

PREPARATION OF BIOCHARS FOR CO-GASIFICATION FROM SWEET SORGHUM BAGASSE

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ABSTRACT: Biochar is a solid product obtained through torrefaction, liquefaction or pyrolysis of organic material. It can be used for soil amendment, activated carbon for sequestration, or as bio-coal for gasification or co-gasification. A recent patent on GreenCoal showed the potential of biochar to lower sulphur emissions and increase coal reactivity during co-gasification with low grade discard coal. Co-gasification of biochar and coal with increased reactivity, translated to increased syngas production using existing synthetic fuel plants without the need for modifications to accommodate biomass in the feed. In this study biochar for co-gasification purposes was produced from sweet sorghum bagasse using hydrothermal liquefaction at low heating rates ($2.5 \text{ K}\cdot\text{min}^{-1}$) in large (1 L) reactors. The effect of reaction temperature and biomass loading on biochar yield and characteristics were investigated with and without the addition of a calcite (CaCO_3) catalyst. Prepared biochars were characterised using SEM, ultimate analysis, proximate analysis, BET, XRD/XRF and FTIR. High biochar yields ($558.7 \text{ g}\cdot\text{kg}^{-1}$ bagasse) were obtained with very little oil and gas products forming. Biochar yields decreased with an increase in temperature and increased with an increase in biomass loading. Elemental analysis showed an increased higher heating value (HHV) for all the prepared chars compared to the original bagasse. Characterisation of the chars showed that the additional of a calcite catalyst increased the biochar yields and significantly changed the structure of the chars. The study showed that lignocellulose materials such as sweet sorghum bagasse can be used to prepare biochars with characteristics similar to young lignite coal, without the minerals and sulphur present in it.

Keywords: Biochar, coal, co-gasification, bagasse, liquefaction.

1 INTRODUCTION

Coal is one of the most important sources of energy, accounting for 36% of worldwide electricity production. The last decade has seen a rapid increase in bio-energy research to find alternative sources of energy to alleviate the pollution that is associated with the use of coal [1].

Coal drying techniques result in the production of high volumes of coal fines due to the weak structure of coal caused by the removal of water. Coal fines negatively influences the environment, adds pressure to the resources demand and creates a number of safety hazards [2]. According to Reddick et al. [3], South Africa disposes of approximately 10 million tons of ultra-fine coal ($<150\mu\text{m}$) annually, as high dewatering costs surpasses the value of the coal.

International standards consider the coal in South Africa as low grade coal. Approximately 89% of mined coal is usable in gasification and electricity generation, while the rest consists of fine coal that has a high moisture and ash content, making it unsuitable for industrial use as it decreases the equipment lifespan of the coal fired-furnace plants. Environmental and economic pressures associated with fine coal storage and processing is creating urgency for the recovery and utilization of fine coal discards. Methods that convert ultra-fine coal to a more valuable product include extrusion, pelletizing and briquetting [3,4].

According to Osman et al. [2], briquetting minimizes the moisture content in the fine coal, facilitates the correct size of particle and increases the calorific value and density of the coal. Coal binders are required to bind the fine coal into a briquette that can then be used in a similar manner than lump coal. The raw material properties, process conditions prior to agglomeration and the amount of binder added to the fine coal mainly influences the stability of the briquette.

Thermochemical liquefaction involves the conversion of organic compounds through a complex set of repolymerisation and oxygen removal reactions into a liquid, solid and gas products in the presence of a suitable

catalyst [5]. The use of biochar as binder for fine coal briquettes has potential for lowering the sulfur emissions during gasification and increasing the coal reactivity through the presence of alkaline earth metals present in the biomass [6].

In this study the production of biochar from sweet sorghum bagasse to be used as binder for fine coal briquettes for co-gasification was investigated. The biochar was produced at high solids loadings and the influence of a calcite catalyst on the char structural and compositional characteristics were investigated.

