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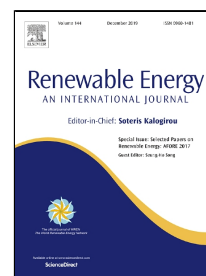
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Batch Pyrolysis of Cotton Stalks for Evaluation of Biochar Energy Potential

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Abstract. The thermal cracking of cotton stalks (CS) through pyrolysis was undertaken using a laboratory scale batch pyrolysis reactor. The distribution of pyrolysis products were studied dependent on the final pyrolysis temperature which ranged from 300 to 800°C by 100°C intervals. The maximum biochar yield of 46.5 % was obtained at 400 °C.mAs the pyrolysis process temperature increased, the solid char product yield decreased. The largest higher heating value (25.845 MJ kg^{-1}) was obtained at 600°C. All biochar samples produced between 500° and 700°C had an energy densification ratio of 1.41, indicating a higher mass-energy density than the initial feedstock. A larger share of syngas and bio-oil were produced at higher temperatures, as estimated. Preferential selection of a char based on the energy yield would lead to a selection of the 400°C product, while selection based on the energy densification ratio would be for a product obtained between 500° to 700°C. An energy simulation was conducted which determined that the process is self-sustaining at and above 400°C. Furthermore, the global energy potential was determined from CS pyrolysis, which was estimated at 380 PJ yr^{-1} could contribute to roughly 0.1% of the actual global total primary energy supply of 576 EJ yr^{-1}.

Keywords: cotton stalks; pyrolysis; biochar; energy

1 Introduction

Cotton stalks (CS) are a common agricultural residue with little economic value. They may be utilised without direct competition to food or feed provision. Cotton waste production by weight is estimated at 2.9 – 3.8 times larger than commercial cotton production [1]. Global cotton production was estimated to roughly 29.136 million tons in 2017/2018 [2], yielding roughly 80 million tons of CS. This significant quantity of CS waste from agricultural production is a potential source of revenue [3]. However, at present, CS is either mulched into the soil, removed from the cropland, or directly incinerated on farm-land to restrict future pest infestations. Furthermore, in less developed regions, CS is utilized as a fuel in simple

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cooking stoves, causing economic costs and environmental concerns [4]. Therefore, innovative technologies for environmentally friendly disposal of CS are urgently needed.

In this context, several studies have encouraged the conversion of agricultural residues into useful products as a method of carbon sequestration rather than their direct combustion [5, 6]. Some of these useful products include paper, boards, and biofuels. Unfortunately, due to the recalcitrant nature of lignocellulosic biomass, direct bioconversion to ethanol or biogas without pre-treatment or co-fermentation always results in an extremely low yield [7-10]. Therefore, many studies have focused on biochar production from agriculture residues[11-13]. Biochar is a solid carbon-rich residue left after pyrolysis of carbonaceous biomass. Researchers have indicated that biochar can be readily used as a biofuel feedstock for domestic use and in existing coal power plants, but also as fuel to heat the pyrolysis process [14, 15].

Utilization of cotton waste as an energy feedstock has been a subject of many studies in recent years [16-21]. These studies confirm that CS can be utilised as a biofuel with respect to its energy content, with a reported lower heating value (LHV) ranging from 16.4 to 18.26 MJ/kg [16]. Clean and energy-efficient utilization of CS in combustion plants is prevented by high contents of alkali elements such as Cl, K and Na which decrease the ash melting point of SiO_2 and lead to an increase in corrosion and fouling in the boiler plant. Therefore, CS are not a suitable feedstock for conventional combustion plants [6]. Instead, low-temperature thermochemical conversion such as pyrolysis could be applied to yield three types of products, biologically stable biochar containing the critical ash constituents, and the ash-free volatiles consisting of bio-oil and syngas. These products can be further utilised in high-temperature conversion routes such as combustion in gas boilers or cofiring in pulverized coal boilers [16]. Consequently, pyrolysis can effectively advance the biomass-conversion efficiency and provide a higher energy yield from the three products in comparison with the process generating a single product only, such as liquid oil or biogas.

Past pyrolysis experimentation of CS has been undertaken for the coproduction of char, oil, and gas [22,23]. The liquid bio-oil and synthesis gas have direct use as a fuel or as an intermediate pre-treatment step for converting biomass into a high-energy liquid, which can be further processed for power, heat, biofuels and chemicals [24]. Venkatesh et al. investigated biochar production technology for conversion of CS. They indicated that CS biochar produced at 450-500°C showed the greatest potential for use as a soil amendment to improve the fertility of rainfed soils as well as to sequester carbon [25].

The optimum quality of the three products obtained from biomass-based pyrolysis technology is critical, but in this context, for CS, there are not enough experimental details in literature. This article focuses on the characteristics of the CS pyrolysis products across a wide temperature range from 300° to 800°C in order to determine its energy potential with a special focus on the biochar.

2 Materials and methods

2.1 Material

CS samples were obtained from Syrian agricultural production. The CS was a mixture of small pieces of the main stem, branches, burs, boll rinds, bracts, and peduncles in various shapes and sizes. The CS was ground and sieved to produce a granular powder with a particle size of 1-3 mm. The chemical analysis of the raw CS feedstock and of each pyrolysis char was conducted in the laboratory of the Institute of Chemical and Energy Engineering (IVET),

University of Natural Resources and Life Sciences, Vienna (BOKU). The dry matter (DM) content of the CS was determined by drying samples at 105°C until a constant weight could be measured according to ASTM D4442-16 2016 [26]. Ash content was determined by combustion at 575°C for 3 hours according to ASTM E1755-01 2015[27] and volatile solids (VS) content was determined by heating at 950°C in covered crucibles to avoid oxidation by air according to ASTM E872-82 2013 [28]. The HHV of the CS feedstock and of each pyrolyzed char was determined using a Parr 6400 Automatic Isoperibol Calorimeter at the University of Copenhagen, Denmark in accordance with ASTM D5865-13 2013 [29]. Ultimate analyses of the dried samples for carbon, hydrogen, nitrogen, and sulfur were carried out with a CHNS/O elementary analyser (LECO TruSpec-CHN) with the methodology defined in ASTM D5373-16 2016 [26].The air dried CS samples contained 44.75% C, 5.75% H, 48.57% O, 0.9% N, and 0.03% S on a dry ash free basis (DAF). Proximate analysis performed on a dry sample indicated that it contained 76.44% volatile matter and 5.08% ash, resulting in a fixed carbon amount of 18.48%. The HHV of raw CS was 18.32 MJ kg^{-1}.

