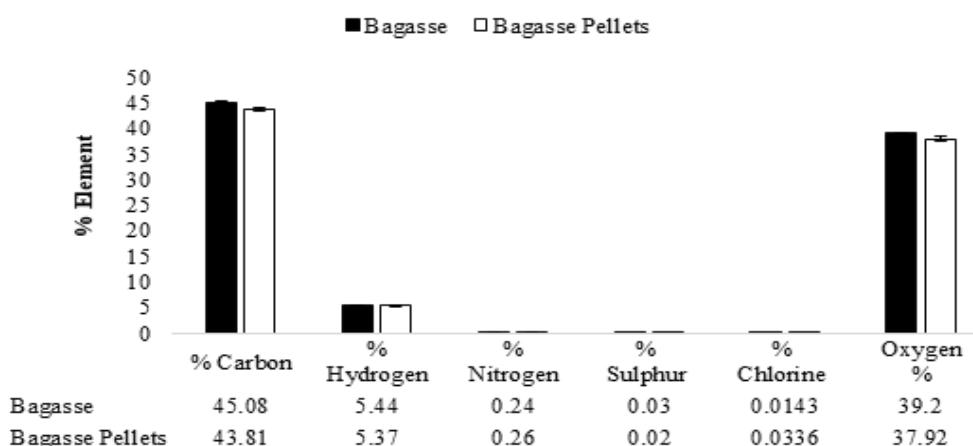


Figure 18: Ultimate analysis results for bagasse and bagasse pellets (% wet mass).

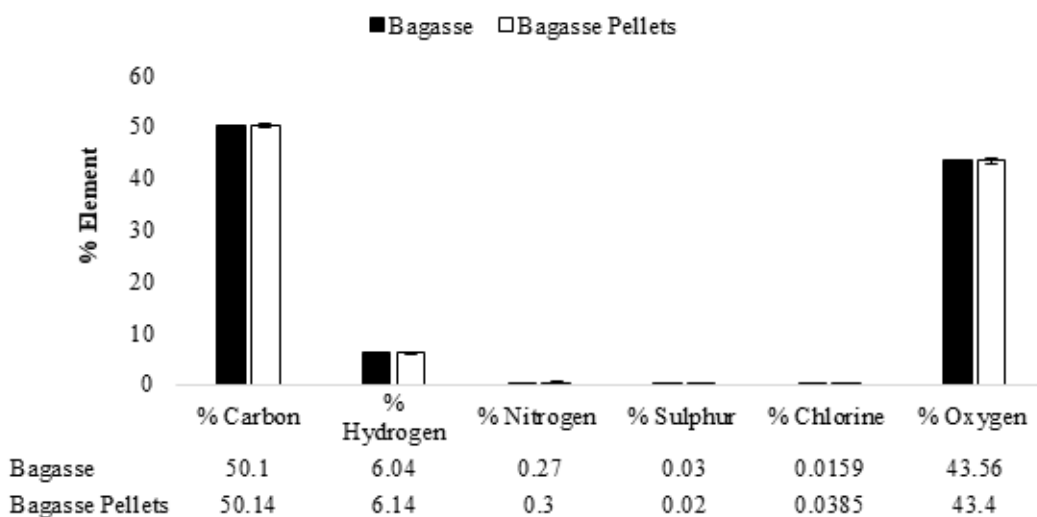


Figure 19: Ultimate analysis results for bagasse and bagasse pellets (% DAF).

compared on a dry ash-free basis.

According to the Vandralek formula and Dulong's equation, biomass's higher heating value is significantly and directly related to the quantity of carbon, hydrogen and sulphur in a sample (Nzihou *et al.*, 2014). The quantity of elemental oxygen in a sample is theoretically a limiting factor for its calorific value. The calorific value, also known as the heating value (HV), is influenced by the chemical content of the material and is independent of moisture content (Celignis Analytical, 2022). The heating value and the carbon content of a biomass sample have a direct proportionality relationship, whereas oxygen, nitrogen and inorganic components (ash) tend to lower the value (Celignis Analytical, 2022). For lower heating value, hydrogen is additionally a reducing factor.

