



Research article

A feasibility assessment of the production of char using the slow pyrolysis process



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ABSTRACT

There is a growing need for the production and use of sustainable biofuels worldwide. One noteworthy approach is the production of biofuels via the thermochemical conversion of lignocellulose biomass. This work studied the production of char via the slow pyrolysis of corn-stover as a suitable supplement or replacement of coal in industrial processes. The char quality was assessed according to the ASTM D388 (American Standard Testing Method), which ranks coals according to their higher heating value (HHV), volatile matter and fixed carbon. Furthermore, an evaluation of the techno-economic feasibility of an industrial scale 30 t/day slow pyrolysis plant was conducted. The techno-economic study was conducted at a char baseline price of \$100/ton. A two-level three-factor central composite design (CCD), with response surface methodology (RSM) was used to study the slow-pyrolysis process conditions. Optimisation experiments were conducted at bench-scale gram-level to study the influences of the process condition of char higher heating value (HHV) and yield. Furthermore, this study assessed the techno-economic feasibility of a 30t/day processing plant. The results showed process temperature had the most significant influence on char HHV and yield. Optimal conditions for char production were at a reactor temperature of 453 °C, and 5 °C/min and 29 min for heating rate and holding time respectively. Under these conditions char with HHV of 26.25 ± 1.5 MJ/kg and yield of 34.5% were produced. These chars are comparable to sub-bituminous A coals. A high energy efficiency of ~82% was also associated with the process. The economic feasibility of the plant is highly sensitive to the cost of CS feedstock. The process had a net present value (NPV) of -\$1.17 million at the \$20/ton CS baseline assumption. A cost sensitivity analysis showed that when the cost of CS was lowered to \$3/ton, the NPV was zero. Uncertainties in the price estimation of the volatile by-products remained a concern.

1. Introduction

Between 2015 and 2040 the world's energy consumption is expected to increase by 28% (EIA, 2017). This increase is attributable to strong economic growth, increasing populations leading to higher energy demands and access to marketed energy. Of the current global energy supply, 78% is comprised of fossil fuels, with consumption of coal being the second-largest closely behind petroleum (EIA, 2017). The use of fossil fuels poses serious environmental problems associated with the release of greenhouse gases and the eventual depletion of these energy sources. Despite the majority of coal being used for electricity generation by the national utility Eskom, a minority of South Africans use coal domestically in low-income households (Balmer, 2007). This is most prevalent in communities located close to coal mines. The coal is used for cooking and

heating purposes in the homes. The intrinsic dangers with the use of coal in households are extreme air pollution, respiratory diseases associated with smoke inhalation as well as suffocation/poisoning due to carbon monoxide inhalation. Charcoal and firewood are also popular fuels in South Africa, particularly for rural domestic dwellers. The production of charcoal and firewood have devastating ecological and environmental issues associated with widespread deforestation (Chidumayo and Gumbo, 2013). The traditional production of charcoal via earth-kilns is highly inefficient with almost half of the energy input lost during production (Kammen and Lew, 2005; Adam, 2009; Chidumayo and Gumbo, 2013; Chidumayo, 2013).

It is common practice in many countries to utilise biomass for bio-energy production (Kretschmer et al., 2012). The European Union (EU) has identified bio-energy as one of the main renewable, low-carbon

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sources to achieve significant climate and energy targets (Directive 2009/28/EC, 2009). In 2013, 26% of the EU's electricity was generated from bio-energy. The target is to reach 45% power generation by 2030 (COM, 2015). In South Africa, the Department of Energy's Integrated Energy Plan (IEP) estimates 26% of the country's energy mix will be derived from renewable resources by 2030 (Department of Energy, 2018). Accounting for a total system's capacity of 89 532 MW. From a socio-economic point of view, it is estimated bioenergy and biomass resources have the potential of creating 3700 jobs per MW (megawatt) energy produced. Biomass is a sustainable energy source that not only reduces the unwanted impacts of waste on the environment but also serves as a regenerative energy source in comparison to the depleting fossil fuel sources. The application of biofuels not only provides great economic opportunity but also promotes a sustainable future. In 2015 alone, 9–13% of the global energy supply was attributed to biomass resources, which amounts to approximately 60 EJ of energy (Wang et al., 2017). Biomass can be divided into five basic categories of materials namely; virgin wood, energy crops, agricultural residues, food wastes and industrial wastes and co-products (Demirbas, 2000; Varol and Atimtay, 2007). Agricultural residues are considered to be less contentious, low cost, carry few risks (WBGU, 2009) and thus making them ideal for countries with a large agricultural base. South Africa, in particular, has great potential for bio-energy due to large agricultural production where significant amounts of biomass are available for energy purposes (Potgieter, 2011). Mohlala et al. (2016) states that 30% of the agricultural residues in South Africa have a potential of 463 MW of power generation. South Africa remains the largest producer of maize in Africa followed by Nigeria and Egypt (Mohlala et al., 2016). Approximately 9.7 million metric tonnes of maize residues are produced annually (Batidzirai et al., 2016). These maize residues are commonly referred to as corn-stover (CS). A portion of approximately 47.4% of the biomass is used as animal feed and to provide nutrients to the soil. As a result, 5.1 million tons of corn-stover per annum (52.6%) are available for potential valorisation processes (Batidzirai et al., 2016). The advantage of CS over other biomass feedstocks is that it does not interfere with food supplies and its use leads to minimal to no land destruction as compared to energy crops (Batidzirai et al., 2016). The lignocellulosic nature of CS and its ample availability make it a strong candidate feedstock for renewable energy.

Slow pyrolysis of corn-stover (CS) is a promising approach for the production of high-value char and volatile by-products. However, limited data is available on the modeling of the devolatilisation process, in addition to the techno-economic feasibility of an industrial scale process which emphasises the production of char. Authors have well established the main factors influencing the production of biofuels as feedstock composition, process temperature, heating rate and holding time (Demirbas and Arin, 2002). However, the researchers have rarely reported on the interactions among these variables, particularly as it pertains to the production chars for combustion applications and volatile by-products through the slow pyrolysis of agricultural residues. Despite the extensive research into the pyrolysis process, the technical feasibility study into the production of char and volatiles for the supplementation of coal remains inadequate. Typically, previous studies have focused on the techno-economic feasibility of producing liquid biofuels (Thilakarathne et al., 2014).

Wright et al. (2010) compared the profitability of two pyrolysis scenarios; fast pyrolysis producing char and transportation fuel versus slow pyrolysis producing fuel gas and char. The fast pyrolysis scenario produced products with substantially higher economic value compared to those of slow pyrolysis. A downside of the fast pyrolysis scenario was that it required a capital investment of \$200 million which was significantly higher than \$132 million capital investment required for the slow pyrolysis scenario. The slow pyrolysis internal rate of return (IRR) assuming a feedstock price of \$0 per metric ton, the resultant IRR ranged from 8% to 17%. The authors, however, did concede the true price of feedstock could be as high as \$83/ton. According to Mullaney et al. (2002), it is possible to produce enough energy to heat both the pyrolysis process and

provide process heat for other applications using pyrolysis products. By refining bio-oil, 'green' gasoline and diesel can be produced. Biogas, on the other hand, can be used as a substitute for natural gas for heating or power generation purposes (Wright et al., 2010). The study, however, did not extend to the utilisation of char for combustion purposes. It is necessary to study a pyrolysis system that centers on the production of char as a substitute or supplement for coal while also taking into account the production of volatile by-products.