2.2 Experimental procedure

CS pyrolysis experiments were conducted using a laboratory batch pyrolysis reactor. The stainless-steel reactor was cylindrical, airtight, and batch designed. The reactor lid measured 18 cm wide and 2 cm high, the holding container 14 cm wide and 12 cm high. The reactor was modified with a steel pipe connected to a valve to allow input of N_2 to create an O_2 free environment and an output of syngas and liquid coproducts released during experimentation. Six temperature settings for pyrolysis were selected: 300°, 400°, 500°, 600°, 700°, and 800°C. The residence time for the pyrolysis of each sample was fixed at 30 minutes. For each pyrolysis experiment the temperature was set at each respective temperature and residence time. Approximately 20 grams (± 0.5 grams) of the prepared CS was loaded into the steel reactor for each run. After loading the CS and before the start of each run, N_2 was purged into the reactor at a rate of roughly 0.5 litres min^{-1} for fifteen minutes. Following the initiation of each run, N_2 input into the reactor continued until the furnace reached the desired temperature. At the desired temperature N_2 input stopped, the tube removed, and the same inlet was used as an outlet for the gaseous and liquid products. The heating rate was calculated by measuring the length of time to reach the desired temperature from ambient room temperature at 25°C yielding an estimated heating rate of 13K per minute. During each experiment the gaseous products were allowed to escape, while the liquid condensates (bio-oil) were collected in a small container. After pyrolysis experimentation, the solid char products were collected from the reactor, weighed, and stored in airtight containers. The syngas and bio-oil yields were calculated by estimation based on literature. Each experiment was conducted at least twice to ensure that the pyrolysis tests yielded similar results and the reported yield is the average. Because the standard deviations for char yields were 2% or lower, duplicate experiments were deemed satisfactory as suggested by Louwes et al [30].
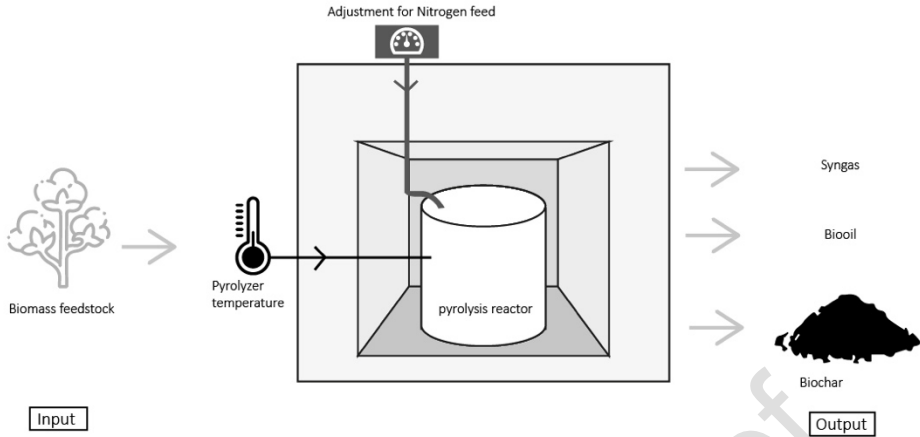
Fig. 1: Design of pyrolysis experimentation

Table 1. Design of pyrolysis experimentation with heating rate 13°C/min and Residence Time 30 min

Experimental Temperature	Initial Mass (g)	Nitrogen Flow (liters min^{-1})	Replication
300°C	20	0.5	3
400°C	20	0.5	3
500°C	20	0.5	3
600°C	20	0.5	2
700°C	20	0.5	2
800°C	20	0.5	2

2.3 Calculations

The input of biomass was compared to the quantity of outputs. 100% conversion efficiency was assumed, as well as a conversion efficiency with a gas loss of 16%. Char yield was calculated with equation (1) in which M_C is the mass of the produced char, M_{Feed} is the mass of the feedstock, and Y_{Char} is the calculated percentage yield [31]:

$$Y_{Char}\left(\%\right) = \frac{M_C}{M_{Feed}} \cdot 100 \qquad (1)$$

Oil yield (Y_{oil}) was determined from previous experiments with similar feedstocks and compared to literature data as mentioned in the section above. The gas yield (Y_{gas}) has been calculated according to equation 2 where Y_{Oil} and Y_{Gas} are defined analogous to equation 1.

$$Y_{Gas} = 100 - Y_{Char} - Y_{Oil} \qquad (2)$$

The energy yield was calculated from the mass yield, and the lower heating values (LHV) of the char and feedstock according to equation 3.

$$Y_{Energy}(\%) = Y_{Char}\frac{LHV_{Char}}{LHV_{Feed}} \qquad (3)$$

The mass energy density or the, energy densification ratio, was calculated by equation 4 from the mass yield and energy yield.

$$Energy\, densification\, ratio = \frac{Y_{Energy}}{Y_{Char}} \qquad (4)$$

A simple energy balance for the pyrolysis experiments at each temperature was developed from the average product yields under the assumption that product losses were negligible. The chemical energy (E_{Chem}) of the char was calculated by multiplying the char yield (Y_{Mass}) by the LHV of the chars at each respective temperature according to Equation 5.