2 MATERIALS AND METHODS

2.1 Sweet sorghum bagasse

Sweet sorghum bagasse was obtained from Agricol Research Institute ($26^{\circ}43'37.6''\text{S}$, $27^{\circ}04'48.2''\text{E}$) near Potchefstroom, South Africa. The syrup was pressed from the plant stalks and the bagasse left after pressing the syrup from the stalks were sun dried to an approximate moisture content of 10 wt%. The dried bagasse was milled to -1.5 mm using a hammer mill and was then stored in air tight bags in the laboratory at 22°C until used in the experiments. The compositional analysis of the dried and milled bagasse is given in Table I.

Table I: Compositional analysis of sweet sorghum bagasse used in this study.

Component	Wt%
Dry matter	92.6
Moisture	7.4
Protein ¹	9.4
Fat ¹	1.1
Ash ¹	8.5
Total carbohydrates ¹	69.6
Cellulose ¹	31.3
Hemicellulose ¹	25.4
Lignin ¹	5.3
Volatile matter ($\text{g}\cdot\text{kg}^{-1}$)	699.5

Fixed carbon (g.kg ⁻¹)	174.0
C content ²	47.4
H content ²	6.2
N content ²	0.4
O content ²	60.5
HHV (MJ.kg ⁻¹)	15.34

1 Reported on a dry basis

2 Calculated on a dry ash free basis

2.2 Experimental method

Thermochemical liquefaction was performed using a grade 316 stainless steel autoclave equipped with a removable heating jacket and magnetic stirrer. The autoclave having a volume of approximately 0.954 L is illustrated in a schematic representation in Figure 1.

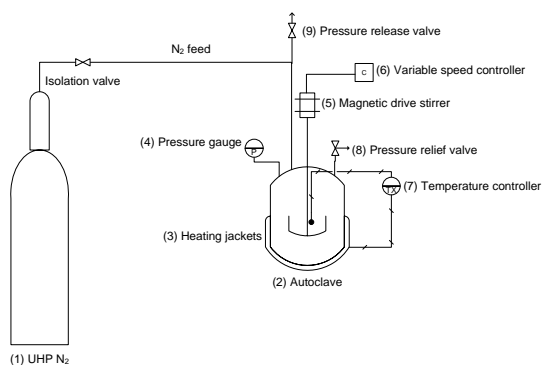


Figure 1: Schematic of liquefaction reactor

In a typical experiment, the required amount of milled bagasse (10-90 wt%) and water was added to the reactor. The sealed reactor was purged with nitrogen for 10 minutes to remove all residual air. The initial pressure in the reactor was 5 bar nitrogen pressure and experiments were done at temperatures of 280°C and 320°C at a heating rate of 2.5 K/min. After the desired temperature was reached, the temperature was kept constant at the chosen reaction temperature for 30 minutes at a constant stirrer speed of 720 rpm. After completion of liquefaction, the reactor was allowed to cool down to room temperature after which a gas sample was taken for analysis. After the residual gas was purged, 100 mL of chloroform was added to the reactor products and stirred for approximately 10 minutes to enable successful extraction of products.

The solid products were recovered from the chloroform mixture through vacuum filtration (Whatman no.10). The char was washed repeatedly with chloroform to remove all oil residues. After vacuum filtration, the solid char was dried in an oven at 105°C for 12 hours to remove any residual chloroform or moisture. The filtrate was transferred to a separation funnel and washed with water to remove all water soluble components. The water and chloroform layers were allowed to settle by gravity. After decantation, the chloroform was removed from the oil by means of vacuum evaporation. The oil layer was then dried at 105°C for 12 hours to remove all residual moisture. The dried char and oil weights were recorded to determine the biochar and bio-oil yields.

2.3 Compositional analysis

2.3.1 Proximate analyses

A Thermo-gravimetric Analysis (TGA) system from U-THERM (China) was used to perform a proximate analysis on the samples. This analysis determines the weight percentages of fixed carbon (by difference), volatile matter, moisture and ash content in the biochar and original biomass sample. The moisture of the biomass was determined using a standard method (ASM013) by drying in an oven at 105°C for 16 hours.