As opposed to the aforementioned investigations, the current study examined the production of solid fuel and volatile by-products which do not require extensive further processing before use in energy applications. The study focused on the effect of process parameters; temperature, holding time and heating rate on char production. There is a dearth in the literature on the effects of the aforementioned conditions on the production of high energy content char, especially as it pertains to the slow pyrolysis process. Most studies typically focused on torrefaction or made use of slow pyrolysis to produce soil additive chars. The techno-economic feasibility study was conducted on the production of char and volatile by-products produced from the slow pyrolysis of CS.

2. Materials and methods

2.1. Biomass

Corn stover (CS) biomass was harvested from a farm in the North West province, South Africa. The biomass was then packed into 20L polyethylene bags and transported to the University of Stellenbosch. Upon arrival, the biomass was stored in a cool dry storage room before processing. Pre-processing of the biomass entailed milling approximately 40 kg CS using a lab-scale Type SM 100 mill (Retsch GmbH, Haan, Germany). A particle size distribution (PSD) of 800–3500 μm was selected using appropriate sieves. The selected PSD was sufficient to allow higher heating rates during the pyrolysis reaction. The milled CS was then packed back into the polyethylene bags prior to the experimental runs. To ensure a good representation of the CS, sampling was done by taking a sample of CS from the top, mid-way and bottom of the polyethylene bag. The samples were then mixed into a different bag. From this bag, CS was scooped and weighed for each experimental run.

2.2. Pyrolysis experimental set-up

The slow pyrolysis set-up consisted of a furnace that houses a removable 1m long stainless-steel reactor. The reactor was connected via rubber pipes to a condensation train consisting of 5 glass condensers in series immersed in dry ice (CO_2). The utilities encompassed in the set-up are a flow meter used to regulate the flow of nitrogen into the reactor and two platinum thermocouples were placed from one end of the reactor with their tip-ends at the centre of the reactor for reactor temperature regulation. The top thermocouple placed closed to the reactor wall controlled the heating by measuring the reactor temperature. While the second thermocouple placed near the reactor centre was used to measure the temperature of the CS sample.

A vacuum pump connected to the 5th condenser was used to ensure the system had no leaks. CS biomass samples of the particle size distribution (PSD) ranging from 800 to 3500 μm were fed into a bed-scale horizontal steel reactor (1m long, 60mm outside diameter) in 20g batches. The conditions of the desired process condition for the specific each run were entered on the control board. The control board ensured the desired process conditions could be reached by carefully inputting the appropriate conditions. To input the CS, a quartz sample holder with 20g of CS was placed in the middle of the reactor. Refer to Figure 1 for an illustration of the set-up of the pyrolysis bench-scale process.

The variable parameters employed in this study were holding time (5–30 min), heating rate (5–20 $^{\circ}\text{C}/\text{min}$) and reactor temperature (300–500 $^{\circ}\text{C}$). The reaction begins at room temperature until the set-point temperature. As the reaction commenced, the volatiles produced

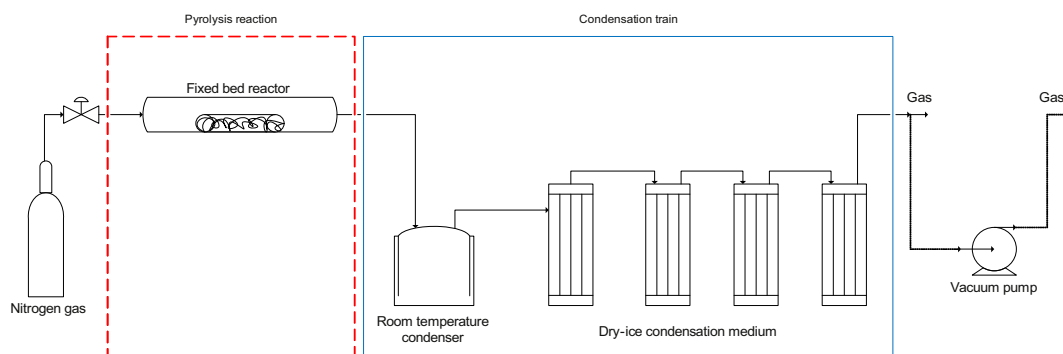


Figure 1. Schematic of the pyrolysis process bench-scale set-up.

would flow into the condensation train where the condensable gases were retained. The non-condensable gases were captured into 10L Tedlar bags preceding the last condenser, then analysed on the gas chromatography instrument (Compact GC^{4.0}, Global Analyser Solutions™, Breda, Netherlands) for their composition. The residual product in the reactor once the reaction concluded was the desired char.

2.3. Proximate analysis

The proximate analysis of samples was carried out using a TGA/DSC Star Systems analyser (Mettler Toledo, Ohio, USA). The standard ASTM E1131 test method was used. For the experiment, a ceramic sample crucible of 600 μL was filled with 20 mg CS. The CS sample was then heated from 30 to 900 $^{\circ}\text{C}$ at heating rates of 1–20 $^{\circ}\text{C}/\text{min}$. A nitrogen inflowing at 100 mL/min was used as the inert gas medium. Whilst the sample was being heated, the weight loss (wt.%) of the sample was continuously measured by the software. After heating, the samples were held isothermally for 5 min to ensure complete removal of excess moisture. A graph that presents the rate of mass change of the fuel was then provided by the software. The mass loss was due to the pyrolysis heating step. The proximate analysis was then calculated using Eq. (1).

$$100 \text{ wt.}\% = a(\text{wt.}\%) + b(\text{wt.}\%) + c(\text{wt.}\%) + d(\text{wt.}\%) \quad (1)$$

Where $a(\text{wt.}\%) = \text{Moisture content}$, $b(\text{wt.}\%) = \text{volatile matter}$, $c(\text{wt.}\%) = \text{Fixed carbon}$ and $d(\text{wt.}\%) = \text{Ash content}$.

2.4. Elemental analysis

The analysis was conducted using a Vario EL Cube elemental analyser (Elementar, Langensfeld, Germany). The test determined the elemental percentage of carbon (C), nitrogen (N), hydrogen (H) and oxygen (O) of the sample in accordance with DIN 51721 standard method. The C and H contents were analysed by an infrared detector and N content by a thermal conductivity detector. A sample mass of 100 mg was combusted in the elemental analyser at a temperature of 950 $^{\circ}\text{C}$.

2.5. Bomb calorimetry

For this study, a bomb calorimeter model Cal²K ECO 2013 (DDS Instruments, Rheinland, Germany) was used to determine the higher heating value (HHV [MJ/kg]) of samples.

2.6. Gas chromatography

Gas chromatography is ideal for measuring gases and light hydrocarbons in laboratory operations. A Compact GC^{4.0} (Global Analyser Solutions™, Breda, Netherlands) was employed for this purpose due to its reliability and highly sensitive detectors. The analysis produced the volume composition of each compound in the sampled gas. The gas exiting the pyrolysis system was collected into 10L Tedlar bags within

two-minute intervals. The collection was done throughout the duration of the experiment. The CompactGC^{4.0} instrument was calibrated to analyse C₁–C₆ hydrocarbons, including H₂, N₂, O₂, CO and CO₂ gases in terms of their volume per mole composition.

The mass of the gas was then determined using Eq. (2)

$$X_x = \frac{\text{Vol}(x\%) \cdot N_2 \text{ feedrate to pyrolysis reactor (L/min)}}{\text{Vol}(N_2\%) \cdot \text{Standard gas volume (L/mol)}} \cdot MM_x \left(\frac{\text{g}}{\text{mol}}\right) \cdot \text{sampling time (min)} \quad (2)$$

Where:

$X = \text{Mass yield (\%)}$, $x = \text{Gas compound}$, $MM = \text{Molar mass gas compound}$.