$$E_{Chem} = Y_{Char} \bullet LHV \qquad (5)$$

The bio-oil and syngas chemical energy were estimated from an energy simulation heat balance. The bio-oil to syngas ratio was used to calculate the remaining energy from the CS feedstock allocated to the bio-oil while the syngas chemical energy was estimated as the remaining energy difference from the chemical energy of the bio-oil and that of the char. To calculate the LHV's of the bio-oil and syngas, the chemical energy from the energy simulation were divided by the percent weight product yields of the bio-oil (Y_{Oil}) and syngas (Y_{Gas}) products according to Equations 6 and 7.

$$LHV = E_{Chem}/Y_{Oil} \qquad (6)$$

$$LHV = E_{Chem}/Y_{Gas} \qquad (7)$$

To measure the total potential energy from CS and the pyrolysis products we must first calculate the collectible dry biomass. The collectible dry biomass C_B can be calculated from Eq. 8, with the annual crop production, C_P, the residue factor, R_F, the dry weight factor, W_F, and the availability factor of the residues, A_F [31]:

$$C_B = C_P \text{ x } R_F \text{ x } W_F \text{ x } A_F \qquad (8)$$

For cotton, the availability factor is 0.6 and the dry weight factor is 0.5 [29]. A value of 3.0 was selected for the residue factor [32].

The global energy potential per year from raw CS, denoted by E_{CS} may be calculated by multiplying the dry cotton residue by the LHV of the residue (LHV of 17.063 MJ/kg) determined from the current study [33]. The LHV was used rather than the HHV because this is the typical value for bioenergy processes [34]. Whereas the char energy potential, denoted by E_{Char} can be calculated by also including the char mass yield (Y_{Mass}).

$$E_P = C_B \text{ x LHV} \qquad (9)$$

$$E_P = C_B \text{ x } Y_{Mass} \text{ x LHV} \qquad (10)$$

In this calculation an optimal situation is assumed in which the energy for the pyrolysis process comes from an external source with enough free energy available for the process. This could be the case if the pyrolysis plant is situated next to a power station or industrial boiler which has enough excess heat production with sufficient temperature. Losses from the process were estimated at 8% of total energy as suggested by a study by Pröll et al. These losses are not distributed evenly throughout the products. The majority of losses occur in the oil scrubber in which gas and liquid products are separated and a small portion in the reactor is lost as heat, therefore the heat loss was distributed amongst the gas and oil energy yield [23].

3 Results and discussions

3.1 Products distribution

Pyrolysis yields (wt%) of CS at different temperatures are shown in Figure 2. Overall, increasing the process temperature results in a decrease of char yield and an increased yield of liquid and gases. Char yield fraction varied from 86.5% to 28.0% for all samples with the highest value for char yield at 300°C, and subsequently decreasing with an increase of the pyrolysis temperature to the lowest char yield at 800°C. Of special consideration is that at 300°C, it is torrefaction rather than pyrolysis which leads to a minimal release of volatiles, and therefore, the char produced at 300°C had not undergone full carbonization. A similar study conducted earlier investigated the char yield of other feedstocks such as wheat and rice straw, corn stover, and rape stalk with results indicating a similar proportional char yield reduction at their respective temperatures. For example, the yield of rice straw was reduced from 74.49% at 300°C to 35.59% at 600°C which is within 2% of the yield of CS char at those temperatures [35]. The products from biomass pyrolysis are a combination of the individual pyrolytic products of cellulose, hemicellulose, lignin, and extractives. Secondary reaction products result from cross reactions with the products of primary pyrolysis and molecules from the original feedstock. Cellulose degradation generally occurs between 240°C and 350°C; hemicellulose degradation occurs between temperatures of 200°C and 260°C while lignin degradation occurs between 280°C and 500°C [36].
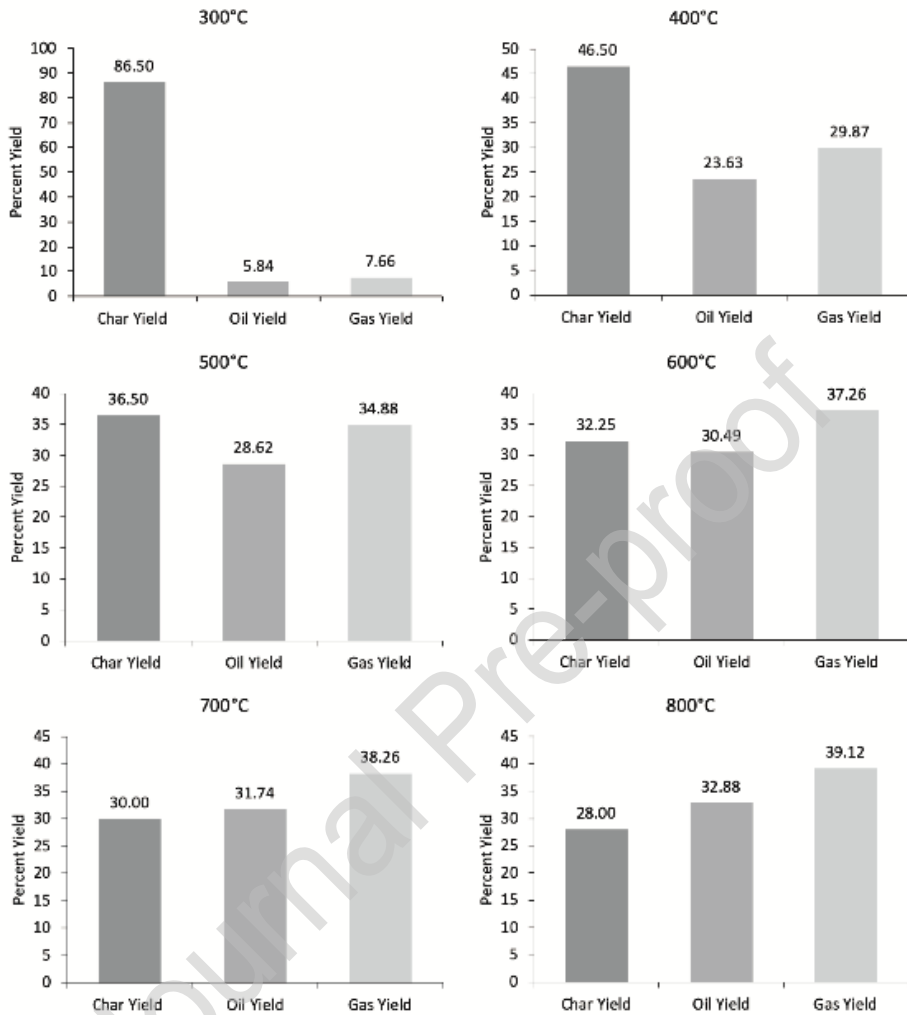
Fig. 2. Yields of pyrolysis products at each temperature