Bagasse and bagasse pellets derived from sugarcane in Western Kenya contain trace quantities of nitrogen, sulphur and chlorine. Nitrogen ranges from 0.24 - 0.30 %, sulphur from 0.02 - 0.03 % and chlorine from 0.0143 - 0.0385 %. Carbon is the most abundant element by weight in the sugarcane bagasse materials, followed by oxygen and hydrogen, respectively. The elemental concentration varies as follows: carbon 43.81- 50.14%, hydrogen 5.37 - 6.14% and oxygen 37.92 - 43.56%. The presence of trace levels of nitrogen, sulphur and chlorine in biomass provides it an advantage over other fossil fuel sources that contain significant amounts of these components and hence cause environmental pollution. The high concentration of oxygen in bio-oil is due to the high oxygen content of the biomass feedstock used to produce it.

Pyrolysis of Bagasse and Bagasse Pellets

Figure 20 summarises the yield of bio-oil, char and gases for the pyrolysis of bagasse and bagasse pellets.

The yield of bio-oil from pyrolysis of bagasse and bagasse pellets is shown in Table I. The highest oil yield from bagasse and bagasse pellets was 46.21 wt.% and 43.69 wt.%, respectively. The difference in pyrolysis oil yields between bagasse and bagasse pellets might be attributable to their different ash and volatile matter contents; bagasse contains more volatile matter and less ash than bagasse pellets. Volatile matter inherent in biomass is critical for bio-oil production, as a higher level of volatile matter results in enhanced bio-oil production (Paul *et al.*, 2020; Singh and Anil, 2013). The ash concentration of biomass indicates the existence of alkali metals, which have an effect on the generation of bio-oil.

TABLE I-BAGASSE BIO-OIL YIELD (WT. %).

Run	1	2	3	Mean
Bagasse	44.05	46.21	46.03	45.43
Bagasse Pellets	42.17	43.36	43.69	43.07

A higher amount of alkali and other metals, such as Na, K, Ca, Mg, Zn and Cd during fast pyrolysis results in the formation of charcoal, the formation of more ash, a reduction in volatile matter, the development of sludge and promotion of gasification (Minowa *et al.*, 1995; Pattiya, 2011; Peacocke and Bridgwater, 1994; Samolada *et al.*, 1990; Singh and Anil, 2013).

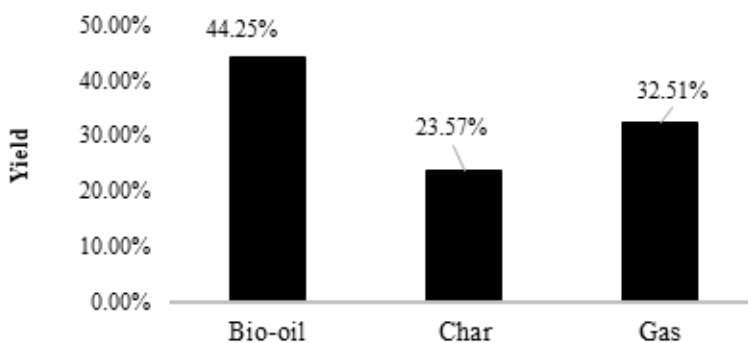


Figure 20: Average overall yield of pyrolysis products for bagasse & bagasse pellets.

Analysis of Untreated Pyrolysis Bio-oil

The following characteristics were determined for raw pyrolysis oil derived from bagasse biomass: water content, pH, density, elements (C, H, N, S and O), calorific value and chemical functional groups (FTIR).

Water content, pH, density, elements (C, H, N, S and O) and calorific value

Table II summarises the findings of the Bio-oil Characteristics: water content, pH, density, elements, and calorific value. Using the methods described, neither ash nor nitrogen were detected in the bio-oil sample. The water content of 21.21% and the oxygen content of 47.05% render the pyrolysis oil unsuitable for use as fuel, necessitating an improvement to bring the water content and oxygen level closer to that of conventional motor fossil fuels. The high amount of oxygen decreases the energy capacity of bio-oil by 50% when compared to ordinary hydrocarbon fuels and also renders it insoluble in conventional petroleum fuels, hence the difficulty in blending (Muley *et al.*, 2015; Zhang *et al.*, 2007). The lower heating value of between 16.68 - 21.17 MJ/kg and higher heating value of between 18.95 and 24.05 MJ/kg is still relatively not suitable for ignition and can improve after catalytic reformation of the bio-oil or hydrodeoxygenation. The low acidity, with a pH of 2.42, is mostly due to the presence of carboxylic acids. Acidity renders bio-oil very corrosive and particularly harsh at high temperatures (Zhang *et al.*, 2007). The main benefit of oil obtained from biomass is the existence of trace or no amounts of nitrogen and sulphur, as shown by the data in Table II and as compared with the elemental amounts in fossil fuels. The pyrolysis oil produced from bagasse had a low content of nitrogen below the detection limits of the instrument and 0.0028% (28.4 mg/kg) of sulphur. In 2007, the sulphur content of motor gasoline, diesel, light fuel oil and heavy fuel oil derived from crude oils, coal or bituminous sand in Canada was 0.41%, 0.96%, 2.30% and 85.91% respectively (Raseeka *et al.*, 2009). Therefore,