2.7. Design of experiments

Optimisation and statistical analysis were performed following the response surface methodology (RSM) and design of experiments (DoE), using DesignExpert® Software Version 11 (Stat-Ease, Inc., Minneapolis, USA). A full-factorial central composite design (CCD) was used to study the effects of process variables on char HHV (MJ/kg) and yield (wt.%). The choice of process variables was based on screening tests and literature. Screening tests on char yield defined the conditions of the process variables in question. The char yield screening tests were conducted through experimental pyrolysis runs as described in section 2.2 at temperatures between 200 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$. Once the char yield range was clearly established, the experiment variable ranges were defined.

Based on char product yields from screening tests, minimum and maximum temperatures were defined as 300 and 500 $^{\circ}\text{C}$ respectively. With a centre temperature point at 400 $^{\circ}\text{C}$. The heating rate minimum and maximum were defined as 5 and 20 $^{\circ}\text{C}/\text{min}$ respectively. With a centre heating rate point at 12.5 $^{\circ}\text{C}/\text{min}$. Finally, the holding time was defined as 5 and 30 min with a centre point at 17.5 min. The DoE detailed a 20 run experimental design matrix, with three process variables. All experiments were duplicated to ensure reproducibility. An analysis of variance (ANOVA) was performed in order to assess the impact of temperature, heating rate and holding time on char HHV (MJ/kg) and yield (wt.%). The significance of the process variables was expressed by the p-value statistic. A $p < 0.5$ denoted a significant variable with 95% confidence. The aim of the optimisation study was to produce chars with a minimum HHV of 25 MJ/kg at a minimum yield of 30%.

2.8. Process techno-economics

This project employed Capcost® software to estimate the process costs of a slow pyrolysis plant and used Turton et al. (2013) investment factors to calculate the capital expenditures of the project. This methodology estimates costs within a 30% margin of error. The profitability of the project was determined by calculating the discounted cash-flow

(DCF) and net present value (NPV) of a process based on anticipated product sales, manufacturing costs and feedstock costs. The techno-economic analysis relies on risk analysis formulas that take into account key process assumptions. Construction duration of fewer than 2 years was assumed. It is estimated the online time of the plant is 90% (330 days). Equipment and installation costs were estimated based on equipment size factors, published data and internal Capcost® equipment database assumptions based on size, process conditions and costs of construction. The CS feedstock price of \$20 per metric ton was estimated based on the literature published by Wright et al. (2010) and Shabangu et al. (2014). The price of char is assumed at \$100/ton which is competitive with established prices of coal. The prices of bio-oil and biogas products from the slow pyrolysis process are not well defined in the literature. Whereas prices of fast pyrolysis volatile products can start from \$260/ton and \$1.8m³ for bio-oil and biogas respectively (Mullaney et al., 2002; Gura, 2017). As such the price of bio-oil and biogas by-products were assumed at \$50/ton and \$1.5/m³ respectively based primarily on purity. A benefit of the proposed process is that it requires no catalyst or additives to the process, thus reducing the costs associated with the operation of the plant. The total plant investment cost takes into consideration overhead and contingency factors for the installed equipment costs. A 25% contingency factor was employed. A straight-line depreciation method was deployed for this study. The study is based on a CECPI of 603.1 (2018).

The disposal services corresponded to water and ash waste management, while electricity was based on compressor and equipment operations. The cost of labour was averaged based on the South African processing plant standards (Payscale, 2019).

3. Results and discussion

3.1. Biomass and char characterisation

3.1.1. Elemental analysis

The CS biomass was characterised via elemental and proximate analyses (Table 1). Characterisation of the biomass provides valuable information that assists in the optimisation of pyrolysis reaction.

The char elemental properties were different from those of raw CS biomass. Increased temperature had a positive effect on the carbon content of char from 300 to 400 °C (Table 1) from 50.07 to 59.36% respectively. The degree of carbonisation and the development of aromatic carbon structures were accelerated by increasing temperature. The increase in char carbon concentration with increasing temperature is similar to those previously reported literature by Naik et al. (2017) and Dhanavath et al. (2019). The study on slow pyrolysis of neem seed cake by Dhanavath et al. (2019) reported an improvement from 57.39 to 64.12% when char was heated from 450 to 575 °C. Likewise, Naik et al. (2017) reported an 18.29% improvement as a result of the pyrolysis of sorghum from 350 to 500 °C. The authors attributed this to the cleavage and cracking of weak char bonds as a result of increasing temperature. The current study also reported a 1.46% reduction in char carbon content (59.36–57.90%) when the temperature was raised from 400 to 500 °C (Table 1). It is believed this reduction is linked to the breaking of C–H chains under high-temperature conditions. Similarly, the study by

Chandra and Bhattacharya (2019) of the slow pyrolysis neem press seed cake also noted a drop in carbon concentration at elevated temperatures above 500 °C. The study linked the reduction to an increased rate of loss of long-chain aliphatic groups due to homolytic dissociation and thermal breaking of C–C and C–H bonds as a result of the char's thermal exposure that crosses the threshold dissociation energy of bonds. Loss in hydrogen from 4.71 to 4.13% and oxygen concentration from 44.25 to 35.22% was noted when the temperature was raised from 300 to 400 °C. The loss in hydrogen and oxygen concentrations could be linked to losses in water vapour, hydrocarbons, carbon dioxide, hydrogen and carbon monoxide through the production of volatiles as the pyrolysis reaction progresses. From 400 °C to 500 °C a slight increase in oxygen concentration (35.22–37.94%) was observed (Table 1). It is believed that the formation of volatiles was limited under these conditions. The study by Chandra and Bhattacharya (2019) noted an increase in oxygen concentration as the temperature was raised from 500 to 600 °C during the production of biochar through the pyrolysis of rice straw. It is, however, important to note the study by Chandra and Bhattacharya (2019) intended the production of biochar for soil applications. The trend was also noted by Gai et al. (2014) who studied the pyrolysis of corn-straw, wheat straw and peanut shell.

Nitrogen concentration increased from 0.98% to 1.29% when the char was heated from 300 °C to 400 °C (Table 1). This positive trend is likely due to the formation of amine functional groups such as NH₄-N, NO₃-N. However, at 500 °C a decline in nitrogen concentration was observed. It is believed that the decline in nitrogen suggests elevated temperatures above 500 °C prohibit the formation of amine functional groups. The decline of this group at 500 °C was also noted by Gai et al. (2014) and Chandra & Bhattacharya (2019). The authors noted a decline in nitrogen concentration at temperatures above 500 °C as a result of loss of volatiles and nitrogen groups such as NH₄-N, NO₃-N. The composition of char, particularly its high carbon concentrations >50% suggests the char produced in this study is suitable for biofuel use (Dhanavath et al. 2019) as high carbon concentrations are linked to improved biofuel properties. Similarly, the reduction of hydrogen and oxygen concentrations with respect to rising temperature implies improvement in fuel properties. The above-mentioned deductions corroborated in section 3.1.3 by measuring the energy content of the chars with respect to temperature.

3.1.2. Proximate analysis

The volatile matter of the char reduced steadily with rising temperatures (300–500 °C) from 62.24 to 29.36% (Table 2). The volatile matter represents the fraction of biomass that will likely degrade to light molecular organics in the form of syngas in the presence of high temperature (Kim et al., 2012). Thus, the loss in volatile matter correctly represents the devolatilisation of the biomass as it was pyrolysed into char. Similarly, the study by Chandra and Bhattacharya (2019) showed a 12.61% reduction in the volatile matter when rice-straw char was heated from 400 to 500 °C.