2.3.2 Elemental analyses (Ultimate analysis)

Elemental analysis determines the weight percentage of carbon, nitrogen, hydrogen, sulfur and oxygen. A CE-440 Elemental analyzer (EAI Exeter Analytical Inc.) was used to determine the elements in the biochar as well as in the biomass. The empirical H/C and O/C ratios were calculated for each sample using the elemental analyses results.

2.3.3 Higher heating value (HHV)

The heating value of the samples was determined using an IKA@C500 bomb calorimeter and compared to a calculated heating value determined by the elemental analyzer results. The calorimeter ignites the sample in an oxygen rich atmosphere and the temperature increase is measured per kilogram of the loaded sample. The analyses results in an energy content (MJ/kg) in order to determine the calorific value for each sample. The higher heating value was also determined using a developed correlation represented by the following equation [7].

$$\text{HHV} = 0.3137\text{C} + 0.7009\text{H} + 0.0318\text{O} - 1.3675$$

2.3.4 Fourier-transform Infrared spectroscopy (FTIR)

Functional groups on the surface of the biochar, biomass and bio-oil samples was determined using infrared spectroscopy on an IRAffinity-1 Fourier transform infrared spectrophotometer, Shimadzu (Japan). The samples were recorded between the ranges of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ and 42 scans per sample.

2.3.5 Gas chromatography

The composition of bio-oil samples were determined with gas chromatography (Agilent 7890, equipped with a 7683B autoinjector and HP-5 capillary column (30m x 320 μm x 0.25 μm) and a flame ionization detector (FID)). Samples were derivatized with trimethyl sulfonium hydroxide (THSH) and dodecane was used as internal standard. Fatty acids were quantified using a set of standard calibration curves.

The composition of the gas phase was qualified and quantified using gas chromatography (Agilent 6890A, equipped with a GS-GASPRO column (60m x 0.32 mm) and thermal conductivity detector (TCD) in series with a FID detector).

2.4 Structural analysis

2.4.1 Scanning electron microscopy (SEM)

A FEI Quanta 250 FEG (Field Emission Gun) ESEM (Environmental Scanning Electron Microscope) in high vacuum was used to analyze the biomass and biochar samples. The voltage of the instrument was maintained at 10 kV.

2.4.2 Brunauer-Emmet-Teller (BET)

The surface area of the biochar was determined using BET analysis. A micromeritics Accelerated Surface Area and Porosimetry (ASAP) system 2020 was used for this analyses. After the samples had been dried at 100°C, absorption atmospheres of N₂ at 273 K and CO₂ at 273 K was used for analysis.

2.4.3 PSD

The particle size distribution (PSD) of the biochar samples was analyzed using a Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd). The analyzer makes use of laser diffraction to measure the PSD of a sample by measuring the intensity of scattered light that passes through each sample.

2.4.4 X-ray diffraction (XRD) and X-ray fluorescence (XRF)

X-ray diffraction (XRD) analyses and the X-ray fluorescence (XRF) analyzes were conducted by Dr Sabine Verryn at the Geology Department laboratory at the University of Pretoria, South Africa. XRD analysis was done to identify the crystalline phases of minerals in the biochar. The material was prepared for XRD analysis using a backloading preparation method and analyzed with a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K radiation. The phases were identified using X'Pert Highscore 4 plus software.

3 RESULTS AND DISCUSSION

3.1 Biochar production without catalyst

The effect of temperature on biochar yield was investigated at 280 and 320°C in this study with a calculated experimental error of 2.07 % at a 95% confidence level. The influence of temperature on product distribution at a solids loading of 60wt% in water is shown in Figure 2.