using bio-oil as a fuel has negligible or no effect on the environment, unlike fossil fuels.

It is anticipated that reforming the oil by hydrodeoxygenation using a catalyst such as Pd/ γ -Al₂O₃, Pt/ γ -Al₂O₃, Pd/ZrO₂ or Pt/ZrO₂ would improve the oil quality and boost its energy density by removal of water and oxygen.

TABLE II- RAW BIO-OIL CHARACTERISTICS.

No.	Analysis Parameter	Unit	Value
1.	Water content [as received]	% Wt.	21.21 ± 0.08
2.	pH	-	2.42 ± 0.04
3.	Density	kg/L	1.20 ± 0.54
4.	Ash [as received]	% Wt.	0.00
5.	Elemental analysis		
	Carbon	% Wt.	46.14 ± 0.89
	Hydrogen	% Wt.	6.80 ± 0.35
	Nitrogen	% Wt.	0.00
	Sulphur	% Wt.	0.0028 ± 0.0001
	Oxygen [calculated]	% Wt.	47.05 ± 0.96
6.	Calorific value/Heating value (calculated)		
	HHV [dry basis]	MJ/kg	24.05 ± 1.36
	LHV [dry basis]	MJ/kg	21.17 ± 0.96
	HHV [as received]	MJ/kg	18.95 ± 1.36
	LHV [as received]	MJ/kg	16.68 ± 0.96

FT-IR analysis

Figures 21 and 22 show the FT-IR spectra of bagasse pyrolysis oil (bagasse feedstock from western Kenya) and pinewood pyrolysis oil from BTG Bioliquids Co. Ltd in Netherlands. The spectra are equivalent in terms of functional groups (peaks), implying similar chemical characteristics, though peak intensity varies.

The FT-IR assignments for the bagasse pyrolysis oil and pinewood pyrolysis oil from BTG Bioliquids are shown in Table III.