The fixed carbon in the char in this study increased from 29.81% to 51.01% with a rise in temperature from 300 to 400 °C (Table 2). A rise in fixed carbon is linked to improved fuel properties through the increase in aromatic carbon (Wu et al., 2012). Hence, the rise in fixed carbon correlates to a rise in HHV (Rafiq et al., 2016). After the initial rise in fixed carbon content, a reduction from 51.02 to 44.87% in fixed carbon was then observed at 500 °C. The reduction implies a drop in the energy content of the char. HHV tests were conducted in the proceeding section to verify this claim. The ash content of the char increased from 7.95 to 25.77% when the temperature was raised from 300 to 500 °C respectively. A rise in ash content was related to the amplification of the mineral concentration during the release of volatiles from the char during heating. Amplification of the mineral concentration is known to cause a reduction in fuel properties as evidenced by Rafiq et al. (2016), the authors showed an ash content increase from 5.7% to 18.7% when corn-stover biomass was heated from 300 to 500 °C.

Table 1. Elemental analysis characterisation of corn-stover and char.

	Elemental analysis			
	C %	H%	O%	N%
Corn-stover	48.8	6.41	44.1	0.65
Char				
300 °C	50.07 ± 2.01	4.71 ± 0.18	44.25 ± 2.21	0.98 ± 0.13
400 °C	59.36 ± 1.02	4.13 ± 0.06	35.22 ± 1.19	1.29 ± 0.14
500 °C	57.90 ± 3.38	3.04 ± 0.07	37.94 ± 3.63	1.12 ± 0.23

Table 2. Proximate analysis for corn-stover and char.

	Proximate analysis		
	AC (%)	VM (%)	FC (%)
Corn-stover	4.96	68.86	17.54
Char			
300 °C	7.95	62.24	29.81
400 °C	16.22	32.76	51.02
500 °C	25.77	29.36	44.87

3.1.3. Energy content

The energy content of the materials was determined by measuring their HHV's. The heating rate and holding time were maintained at 12.5 °C/min and 17.5 min respectively when producing the respective chars. An increase in temperature from 300 to 400 °C improved the HHV from 21.42 to 23.79 MJ/kg. This is evident in the fixed carbon concentration in section 3.1.2 (see Table 3).

Further, heating to 500 °C led to a 1.95 MJ/kg drop in HHV. This drop validates the claim made in section 3.1.2. The assertion was that the reduction in fixed carbon and an increase in ash content had a detrimental effect on the HHV at 500 °C. A previous study by Mundike et al. (2017) attributed dehydrogenation as the cause in the reduction of HHV at higher (above 450 °C) temperatures. Dehydrogenation resulted in char having a higher percentage of inorganic materials such as potassium and silica. The presence of these elements is detrimental to the char's HHV decrease in char's HHV at higher.

3.2. Product yields

The yields of bio-oil and biogas were positively affected by temperature increases. As the process temperature was raised from 300 to 500 °C, bio-oil and biogas increased from 20.05 to 35.88% and 12.51–33.64% respectively. Alongside, the mass yield of char dropped from 66.5% to 27.95% (Figure 2). This is consistent with the theory of pyrolysis (Jahirul et al., 2012; Dhanavath et al., 2019; Chandra and Bhattacharya, 2019). The reduction in char yield with respect to temperature can be linked to the loss of volatiles and organic liquids resulting from the thermal degrading of cellulose and lignin structure of the biomass (Zhan et al., 2015; Chandra and Bhattacharya, 2019).

3.3. Effect of process conditions on char production

The effect of process conditions on char production was studied by RSM using 3-dimensional surface plots of the empirical model. The 3-dimensional plots display the effect of changing two variables whilst maintaining the third constant. The independent variable, the temperature was varied from 300 to 500 °C with a centre point at 400 °C. The heating rate was varied from 5 to 20 °C/min with 12.5 °C/min as a centre point. Finally, holding time was varied from 5 to 30 min with 17.5 min as a centre point. The char yield (Xchar) regression model was relatively high $R^2 = 99.57$ based on the analysis of variance (ANOVA). The adjusted R^2 was 97.20. This indicated the model agreed with experimental results. As such the model can be used to estimate the influence of

Table 3. Energy contents of corn-stover and char.

	Energy content
	HHV (MJ/kg)
Corn-stover	16.59
Char	
300 °C	21.42
400 °C	23.79
500 °C	21.84

independent variables reliably. The effects of all variables on Xchar were significant ($p < 0.05$) (Table 4). The F-value of temperature was highest ($F = 158.51$), indicating it had the highest influence on Xchar. Design Expert® was used to fit the experimental results to quadratic models. The effects of all variables on Xchar were significant ($p < 0.05$) (Table 4). The resultant process model equation is provided by Eq. (3). The equation highlights the significance and interactions among process variables.

$$\text{char yield} = 17.98 - 18.59x_1 - 1.26x_2 - 1.57x_3 + 0.924x_2x_3 - 2.94x_1^2 + 0.67x_1x_2 \quad (3)$$

Optimisation of char HHV sought to produce char with a yield of at least 30%. Analysis of the results indicated that if the temperature is maintained below 470 °C (Figures 2 and 3), Xchar above 30% can be produced. Provided that holding time is maintained below 15 min. The heating rate, on the other hand, should ideally be maintained below 10 °C/min. A linear coefficient describes a linear relationship between the dependent variable and quadratic coefficients imply the response varies parabolically with the dependent variables (Table 4).

3.3.1. Influence of process variables and char yield

3.3.1.1. Effect of temperature and holding time. The linear (L) and quadratic (Q) relationships between the independent variables and char yield are illustrated in Table 4. It is evident that the linear coefficients have a more significant influence on char yield. An assessment of the relationship between process variables and char yield based on three-dimensional surface plots (Figures 3 and 4) was conducted. It is evident from Figure 2 that there is a general decrease in Xchar with respect to temperature and holding time from base conditions of 300 °C and 5 min until around 400 °C and 30 min, where there was a decrease in char mass loss, the relationship between process variables and Xchar was linear under these conditions. Based on the curvature that appears at temperatures beyond 400 °C, it is believed that the quadratic effect of temperature cancelled the linear effect (Table 4). A maximum char yield of 71.45% was obtained at 300 °C (Figure 3). The figure illustrates that increasing temperatures have a negative effect on Xchar. This is further validated by the negative linear coefficients of temperature -18.59 as described by Eq. (3) which indicates that an increase in temperature had a detrimental effect on Xchar. Accordingly, when CS was heated from 300 to 400 °C the Xchar dropped from 66.5 to 38.08% respectively. This observation is consistent with results from previous reports (Wu et al. 2012; Khanmohammadi et al. 2015). The study by Dhanavath et al. (2019) on the slow pyrolysis of neem press seed cake, the reaction temperature was the most predominant process variable and it had negative effects on Xchar. Their study found that by raising the temperature from 450 to 575 °C, the net result was an 18.52% reduction in Xchar. The study by Brown and Brown (2012) also showed that an increase in temperature resulted in a decrease in Xchar. The reduction in Xchar in this study could be attributed to the degradation in the hemicellulose, cellulose and lignin constituents in CS. The interaction between temperature and holding time proved insignificant ($p > 0.05$) effect on char. As a result, it is believed an optimum holding time for Xchar maximisation under the prescribed conditions does not exist.

3.3.1.2. Effect of temperature and heating rate. The linear coefficient of heating rate was -1.26, Eq. (3) which suggests an increase in heating rate will result in a reduction in Xchar. The heating rate had a significant effect on char yield ($p = 0.013$) (Table 4). However, it was observed that when the heating rate was increased from 5 to 20 °C/min there was a 1.91% increase in char yield when the temperature was maintained at 300 °C. This is contrary to the theory of pyrolysis. The theory on pyrolysis systems suggests volatile production is favoured with increases in heating rate (Amutio et al., 2012). Literature generally ascribes such theory to when an operation is at elevated temperature >450 °C, this study suggests the theory does not hold true at 300 °C likely because the temperature is not high enough to initiate rapid devolatilisation of the char.