The lowest bio-oil and syngas yield occurred at 300°C with 5.84% and 7.66% respectively. These values were estimated based upon previous experiments as well as through literature [37, 38]. This can be attributed to the fact that 300°C sample had not undergone full carbonization and therefore produced minimal gaseous and liquid products while yielding the largest quantity of solid product at 86.5%. The largest bio-oil and syngas yields occurred at 800°C with 32.88% and 39.12% respectively, but also with the lowest yield of char at 28%. At higher temperatures, the increase in gas yield can be attributed to the secondary reactions of the pyrolysis vapors within the reactor, while the decreased char yield is attributed to the primary decomposition of the CS feedstock and the secondary decomposition of char at higher temperatures. During secondary decomposition of char at higher temperatures, non-condensable syngas products also contribute to elevated gas yield which occurs parallel to increasing temperature [39, 40]. Preferential selection of pyrolysis temperature is dependent on prioritizing yield distribution. In this study, our main objective is a higher char content, and therefore, the yield at 400°C would be deemed optimal.

3.2 Proximate Analysis
The results of the proximate analysis for all samples are shown in Tables 2 and 3. In Table 2, the proximate analysis for the CS feedstock is measured on an air-dried basis with a moisture of 8.6% while the proximate analysis in Table 3 is on a dry basis excluding moisture for all samples.

Table 2: Proximate analysis of air-dried cotton stalks.

Sample	Volatile$_{ad}$ (%)	Fixed Carbon$_{ad}$ (%)	Ash$_{ad}$ (%)	Moisture$_{ad}$ (%)
Current Study CS	69.9	16.9	4.6	8.6

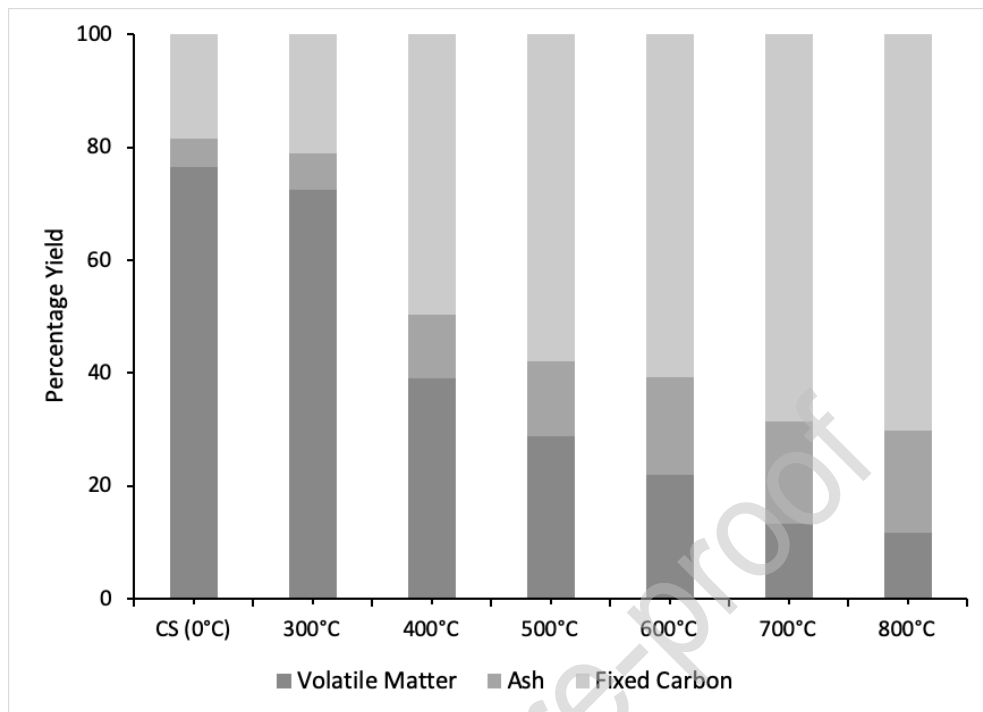Air Dried (ad): includes air dried moisture only

Figure 3: Proximate analysis of product samples on a dry basis.

Table 3: Proximate analysis of product samples on a dry basis.

Experimental Temperature	Volatile$_{db}$ (%)	Ash$_{db}$ (%)	Fixed Carbon$_{db}$ (%)
CS (0°C)	76.44	5.08	18.48
300°C	72.55	6.41	21.04
400°C	39.04	11.22	49.74
500°C	28.88	13.24	57.88
600°C	21.95	17.26	60.79
700°C	13.28	18.09	68.63
800°C	10.61	18.21	71.02