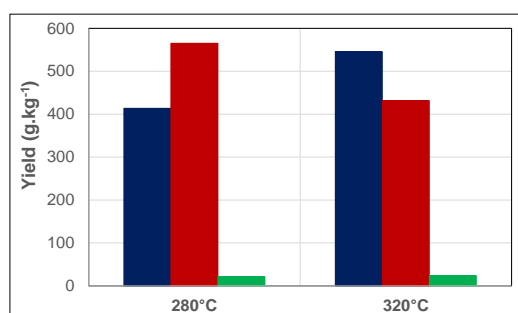


Figure 2: Influence of reaction temperature on product distribution at a constant solid loading of 60 wt% (■ - Biochar, ■ - Bio-oil, ■ - Bio-gas)

The biochar yield increases while the oil yield decreases and the gas yields remains unchanged with an increase in temperature. This is contrary to results obtained in literature [8]. Most literature results [9, 10, 11, 12] reports biochar and bio-oil yields at relatively low solid loadings (< 20 wt%) compared to loadings used in this study. At the higher solid loadings, much more energy is necessary to liquefy the biomass components, and the lower availability of active hydrogen leads to a suppression of the water shift reaction at higher

temperature, resulting in the formation of more CO and biochar instead of CO₂, H₂ and bio-oil.

The influence of solid loading (wt% in water) on the biochar yield is given in Figure 3.

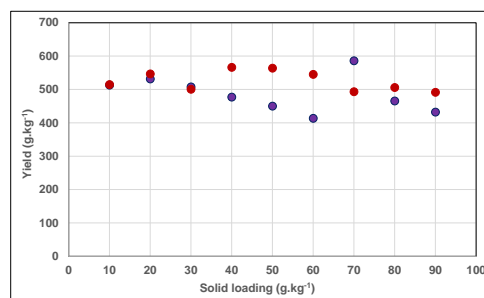


Figure 3: Influence of solid loading on biochar yield at different temperatures (● - 280°C, ● - 320°C)

The effect of solid loading is much more notable at 280°C than at 320°C. At 320°C, the solids loading varies between 500 and 600 g.kg⁻¹, with the highest char yield obtained at a solid loading of between 40 and 50%. The char yield at 280°C changes significantly between 400 and 600 g.kg⁻¹. The reactor filling volume was kept constant during all experiments and thus the influence seen in Figure 3 is purely the effect of an increase in the solid loading. Different reaction mechanisms seems to be present between 10 and 70 wt% and 70 and 90 wt%, with the char yield remaining constant after 70wt% solid loading at 320°C.

3.2 Biochar production with catalyst

The influence of a calcite (CaCO₃) catalyst on biochar yield and product distribution during hydrothermal liquefaction of sweet sorghum bagasse was investigated by adding 5wt% of calcite to the bagasse during liquefaction. The effect of adding a catalyst on the product distribution compared to yields obtained without a catalyst is compared in Figure 4.

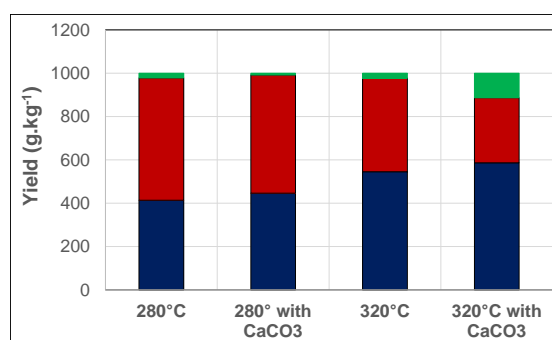


Figure 4: Comparison of product distribution with and without the addition of a catalyst at a solid loading of 60wt% (■ - Biochar, ■ - Bio-oil, ■ - Bio-gas)

From Figure 4 it can be seen that the addition of a catalyst significantly increases the biochar yield and reduces the bio-oil yield with an increase in gas yield. The addition of a catalyst containing oxygen molecules to the reaction mixture promotes hydrolysis of the biomass components, but because less active hydrogen is available to stabilize the fractions, polymerization is promoted and more char and less oil is formed [13].

3.3 Structural analysis of chars

SEM images of the chars produced at various temperatures, with and without the addition of a catalyst is presented in Figure 5.

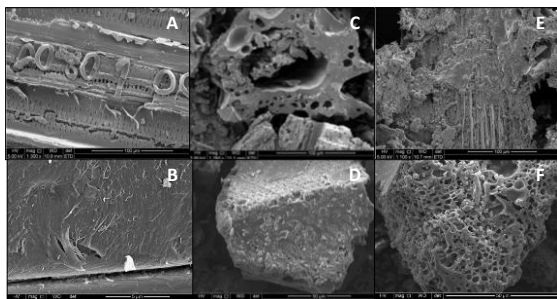


Figure 5: SEM images of sweet sorghum bagasse (A and B), chars produced at 280°C with (C) and without (D) a catalyst and chars produced at 320°C with (E) and without (F) a catalyst.