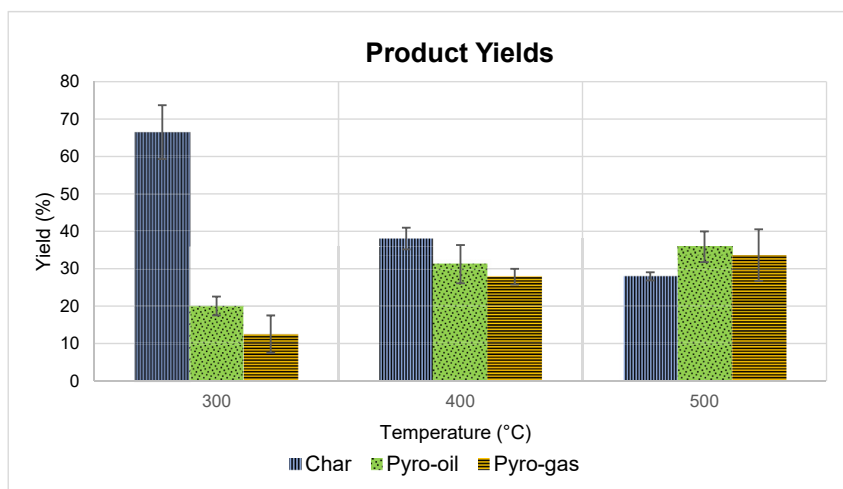


Figure 2. Slow-pyrolysis experimental yields.

Table 4. ANOVA for char yield.

Variable	F-value	p-value	Comment
(X ₁) Temperature (L)	158.51	0.0001	Significant
Temperature (Q)	132.2	0.008	Significant
(X ₂) Heating rate (L)	14.26	0.013	Significant
Heating rate (Q)	0.08	0.52	Insignificant
(X ₃) Holding time (L)	3.35	0.046	Significant
Holding time (Q)	0.042	1.22	Insignificant
(X ₁)L by (X ₂)L	64.1	0.032	Significant

*L: linear; *Q: quadratic.

However, when the final reactor temperature was maintained at 500 °C, a heating rate increase from 5 to 20 °C/min resulted in reduced Xchar from 32.65 to 29.49%. It can be deduced that at higher heating rates of approximately 20 °C/min, particularly at elevated temperatures above 450 °C, the reaction decomposes the feedstock more rapidly. The rapid decomposition of the feedstock into volatiles limits the effect of secondary catalytic reactions between the char and volatiles. The limitation of these reactions favours the production of liquid, hence a reduction in Xchar was observed. This was consistent with the study by Gonzalez et al. (2005). The study showed that char yield increased by 4.2% when the

heating rate was reduced from 20 to 5 °C/min while maintaining the reaction at 500 °C (Figure 4). The 3D surface plot of the relationship of temperature and heating rate from base conditions of 300 °C and 5 °C/min to the upper limit of 500 °C and 20 °C/min with holding time maintained at 17.5 min (Figure 4). ANOVA describes the relationship as being significant (p < 0.05) and linear. Based on the positive coefficient for the interaction of temperature and heating rate as described by Eq. (3), it is suggested that an increase in the two variables would result in an increase in Xchar. However, the progression of Figure 4 suggests otherwise. The latter is likely accurate, the magnitude of the individual effects of temperature and heating rate have a detrimental effect on Xchar supersede that of the interaction between them.

3.4. Effect of process conditions on char HHV

The regression model for char HHV had a high R² value of 96.20, which indicated the model agreed well with the experimental results (Table 5 and Figure 5). As such the model can be used to estimate the influence of independent variables reliably. The p-value and F-value of

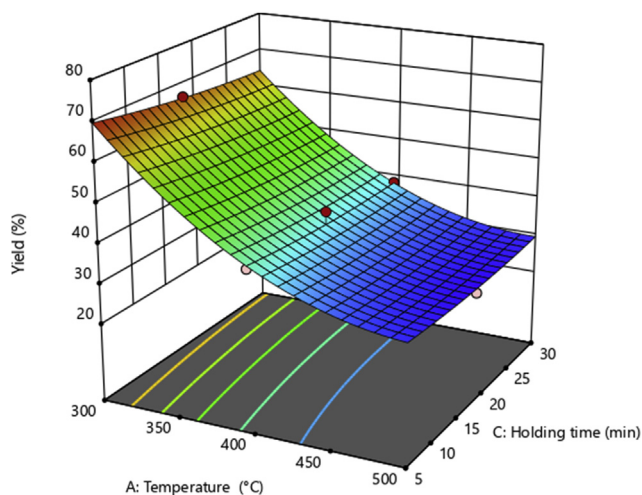


Figure 3. Effect of pyrolysis temperature (X₁) and holding time on char yield at a heating rate of 12.5 °C/min.

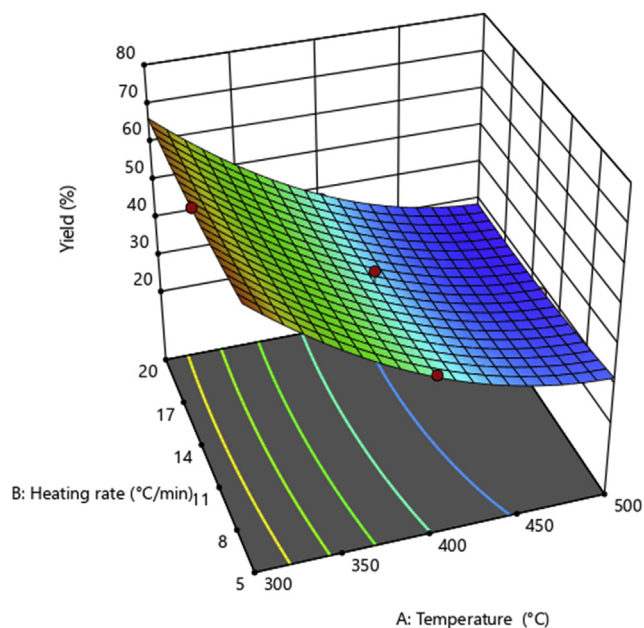


Figure 4. Effect of temperature (X₁) and heating rate (X₂) on char yield at holding time of 17.5 min.

Table 5. ANOVA for char HHV.

	Variable	F-value	p-value	Comment
Adjusted R ² = 92.79	(X ₁) Temperature (L)	142.51	<0.0001	Significant
	Temperature (Q)	39.27	<0.0001	Significant
R ² = 96.20	(X ₂) Heating rate (L)	12.6	0.0053	Significant
	Heating rate (Q)	0.78	0.0815	Insignificant
	(X ₃) Holding time (L)	1.35	0.2723	Insignificant
	Holding time (Q)	0.04	0.8512	Insignificant
	(X ₁)L by (X ₂)L	11.65	0.0066	Significant
	(X ₂)L by (X ₃)L	6.87	0.0255	Significant

the model were 0.0001 and 28.16 respectively, which suggests model significance. The p-value which indicates the significance of the process variables showed the coefficients of X₁, X₂, X₁X₂, X₂X₃, X₁² quadratic terms were significant (p < 0.05) (Table 5). The resultant process model equation is provided by Eq. (4). The equation highlights the significance and interactions among process variables.

$$\text{Char HHV} = 24.26 + 1.69x_1 - 0.501x_2 - 0.539x_1x_2 - 0.414x_2x_3 - 1.69x_1^2 \tag{4}$$

In order to produce char competitive with commercial coals, char with an energy content of above 25 MJ/kg was desired. Optimisation of slow pyrolysis experimental process variables yielded char with an energy content of 26.25 MJ/kg. This was achieved via slow pyrolysis at 453 °C, 5 °C/min and 29 min. Under these process conditions, the desired Xchar of 34.5% was attained, which eliminated the need to further maximise the yield production of char. Under optimum process conditions, the slow pyrolysis process was effective in producing product outputs of 34.5% char, 40.9% bio-oil and 24.1% biogas Based on GC results under optimum process conditions the biogas produced had a composition (vol.%) of 18.7% H₂, 2.2% CO, 6.4% CO₂ and 0.1% CH₄ (see Figure 6).