Dry Basis (db): excludes all moisture

On a dry basis, the CS contained the highest volatile matter (VM) at 76.44%, the lowest ash content at 5.08%, and the lowest fixed carbon (FC) at 18.48%. On the other hand, the char produced at 800°C had the lowest VM at 10.61%, the highest ash content at 18.21%, and the highest FC at 71.02%. The largest changes occurred between 300°C and 400°C with a reduction of VM at 33.51%, an increase in ash content at 4.81%, and an increase in FC at 28.7%. The FC and ash content increased continuously with increasing temperature. The

measured FC content was higher than the VM in all samples above 300°C. Because the char at 300°C did not undergo full carbonization, the lower FC content may be attributable to the low carbonization degree of the sample [41]. The smallest decrease in VM and increase in FC content occurred between 700°C and 800°C at 2.67% and 2.39% respectively. The carbonization process consists of two major reactions, the de-polymerization reaction dominant in the preliminary carbonization stage and the polycondensation reaction dominant at higher carbonization temperatures. The decrease in biochar yield at higher temperatures is due to the conversion of VM into carbon black by polycondensation reactions. Conversely, during dominance of polycondensation reactions, formation of FC and the decomposition rate of volatiles may increase or remain unchanged [42]. Therefore, the reduction in biochar yield at higher temperatures decreases, observed above 600°C in this study, while that of VM and FC yield decreases at temperatures above 700°C in this study. This study suggests that CS char would be more appropriately used as a fuel than a fertilizer due to its relatively low ash content, low VM, and high FC compared to other feedstocks [41]. Preferential selection of a char for use as fuel would be the char produced at 800°C because it has the lowest VM, a suitable ash content, and the highest FC.

The distribution of VM, ash, and FC yields are similar to previous related studies. He et al. reported an initial value of 82.4% VM, 7.45% ash, and 10.2% FC for feedstock CS, of which the values changed to roughly 19%, 21%, and 60% respectively at a final temperature of 600°C [41].

3.3   Calorific Value

The results of the heating value analysis including the standard deviation (SD) and standard error (SE) for all samples is shown in Table 4. The HHV was measured by bomb calorimeter while the LHV was calculated based on the elemental analysis as presented in the following section.

Table 4: Heating values of pyrolysis samples.

Experimental Temperature	HHV (MJ kg^{-1}) + Standard Deviation	LHV (MJ kg^{-1}) + Standard Deviation	Standard Error of HHV
CS (0°C)	18.320 ±0.190	17.063 ±0.196	±0.110
300°C	19.629 ±0.454	18.633 ±0.462	±0.110
400°C	25.403 ±0.538	24.638 ±0.545	±0.262
500°C	25.755 ±0.525	25.126 ±0.534	±0.303
600°C	25.845 ±0.171	25.457 ±0.175	±0.121
700°C	25.793 ±0.481	25.582 ±0.493	±0.099
800°C	25.609 ±0.449	25.423 ±0.474	±0.259

As illustrated in Table 4, the highest measured HHV was 25.845 MJ kg^{-1}, which occurred at a pyrolysis temperature of 600°C while the lowest HHV was 19.629 MJ kg^{-1}, which occurred at a pyrolysis temperature of 300°C. For the calculated LHV values, the highest LHV was 19.629 MJ kg^{-1}, which occurred at a pyrolysis temperature of 700°C while the lowest LHV was 18.633 MJ kg^{-1}, which occurred at a pyrolysis temperature of 300°C. A reduction in HHV was measured in samples pyrolyzed above 600°C, while a reduction in

LHV was calculated only in the sample pyrolyzed above 700°C. The ANOVA statistical analysis was conducted on both HHV and LHV; it found that there is a significant difference between both the feedstock CS and char pyrolyzed at 300°C compared to the other samples. However, char produced at pyrolysis temperatures of 400°C, 500°C, 600°C, 700°C, and 800°C did not have a significant difference ($P > 0.5$) between them. Therefore, we are ambivalent to the selection of char based on the temperature of the pyrolysis process as long the process is at least 400°C. The increasing trend of calorific value and subsequent decline with increasing temperatures is a well-documented phenomenon and can be explained scientifically. During low pyrolysis temperatures, large quantities of low calorific value volatiles such as CO, CO_2, and chemically bound water is released and the FC increases thereby increasing the calorific value with the gradually increasing temperature. At higher pyrolysis temperatures there is a decrease in calorific value due to the emission of high calorific value VM constituents such as H_2, CH_4, and tar [41].

The characteristics of the samples were consistent with values found in literature. A study by Xiong et al. reveals that the HHV of CS char has a peak value between 550°C and 600°C at roughly 27.5 MJ kg^{-1} before a slight reduction at higher temperatures [38]. A study by He et al. reported a HHV for CS char of 25.45 MJ kg^{-1} at a temperature of 600°C which is close to the HHV of standard coal indicating its suitability as a fuel [40].

3.4   Elemental Analysis

The results of the elemental analysis for all samples are shown in Table 5 and the molar ratios of H/C and O/C are placed on a Van Krevelen graph in Figure 4 to illustrate the substitution suitability of the chars for various fossil fuels.

Table 5: Elemental analysis of all samples.

Experimental Temperature	C	H	N	S[a]	O*	H/C	O/C
CS (0°C)	44.75	5.75	0.9	0.03	48.57	1.53	0.81
300°C	47.13	4.51	1.09	0.1	47.17	1.14	0.75
400°C	58.8	3.47	1.49	0.14	36.11	0.70	0.46
500°C	67.63	2.86	1.42	0.16	27.93	0.50	0.31
600°C	68.99	1.72	1.4	0.18	27.72	0.30	0.30
700°C	71.25	0.90	1.4	0.2	26.26	0.15	0.28
800°C	72.26	0.78	1.43	0.28	25.25	0.13	0.26