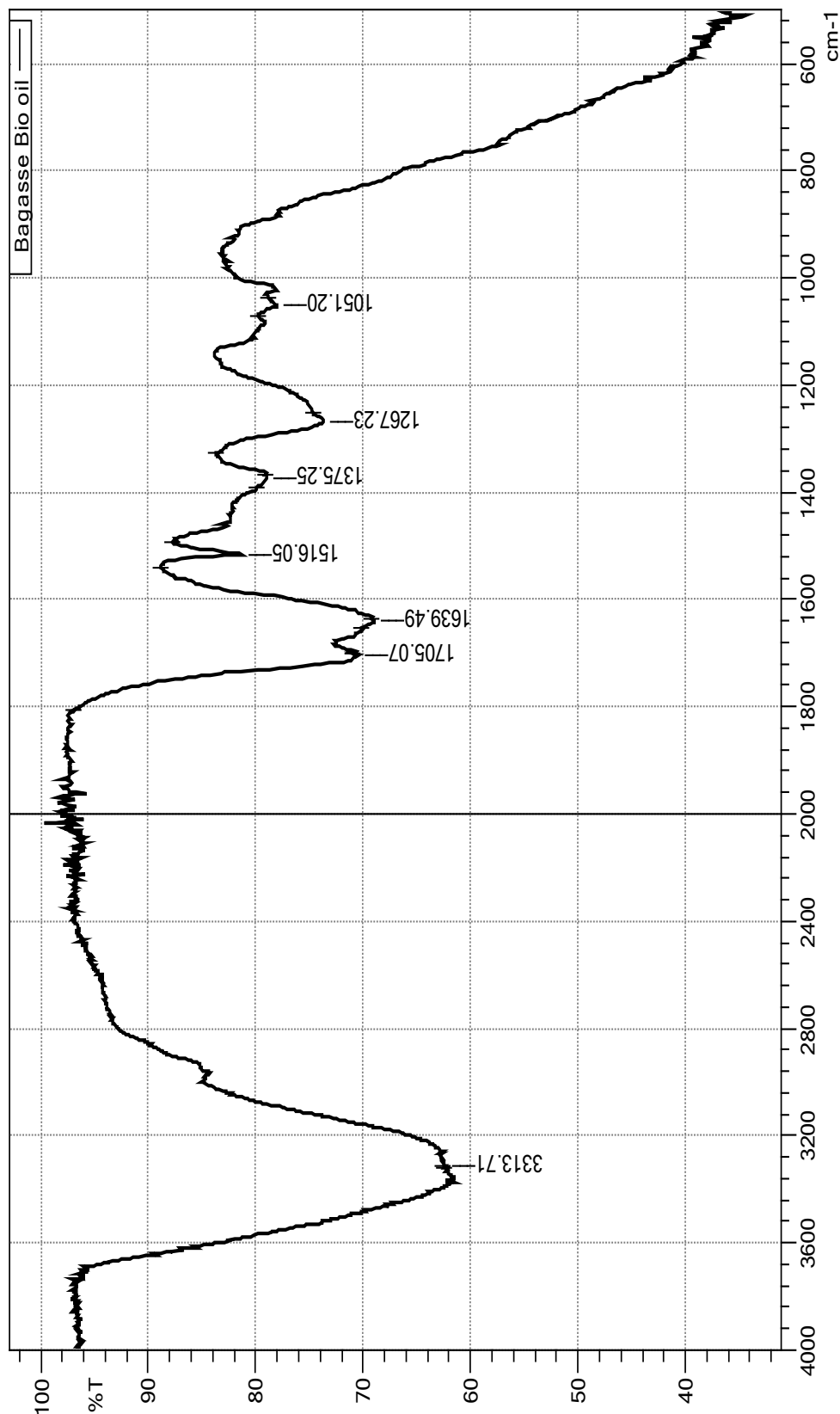


Figure 21: Infrared spectra of raw bagasse pyrolysis oil.