3.4.1. Relationship between process variables and char HHV

3.4.1.1. Effect of temperature and heating rate. The temperature had the highest overall effect of char HHV (p < 0.0001) (Table 5). As such Eq. (4)

details how an increase in temperature has a positive outcome on char HHV. The char HHV increased steadily with rising temperatures as indicated by the positive temperature linear coefficient (+1.69) as described by Eq. (4). The linear and quadratic coefficients of temperature as having a significant effect of char HHV, with the quadratic coefficient being negative (-1.69). This further indicates the possibility of optimum temperature for char HHV maximisation. By heating corn-stover biomass from room temperature to 300 °C, a 3.44 MJ/kg (29.13%) fuel improvement was attained. Peak temperature effects were observed at temperatures exceeding 350 °C. The heating rate as a parameter had a significance of p-value = 0.0053 on the HHV of char. While its linear coefficient was -0.501, suggesting that an increase in heating rate resulted in a reduction in the char's HHV. Indeed, when by raising the heating rate from 5 to 20 °C/min a 1.76 MJ/kg (7.01%) reduction in char HHV was attained while the temperature and holding time were maintained at 400 °C and 17.5 min respectively. This study also showed that at 500 °C, a 1.56 MJ/kg (7.9%) reduction in HHV was attained when the heating rate is raised from 5 to 20 °C/min. It was clear the negative effects of heating rate on HHV were more prominent at higher temperatures >400 °C. Higher heating rates lead to rapid devolatilisation, which may limit secondary and tertiary char reactions. By limiting secondary and tertiary char reactions the pyrolysis mechanism does not favour the production of carbon-rich volatiles. Interestingly, the study by Angin (2013) produced results contrary to this fact. Rising heating rates showed positive effects on HHV, especially at 400 °C. However, these results could be considered negligible as the rise accounted for in energy differences of <0.2 MJ/kg per 100 °C increases. A general parabolic relationship between temperature and heating rate (Figure 5). A parabolic relationship confirms there exist optimum process conditions for temperature and heating rate that would result in maximal char HHV production. The significance of the interaction between the two variables (p = 0.0066) further validates this point (Table 5).

3.4.1.2. Effect of temperature and holding time. Holding time had a statistically insignificant (p > 0.05) effect on char HHV (Table 5). However, it is important to note that holding time had a positive linear coefficient of +0.1640 as described by Eq. (4). This suggests that increasing the holding time would have a positive effect on char HHV. The literature on slow pyrolysis systems describes how prolonging holding times affect the fuel properties of char positively (Gheorghe et al., 2010). Rossen et al. (2013), showed that by increasing the holding time from 15 to 30 min a

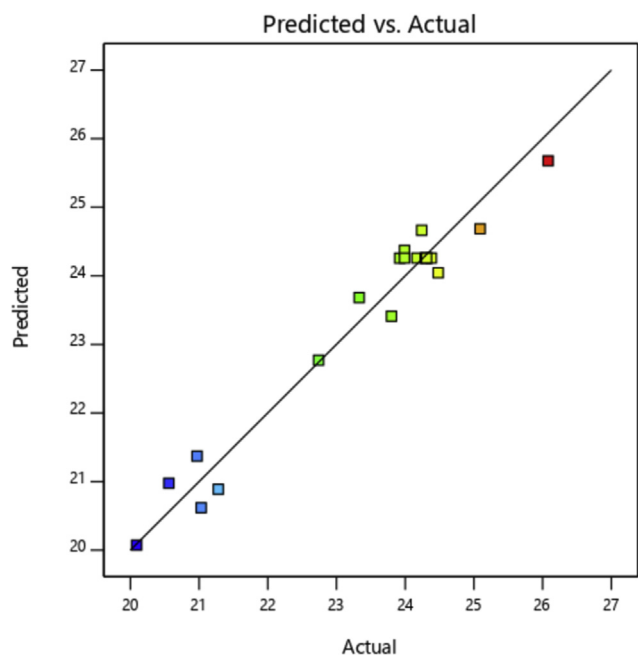


Figure 5. Char HHV prediction model.

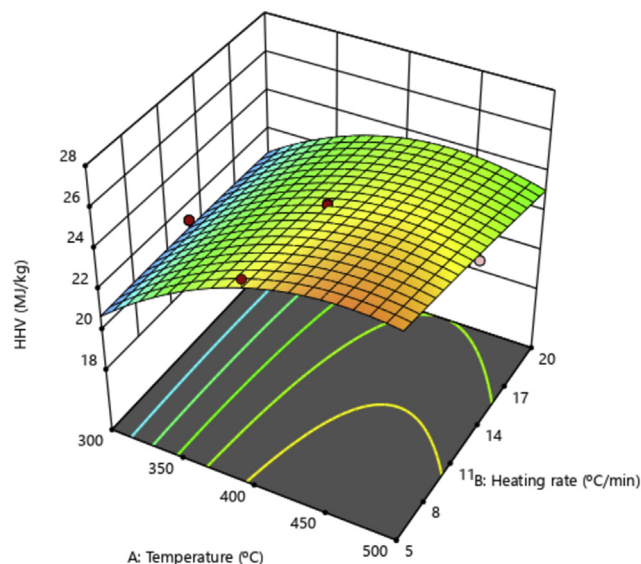


Figure 6. Effect of temperature (X₁) and heating rate (X₂) on char HHV at holding time of 17.5 min.

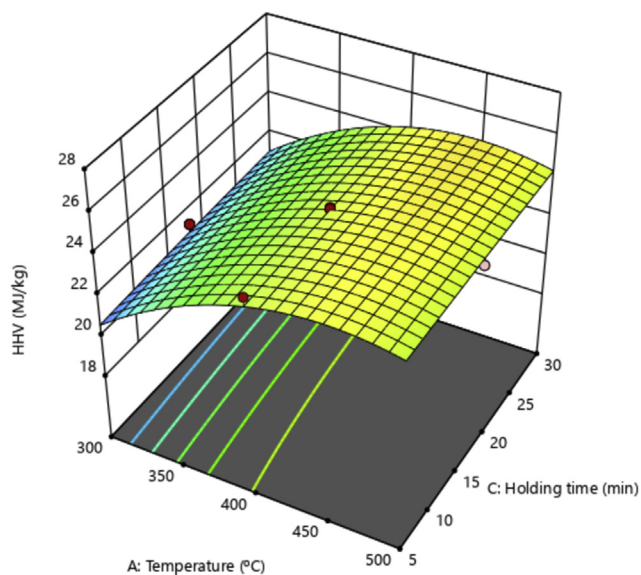


Figure 7. Effect of temperature (X_1) and holding time (X_3) on char HHV at heating rate of 12.5 min.