[a]Adapted from Chen 2012
*Calculated by difference
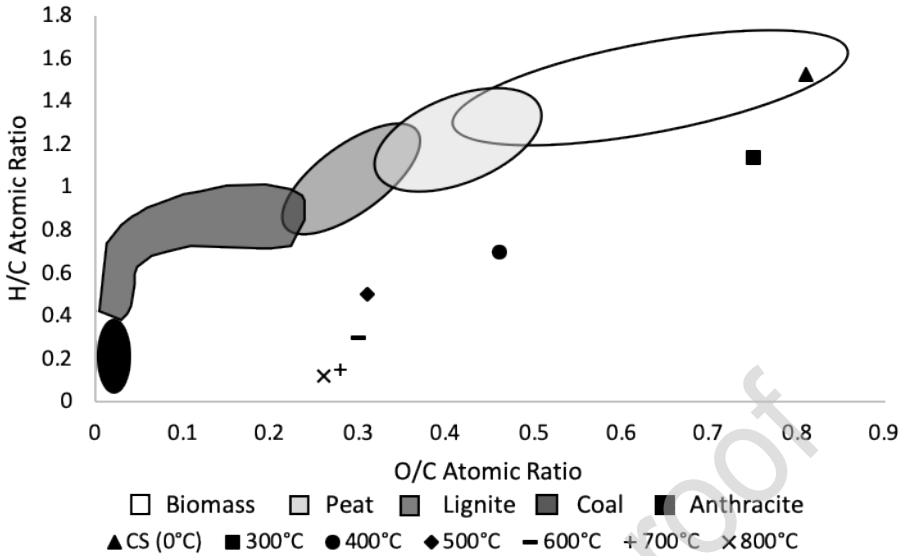
Fig. 4. Van Krevelen diagram with molar ratios of H/C and OC (Bilgic 2016).

The C content in the char samples increased as a function of increasing temperature while the H and O contents decreased. The highest C content at 72.26% was found at a pyrolysis temperature of 800°C, while the lowest was found in the feedstock CS at 44.75%. The highest H and O contents were found in the feedstock CS at 5.75% and 48.57% respectively, while the lowest were found at 0.78% and 25.25% respectively in the char pyrolyzed at 800°C. The N content initially increased with increasing temperature to its highest content at 1.49% in the char which underwent pyrolysis at 400°C until it stabilized into a decreasing trend. The C content conversion efficiency displayed a decreasing trend until the char pyrolyzed at 500°C and then displayed a slight increasing trend with exception to the char pyrolyzed at 800°C. The slight increasing trend of C content conversion efficiency at higher temperatures may be attributable to the secondary decomposition of dextran tar to produce C, gas, and non-condensable gas. H and O reduction is attributed to deoxygenation and dehydration reactions during the production of VM at increased pyrolysis temperatures. The separation of H and O is mainly caused by the breaking of chemical bonds with increasing pyrolysis temperature [41]. The molar ratios of H/C and O/C underwent a significant decrease as pyrolysis temperatures increased. From an initial feedstock value of 1.53 for H/C and 0.81 for O/C to values of 0.13 and 0.26 for the char pyrolyzed at 800°C respectively. The decreasing trend slowed as the samples were pyrolyzed at higher temperatures. The H/C and O/C molar ratio decrease indicates that the degree of carbonization and aromaticity elevates gradually [41]. As illustrated in the Van Krevelen diagram in Figure 4, the H/C and O/C molar ratios of the pyrolyzed samples indicate their suitability as a fuel. In particular, pyrolysis temperature at and above 400°C are most suitable because they are close to the ratios given by peat, lignite, coal, and anthracite. Preferential selection of char sample based on pyrolysis temperature would lead to the conclusion that a pyrolysis temperature of 800°C is the highest quality char for fuel because it displays higher carbonization and the H/C and O/C molar ratios reveal that is an appropriate substitute for coal.

The characteristics of the samples were consistent with values found in literature. He et al. reported a gradual increase in C content from 300°C to 600°C and a decrease in H and O content. The C content conversion efficiency decreased until 500°C, after which an

increasing trend was observed. The N content of the chars initially increased until 400°C, after which it decreased until the final measurement of 600°C. The S content increased in all char samples as temperatures increased [41]. Chen et al. also pyrolyzed CS from 250°C to 950°C and reported an increase in C content and a decrease in H and O content. The C content conversion efficiency decreased until 650°C, after which an increasing trend was observed. The N content increased until 350°C after which it displayed a decreasing trend. The S content also increased in all char samples as temperatures increased [42]. He et al. reported a decrease in H/O and O/C molar ratios for CS and a variety of feedstocks and illustrated that the values for char were lower than those for wood, grasses, manure and crop residues [41].

3.5 Solids Energy Yield, and Mass Energy Density

The char energy yield of the samples is displayed in Table 6. It is a comparison of the energy retained after pyrolysis with the energy content of the initial biomass feedstock.

Table 6. Mass and Energy yields of CS and char samples.

Experimental Temperature	Solids Mass Yield (%)	Solids Energy Content (HHV) (MJ kg^{-1})	Solids Energy Yield (%)	Energy Densification Ratio
CS (0°C)	100	18.32	-	1
300°C	86.5	19.63	92.68	1.07
400°C	46.5	25.40	64.48	1.39
500°C	36.5	25.765	51.31	1.41
600°C	32.25	25.855	45.50	1.41
700°C	30	25.80	42.24	1.41
800°C	28	25.61	39.14	1.40

For char samples at all temperatures the energy yield was greater than the mass yield. The highest chemical efficiency was exhibited in the char pyrolyzed at 300°C at 92.68%, however, this sample did not undergo full carbonization and was therefore eliminated from consideration. The second highest chemical efficiency was found in the char pyrolyzed at 400°C at 64.48%, while the lowest was found in the char pyrolyzed at 800°C at 39.14%. The energy densification ratios of all samples increased with increasing pyrolysis temperature. In comparison with the energy density of the feedstock with a value of 1, chars pyrolyzed at 500°C, 600°C, and 700°C all had the highest energy densities at 1.41. This signifies that at a lower mass, there is an increase in energy content, producing a higher quality product. Preferential selection of a sample based on the energy yield would lead to a selection of the char pyrolyzed at 400°C, while selection based on the energy densification ratio would be the chars which underwent pyrolysis between 500°C and 700°C. A study by Poudel et al. reports a similar decrease in energy yield from 95% at 150°C to 25% at 600°C during pyrolysis of food waste [43].