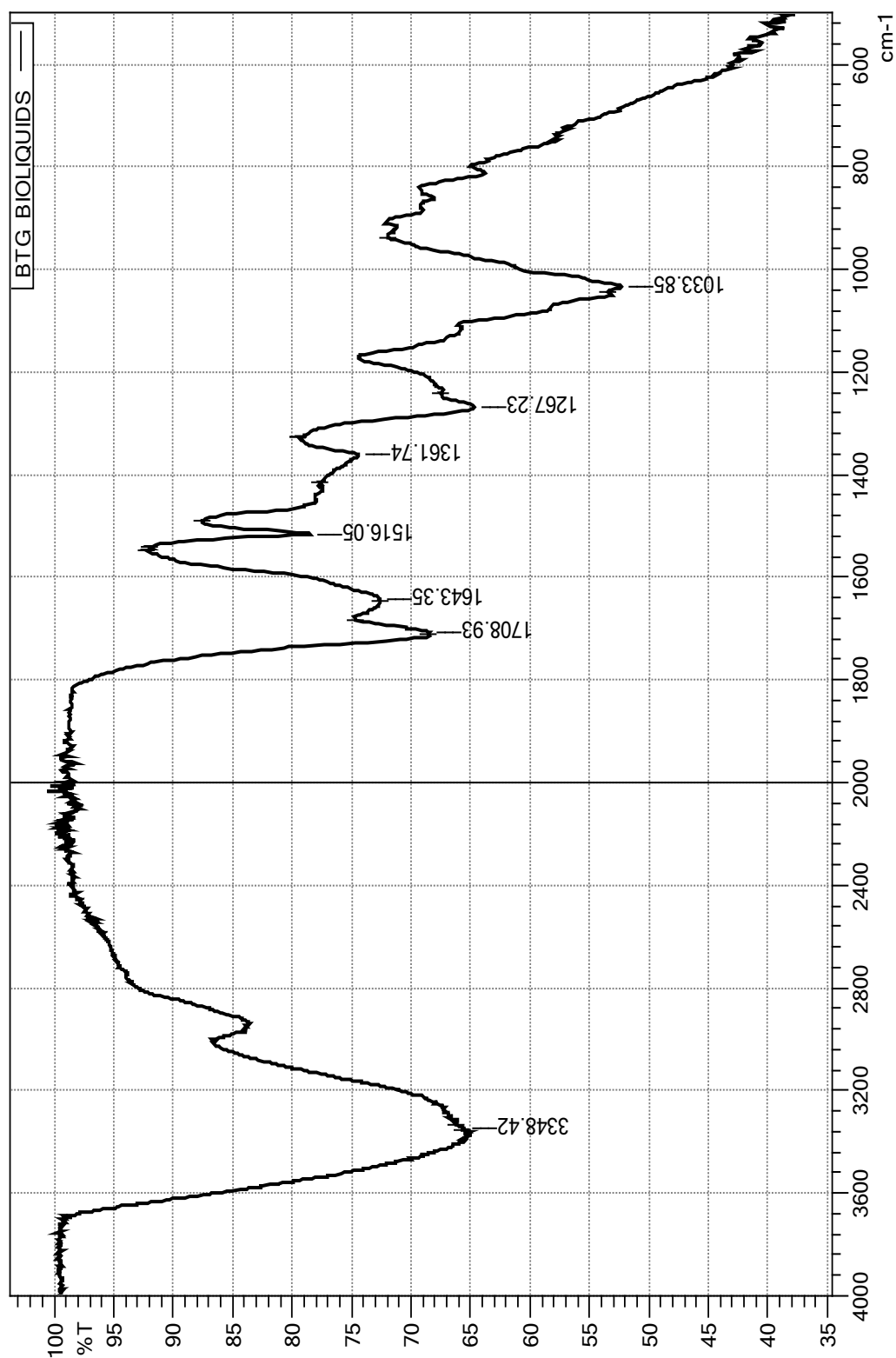


Figure 22: Infrared spectra of raw pinewood pyrolysis oil from BTG bioliquids.

TABLE III- FT-IR ASSIGNMENTS FOR BAGASSE AND PINEWOOD PYROLYSIS OILS.

Bagasse Bio-oil	Pinewood Bio-oil	Type of Vibration	Nature of Functional Group
3313.71/cm	3348.42/cm	O-H stretching	Phenols and alcohols
1705.07/cm	1708.93/cm	C=O stretching	Aldehydes, ketones, carboxylic acids, esters
1639.49/cm	1643.35/cm	C=C stretch, Aromatic skeletal vibration (C=C)	Olefins (alkenes), benzene ring
1516.05/cm	1516.05/cm	C=C aromatic skeletal vibration, guaiacyl > 5	Phenolic compounds, aromatic hydrocarbons
1375.25/cm	1361.74/cm	C-H scissoring and bending	Alkanes
1267.23/cm	1267.23/cm	C-O of guaiacyl ring, ether C-O stretching	Phenolic compounds
1051.20/cm	1033.85/cm	C-O stretch	Alcohols

The peaks wavenumbers as illustrated in Table III reveals that the raw pyrolysis oil samples (bagasse oil and pinewood oil from BTG Bio-liquids) contain compounds with similar functional groups, indicating identical chemical composition. The chemical components are phenolic compounds / alcohols, carbonyl compounds (aldehydes, ketones, carboxylic acids and esters), olefins (alkenes), alkanes and aromatic hydrocarbons.

CONCLUSIONS

Bagasse and its processed components have the potential to be used as a solid biofuel as well as in the production of bio-oil through fast pyrolysis. Bagasse has an estimated potential energy value of 20.88 MJ/kg on a dry basis and 21.59 MJ/kg on a dry ash free basis (DAF). The pyrolysis experiment carried out under this study produced a maximum yield of 46.21% of bio-oil with a maximum mean average for the runs at 45.43%.

Untreated sugar factory bagasse has superior combustion characteristics and yields more pyrolysis bio-oil than treated bagasse (bagasse pellets). Fresh bagasse yielded a maximum of 46.21% bio-oil while bagasse pellets produced a maximum yield of 43.69%.

Biomass (bagasse) is an abundant natural resource waste that can be recovered for the production of clean green fuel with extremely low emissions of sulphur and nitrogen pollutants into the environment.

Bagasse pyrolysis oil contains a wide range of chemical constituents, including phenols, alcohols, alkanes, olefins, aldehydes, ketones, carboxylic acids and esters; these components may be converted into sustainable fuel or used to manufacture specialized chemical compounds.

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