+0.6 MJ/kg was attained when heating cherry sawdust at 450 °C. Although this study detailed holding time as having no significant effects on HHV, deductions could be drawn from the statistical analysis. Positive trends were observed. By raising the holding time from 5 to 30 min at 300 °C, a 0.47 MJ/kg improvement was attained. Similarly, a 0.29 MJ/kg fuel improvement at 400 °C (Figure 7). The constituents of CS are readily decomposed under temperatures above 300 °C, as such prolonging the reaction time theoretically accelerates degradation, hence an increase in HHV. The relation between temperature and holding time was insignificant ($p > 0.05$), it is believed the currently defined holding time upper limits were not high enough to cause any major change in char HHV when contrasted with temperature. By raising the temperature from 350 to 450 °C a 1.76 MJ/kg (11.37%) improvement in HHV was attained while maintaining heating rate and holding time at 12.5 °C/min and 17.5 min respectively. As mentioned earlier, proximate analysis tests on chars within this temperature range indicate an increase in fixed carbon concentration, which is a primary indicator of improved fuel properties. A similar trend was reported by Xiong et al. (2014) as bamboo sawdust was heated from 400 to 600 °C, an HHV increase from 28 to 32 MJ/kg was noted. Within 300–500 °C temperature range is where the degradation of lignin and cellulose constituents takes place. These constituents are primarily responsible for char formation. The results of this study also showed that an increase in temperature from 450 to 500 °C was associated with HHV decrease from 24.27 to 21.84 MJ/kg. As previously mentioned dehydrogenation and amplification of the mineral concentration were linked to the decline in HHV. The results of Mundike et al. (2017) agree with this finding. Mundike et al. (2017) describes a release of hydrocarbons composed of C–C and C–H bonds when the temperature was raised from 525 to 570 °C as the cause of their 0.74 MJ/kg loss in HHV.

4. Techno-economics

A summary of process costs showing the disposal, utilities and labour costs of the proposed plant is shown in Table 6. The mass balance relies on bench-scale slow pyrolysis experiments published by Soka (2020) with CS as feedstock. The experiments estimated product yields of 34.5% char, 40.9% bio-oil and 24.1% biogas with 0.5% mass loss. These results formed the basis of the 30t/day proposed pyrolysis plant (Figure 8).

The capacity of the plant was selected to mirror the corn-stover production in South Africa. Based on the assumptions and estimation

Table 6. Summary of process costs.

	Cost	Unit
Raw materials		
Corn-stover	\$20	ton
Disposal services		
Disposal (solid and liquid)	\$53.48	ton
Utilities		
Electricity	148.27 c	KWh
Cooling water	\$9.95	m ³
Medium pressure steam	\$10.86	ton
Labour		
Process engineer	\$27 168	year
Operator	\$9 190	year

of process costs, the expected revenue from the sale of these products was \$575 167. The total purchased cost of equipment (TPCE) was \$765 600 while the working capital required was \$115 200. The total capital cost of the process was estimated at \$980 440 annually (Table 7). In comparison, a study by Thilakarathne (2016) on pyrolysis of woody biomass for hydro-carbon biofuel production, a TPCE of \$89.7 million with a working capital requirement of \$67.8 million were estimated. Their total capital costs requirement exceeded \$384 million. It is clear that a pyrolysis process that centres on the production of solid fuels are less capital intensive. Zhang et al. (2013) modeled a 2000 metric tons per day (MTPD) bio-refinery processing red oak feedstock and employing pyrolysis followed by hydroprocessing to produce diesel. The hydro-processing and reforming units were the largest drivers of the capital cost. The process had a total project investment of \$379 million. Many of these case studies involved pyrolysis followed by hydroprocessing to obtain the desired liquid biofuel products. The inclusion of additional processing units drives up production costs. In the study by Bridgwater (1996), biofuels market selling prices were 158% higher than contemporary diesel fuel. In the case where the production of solid char is prioritised, the need for liquid fuel upgrading is eliminated.

It is believed that the economic feasibility of the process is most sensitive to the cost of feedstock and pyrolysis products. Therefore a sensitivity analysis was conducted to study the convergence of product and CS prices with respect to profitability. The variance in product costs was based on previously published costs and assumptions based on the possible allowable market prices. CS as a pyrolysis feedstock has been investigated by Wright et al. (2010) and Shabangu et al. (2014). The former estimated the cost of CS at between \$0 and \$83/ton. The authors described the possibility of obtaining the CS at zero cost (excluding transportation costs) as an outcome of it being waste material. It is

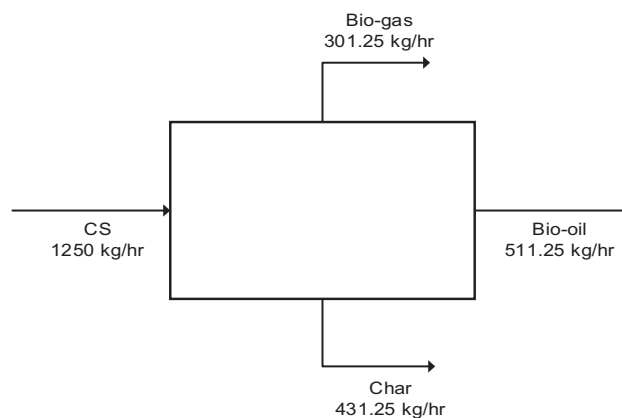


Figure 8. Mass balance of the pyrolysis process.

Table 7. Summary of economic results.

Slow pyrolysis	
Capital cost (\$/yr)	980 440
Cost of labour (\$/yr)	63 925
Annual operating costs (\$/yr)	645 476
Annual feedstock costs (\$/yr)	20 8050
Revenue (\$/yr)	575 167
Working capital (\$/yr)	115 200
TPCR (\$)	765 600

Table 8. By-product price assumptions.

By-products	\$/unit	source
Pyro-oil	50/ton	a*
Pyro-gas	1.5/m ³	a*

a* assumption based on purity.

believed that the valorisation of CS would relieve farmers of the burden of having to dispose of their CS through undesirable methods such as landfill dumping. Shabangu et al. (2014) estimated the cost of CS at \$50/ton inclusive of transportation costs. The current study estimated the cost of char at \$100/ton, which is based on reported studies and is comparable to the price of coal. Gura (2017) assessed the economics of a plant processing lignin into valuable phenols and other liquid biofuels. The author estimated the cost of biofuels ranging from \$320 to \$480/ton. While their gaseous fraction was sold at a minimum price of \$1.2/m³. The price of by-products in this study was assumed based on purity (Table 8).

Figure 9 illustrates the effect of variant feedstock and product prices on NPV. From a base price of \$20/ton, every ±20% change in the cost of CS, results in a \$0.27 million change in NPV. The possible variation in the cost of CS to \$3/ton results in an NPV of \$0. The NPV of the process is also highly sensitive to the pricing of char. The \$100/ton base price of char was selected comparatively to the price of coal. When the price of char is raised to \$150/ton, the result is a \$2.71M NPV improvement. On the other hand, there was no set price for bio-oil and bio-gas, hence their prices were assumed based on purity and market demands. A ±20% change in pyro-oil pricing, the resultant change in NPV was approximately \$0.11 million. Pyro-gas showed no significant effects on NPV.

The use of the upper limit prices (Figure 10) results in a positive cash-flow with NPV improved to \$2.41 million. Under these conditions, the process would break-even after 5 years. Provided these price estimates are accepted by the market, such returns could draw investment. The study suggests the payback period of slow pyrolysis is longer than that of faster forms of pyrolysis. Comparatively, the study by Kolokolova (2014) on the techno-economics of biomass pyrolysis into bio-bitumen had a

break-even period of 3 years. While the NPV after 20 years of operation is \$8.55 million.