3.6 Heat Balance

Table 7 displays the energy required for pyrolysis as well as losses and the remaining energy when each respective product is used as fuel. The first column represents the energy requirement and losses associated with the pyrolysis process. The second, third, fourth, and fifth column represents the self-sustaining potential of the process when the respective constituent products are used for heat.

Table 7: Heat balance in pyrolysis, using different fuels.

Experimental Temperature	Pyrolysis Energy (MJ kg^{-1}) Requirements +Losses	Total Gas and Oil Product (MJ kg^{-1})	Portion of Oil from Total Gas and Oil Product (MJ kg^{-1})	Oil Only (MJ kg^{-1})	Gas Only (MJ kg^{-1})	Char Only (MJ kg^{-1})
300°C	2.20	-0.8	-1.1	-1.9	-2.4	13.52
400°C	2.29	4.2	3.0	1.3	-2.0	8.28
500°C	2.45	6.7	5.2	2.8	-2.2	5.51
600°C	2.62	7.7	6.0	3.1	-2.5	4.10
700°C	2.80	8.3	6.6	3.2	-3.0	3.11
800°C	2.98	9.0	7.3	3.3	-3.4	2.10

The simulation indicates that at pyrolysis temperatures above 300°C there is enough energy to heat the process when the syngas is combusted in conjunction with a small portion of the bio-oil. As can be seen in the fifth column, all of the syngas is combusted at each temperature. In the third column, when the total syngas is combusted and a portion of bio-oil is utilized, there is still excess energy after at process temperatures above 300°C. The simulation was conducted using the simulation software IPSEpro. Comprehensive explanation of the simulation software as well as on results of the mass- and energy balance can be found in Schaffer et al. [16].

Of the three products of pyrolysis, syngas is regarded as the lowest energy density product with a low heating value. Regardless, in many pyrolysis processes the syngas has enough energy potential to dry the feedstock and heat the pyrolysis furnace. The output of non-condensable gases consist of a variety of combustible gases including H_2, CO, CH_4, and C_2-hydrocarbons as well as a high concentration of non-combustible CO_2. The gases are produced due to reactions, namely, decarboxylation, demethanation, depolymerization, as well as others which occur under thermal conditions. A study by Crombie et al. found that pyrolysis above 450°C produced enough syngas to provide sufficient energy to maintain the pyrolysis process [45]. Conversely, a study by Xu et al. found that the syngas was insufficient to self-sustain the process and therefore an additional energy source was required. This energy source can come from the co-produced bio-oil for heat as it exits the reactor in the form of vapors. In this way a portion of the bio-oil can be directed to the combustor with the syngas, thereby avoiding its condensation for a more simple process. As illustrated by the study, the process is self-sustaining by combusting the co-produced syngas and fraction of bio-oil and no external energy source is required [46]. There are several other alternatives

available for creating a self-sustaining pyrolysis process in the case that the syngas does not provide enough energy through combustion, these are: combustion of a portion of the produced char, combustion of other raw feedstocks, gasification of the char in conjunction with combustion of the produced syngas, the combustion of fossil fuels, and the use of the produced bio-oil in conjunction with syngas as suggested in this study [47].

3.7 Chemical Energy Balance

Table 8 displays the LHV found within each pyrolysis product. The bio-oil and syngas LHV's were calculated with Eq. 6 and 7, respectively. Table 9 displays the chemical energy of each product and the percentage of the total feedstock they contain. The total chemical energy of the combined pyrolysis output products equals the energy input LHV of the feedstock. LHV and chemical energy values are rounded to the nearest hundredth. Figure 3 displays a Sankey diagram of the chemical energy balance for pyrolysis products at 600°C in which the chemical energy is based on the LHV and the input energy is equal to the output. In normal operating conditions some loss would be expected from the reactor.

Table 8: LHV's of all pyrolysis products.

| Experimental Temperature	Solids LHV (MJ kg^{-1})	Bio-oil LHV (MJ kg^{-1})	Syngas LHV (MJ kg^{-1})
CS (0°C)	17.06	-	-
300°C	18.63	12.35	2.93
400°C	24.64	18.78	3.92
500°C	25.13	22.62	4.07
600°C	25.46	23.77	4.31
700°C	25.58	24.54	4.18
800°C	25.42	25.43	4.05

Table 9: Energy balance of pyrolysis process based on chemical energy of products.

Exp. Temp.	Solids Chemical Energy (MJ kg^{-1})	Solids % of Total Energy	Bio-oil Chemical Energy (MJ)	Bio-oil % of Total Energy	Syngas Chemical Energy (MJ)	Syngas % of Total Energy	Total Chemical Energy (MJ)
CS (0°C)	17.06	100	-	-	-	-	17.06
300°C	16.12	94.5	0.72	4	0.22	1.5	17.06
400°C	11.46	67	4.44	26	1.17	7	17.06
500°C	9.17	54	6.47	38	1.42	8.5	17.06
600°C	8.21	48	7.25	42.5	1.61	9.5	17.06

| 700°C | 7.67 | 45 | 7.79 | 45.5 | 1.60 | 9.5 | 17.06 |
| 800°C | 7.12 | 42.5 | 8.36 | 48 | 1.58 | 9.5 | 17.06 |

*Percentage rounded to the nearest 0.5%.
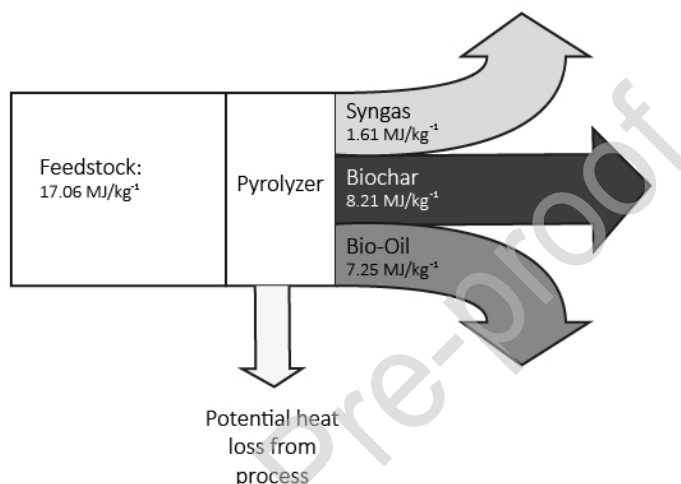
Fig. 5 Sankey diagram of the chemical energy balance for pyrolysis products at 600°C