From Figure 5 it can be seen that all the bio-chars produced were completely charred and that chars produced with a catalyst and at higher temperatures appeared to be more porous. This was confirmed by BET analysis as reported in Table II.

Table II: Average microporous surface areas and particle sizes compared at a solids loading of 60 wt%

	Without catalyst		With catalyst	
	d ₅₀ (μm)	Micropore surface area (m ² .g ⁻¹)	d ₅₀ (μm)	Micropore surface area (m ² .g ⁻¹)
Bagasse	-	142.6	-	142.6
280°C	32.9	154.2	101	248.0
320°C	237.2	168.1	65.4	112.5

As temperature is increased, the surface area increases and the average size of the particles becomes larger when no catalyst was added. At 280°C, the addition of the catalyst resulted in bigger particles and much higher surface area, but at 320°C, the particles are smaller and the surface area drops to below that of the bagasse. The increase in surface area at the lower temperature is due to the evolution of gases, but at higher temperature, the char is converted to oil and gas and thus, a densification of the material is observed. The particle size of all the chars are small (70 to 140 μm) compared to coal for gasification and the char is thus ideal for briquetting with fine coal for co-gasification.

3.4 Compositional analysis

The volatile matter (VM), fixed carbon (FC), moisture and ash content of the chars did not change significantly with a change in the solid loading, and average values are listed in Table III. The average values for the elemental analysis is given in Table IV.

Table III: Proximate analysis of chars (wt%) (air-dried basis)

	VM	FC	Moisture	Ash
280°C	57.9	31.8	4.0	6.3
320°C	50.0	23.0	3.2	7.8
Cat 280°C	61.1	39.1	1.8	14.0
Cat 320°C	54.0	27.8	1.4	16.9
Bagasse	70.0	17.4	8.5	4.2

As expected, the VM content of the bagasse was reduced in all instances, while the FC content was increased. Chars with a higher carbon content were obtained at 280°C than at 320°C; and the addition of a catalyst improved the carbon content, because the carbonates had not decomposed at 320°C and is thus counted as part of the fixed carbon of the chars. Chars produced with the addition of a catalyst showed a relatively high ash content, which is due to the catalyst ending up in the char.

Table IV: Elemental analysis of chars (wt%, daf)

	C	H	N	O	HHV
280°C	74.2	5.7	0.8	19.3	26.4
320°C	77.5	5.4	1.0	14.1	27.2
Cat 280°C	74.4	8.8	1.9	15.0	27.6
Cat 320°C	72.0	7.8	2.2	18.1	24.7
Bagasse	47.4	6.2	0.4	60.5	15.3

An increase in temperature resulted in an increase in elemental carbon content, but the addition of a catalyst did not significantly change the carbon content at 280°C. The hydrogen and nitrogen content of the chars were higher with the addition of a catalyst. The highest oxygen content was observed for chars prepared with the addition of a catalyst at 320°C. Although liquefaction significantly increased the HHV compared to that of the bagasse, no significant changes were observed with a change in temperature or solid loading. The highest HHV was obtained at 280°C with the addition of a catalyst.

FTIR analysis showed complete degradation of all plant materials and the presence of aromatic ring structures in the chars.

XRD/XRF analysis showed the presence of silicon structures in the chars and showed that the alkali earth metals are present as oxides in the char.

4 CONCLUSIONS

Solids loading is an important parameter during hydrothermal liquefaction of lignocellulose material that influences the char, oil and gas yields, but does not significantly influence the composition of the chars. The addition of a catalyst improves the fixed carbon content of the chars, but does not significantly improve the HHV. The catalyst ends up as an oxide in the chars, adding to the overall ash content and lowering the HHV.

5 REFERENCES

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7 LOGO SPACE