5. The energy efficiency of the slow pyrolysis process

During the pyrolysis process, energy is required to maintain the desired temperature conditions inside the fixed bed reactor. As such, the energy efficiency of the process is an important parameter that describes the performance of the pyrolysis reaction. Jahirul et al. (2012) states that a comprehensive energy audit of industrial-scale pyrolysis plants is necessary to have a better understanding of the feasibility of such processes. The energy efficiency of a pyrolysis process can be estimated using Eq. (5)

$$n_{energy} = \frac{E_{biofuel}}{E_{feedstock} + E_{Pyrolysis}} \tag{5}$$

Where:

- n_{energy} is the energy efficiency of the process.
- $E_{biofuel}$ is the energy content of the char (MJ/kg).
- $E_{feedstock}$ is the energy content of CS (MJ/kg).
- $E_{Pyrolysis}$ is the external energy supply of the pyrolysis process (MW).
- $E_{Pyrolysis}$ is the input heating required to decompose the biomass under optimum process conditions. It can be through Eq. (6):

$$E_{Pyrolysis} = E_{reaction} \tag{6}$$

Where $E_{reaction}$ describes the input energy required to decompose the CS at optimum process conditions. It is desired that the energy efficiency be maximised in order to limit energy wastage during the process. Table 9 details the energy contents of the various parameters.

The $E_{reaction}$ was divided by the biomass feedstock feed-rate of 1250 kg/h (0.347 kg/s) to account for the quantity of CS that was decomposed during heating. As such the final Eq. (7) is as follows:

$$n_{energy} = \frac{26.25}{16.59 + 15.48} \times 100 \tag{7}$$

$$n_{energy} = 81.85\%$$

This study shows that ~82% of produced energy is sufficient for running the pyrolysis process. This is a relatively high energy efficiency compared to the results reported by Bramer and Holthuis (2005). The authors studied the energy requirements of running a 30 kg/h biomass system using flash pyrolysis. The study showed that about 5.48% of the energy produced was sufficient for running the process. The analysis conducted by Stals et al. (2010) achieved a better energy efficiency of 35–39% for the flash pyrolysis of heavy metal contaminated hardwoods from phytoremediation. The results of the current study suggest slow pyrolysis systems can have a better energy efficiency than flash pyrolysis systems.

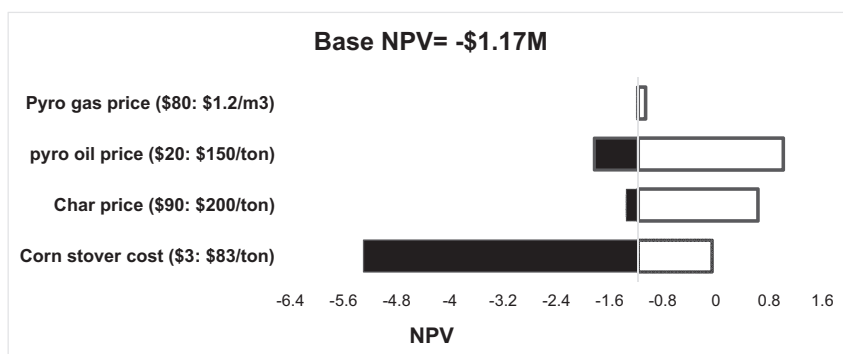


Figure 9. Sensitivity analysis on feedstock and product prices.

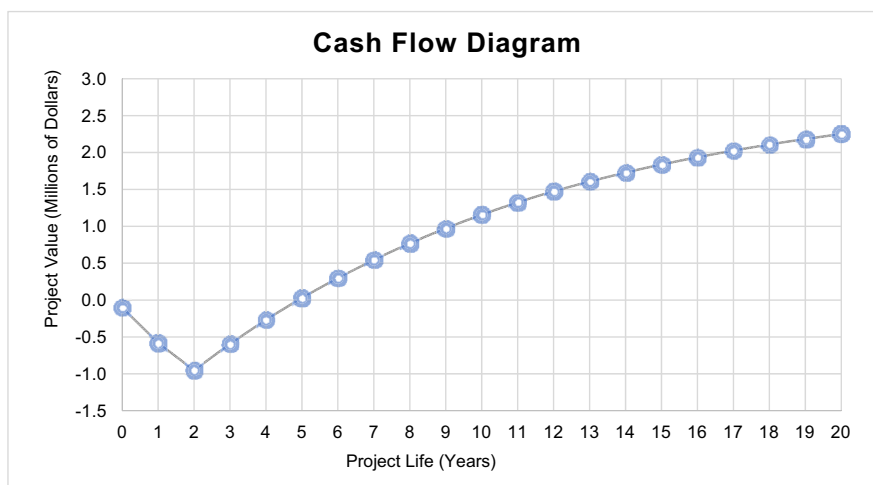


Figure 10. NPV at upper price limits.

Table 9. Energy contents of the different parameters.

Parameter	Energy content	Units
E_{biofuel}	26.25	MJ/kg
$E_{\text{feedstock}}$	16.59	MJ/kg
E_{reaction}	5.37	MW

In addition to energy efficiency, one other important energy measurement is the energy recovery of the process. The energy recovery indicates the percentage of energy transferred to the main product, in this case char. The energy recovery is determined using Eq. (8):

$$\text{Energy recovery} = \frac{\text{mass of pyrolysis char} \times \text{HHV of pyrolysis char}}{\text{mass of biomass pyrolysed} \times \text{HHV of biomass pyrolysed}} \times 100 \quad (8)$$

$$\text{Energy recover} = \left(\frac{6.9 \times 26.25}{20 \times 16.59} \right) \times 100$$

$$\text{Energy recover of char} = 54.59\%$$

This estimate implies char has 54.59% of the total energy transferred to the products. This result illustrates the process adequately favoured the production of char over bio-oil and biogas. In comparison, the energy recovered in the bio-oil and biogas was 28.61% and 16.8% respectively. The study by Stals et al. (2010) determined the energy recovery of bio-oils. The authors cited a 34% energy recovery in bio-oil when Jorunn hardwood was pyrolysed via flash pyrolysis. This determination suggests that processes that focus on the production of char over volatiles have the ability of having better energy management than other forms of pyrolysis which typically focus on the production of volatiles. For this reason more attention should be aimed at improving energy systems of slow pyrolysis processes. It is important to note the literature mentioned in this study utilised laboratory equipment for their determinations. As such it remains unclear the energy performance of industrial scale pyrolysis processes.

6. Conclusion

The optimisation of the slow pyrolysis process proved the process can be used to produce chars that are competitive with coals and are suitable for use in a range of combustion applications as a result of their relatively high energy contents. The work showed that temperature had a

statistically significant influence on both char yield and HHV ($p > 0.0001$). Considering the high HHV and yield, the optimisation of char production was successful. The study defined an objective to produce char with an energy content of above 25 MJ/kg while maintaining a yield of above 30%. At this specification, it is believed the char will be competitive with commercial coals. The optimisation of slow pyrolysis experimental variables produced char with an energy content of 26.25 MJ/kg with a yield of 34.5%. This was achieved at optimum process conditions of 453 °C, 5 °C/min and 29 min. This study also highlighted the economic feasibility of a 30t/day slow pyrolysis process. The process was highly dependent on the price of feedstock CS. It is recommended CS prices be kept as low as possible. The estimated prices of volatiles in this study remain contentious. In previous studies, volatile products were further processed to fit known market standards. Therefore the prices in this study were projected based on market-related products. The volatile products were not upgraded and were marketed as potential feedstock to downstream refinement. For that reason, there remains uncertainty in their price estimations. Corn-stover derived char is a commodity that can compete with traditional fossil fuels used in the South African energy sector. A pyrolysis plant that emphasises only on the production of char is not economically viable under base condition assumptions. Moreover, when the bio-oil and biogas by-products are accounted for, the price of char should be twice as much as that of traditional coals to make the process economically viable. It is unlikely the commercial markets would be receptive to such pricing. The NPV of the plant was highly dependent on the cost of CS and the price of char. At base price conditions, the valuation of by-products does not improve the profitability of the process significantly.

Declarations

Author contribution statement

Oluwaseun Oyekola: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ongama Soka: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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