Table 8 displays the LHV's of each pyrolysis product at their respective temperatures. The lowest calculated LHV for bio-oil occurred in the char pyrolyzed at 300°C at 12.35 MJ kg^{-1} while the highest calculated LHV occurred in sample the char pyrolyzed at 800°C at 25.43 MJ kg^{-1}. The char pyrolyzed at 800°C was the only bio-oil product which had a higher LHV than the char product (25.42 MJ kg^{-1}). The lowest calculated LHV for syngas occurred in the char pyrolyzed at 300°C at 2.93 MJ kh^{-1} while the highest calculated LHV occurred in the char pyrolyzed at 600°C at 4.31MJ kg^{-1}. All syngas products had lower LHV's than those of the char and bio-oil products.

Table 9 displays a simple energy balance for the pyrolysis samples at each temperature based on the chemical energy within the products. For simplification, losses are neglected here; i.e. heat losses are considered equal independently on the process temperature. It was observed that the largest fraction of chemical energy was contained in the char between at 300°C at 94.5% and at 600°C at 48%. Chars pyrolyzed at 700°C and 800°C had the largest fraction of chemical energy within the bio-oil at 45.5% and 48% respectively. Syngas had the lowest fraction of chemical energy in all samples which ranged from its lowest in the char pyrolyzed at 300°C at 1.5% to its highest in the chars pyrolyzed from 600°C through 800°C at 9.5%.

Figure 5 reveals that the largest fraction of the total feedstock chemical energy content is found within the biochar at 48%. The bio-oil constitutes 42.5% while the syngas constitutes 9.5% of the total feedstock chemical energy.

Studies by He et al. and Chen et al. find a similar increase in HHV of syngas from CS at increased pyrolysis temperatures [40, 41]. A study by Mythili et al. on pyrolysis of CS at 450°C reveals a HHV of 19.445 MJ kg^{-1} which is close to the calorific value of the char pyrolyzed at 400°C at 18.78 MJ kg^{-1} [46].

3.9 Global Energy from CS and the Pyrolysis Products

Table 10 displays the global energy potential from CS combustion and pyrolysis products with 8% heat loss. Quantities of dry CS residue were calculated with Eq. 8. Global energy potential per year from raw CS was calculated by Eq. 9. Global energy potential per year from the char was calculated by Eq. 10 (rounded to the nearest whole number) [32].

Table10: Global energy potential from CS and pyrolysis products with 8% heat loss.

Experimental Temperature	Solids Energy (PJ yr^{-1})	Bio-Oil Energy (PJ yr^{-1})	Syngas Energy (PJ yr^{-1})	8% Losses of Energy	Total Energy (PJ yr^{-1})
CS Feedstock	413	-	-	-	413
300°C	380	0	0	33	413
400°C	277	91	12	33	413
500°C	222	140	18	33	413
600°C	199	159	22	33	413
700°C	186	172	22	33	413
800°C	172	186	22	33	413

It was found that direct combustion of CS residues results in an energy potential of 413 PJ yr^{-1} which is under 0.1% of the global TPES of 576 EJ. Pyrolysis of the CS results in identical net energy of 413 PJ, however the distribution of the energy varies and when losses are included the potential energy is reduced from 413 PJ to 380 PJ for all pyrolysis processes. The pyrolysis process at 300°C has the largest quantity of energy within the solid residue at 380 PJ, however the sample had not undergone full carbonization, its calorific value was low, and it has a lower energy density than the other samples. Of the char samples which underwent full carbonization, the pyrolysis process at 400°C has the largest energy potential distribution in the char at 277 PJ. The remaining energy potential is found in the bio-oil at 91 PJ and the syngas at 12 PJ. The pyrolysis process at 800°C has the lowest energy potential found within the char at 172 PJ and the highest energy potential found within the bio-oil at 186 PJ. Meanwhile, the samples with the highest energy potential found within the syngas occurred under pyrolysis temperatures of 600°C, 700°C, and 800°C which all have 22 PJ. Preferential selection of appropriate pyrolysis temperature for energy potential would be dependent on prioritization of higher char or bio-oil yield as these are the highest quality of the three products. Considerations contributing to preferentially selecting a higher char or bio-oil yield are transportation and storage costs, end-use of products, the price of utilizing each product, as well as others. It is estimated that the conversion of biomass to bio-oil can reduce transportation, handling, and storage costs due to its density of roughly 1.2 kg/m^3

which is nearly ten times higher than the density of agricultural residues. A reduction of 87% in vehicle movements and costs is also estimated. The concept of small decentralized pyrolysis units on the magnitude of 100,000 - 300,000 tons yr^{-1} of agricultural residues can be envisioned to produce bio-oil to be processed in a centralized plant for upgrading away from the pyrolysis process. Furthermore, there are proposals to consider a mixture of the bio-oil with the co-produced char to create a slurry with higher energy content than the individual constituents alone [45].

In 2016, the global TPES was 576 EJ [46]. The total potential energy from the combustion of the CS is 413 PJ and of the pyrolysis products is 380 PJ which constitutes less than 0.1% of the TPES. Although the percentage is low, this study provides a proof of concept which can be scaled up by utilizing alternative residuals of which there are considerable quantities globally. Indeed, the estimate of 65 EJ yr^{-1} from only six abundant agricultural residues represents roughly 15% of global TPES which indicates their large-scale potential and viability [47].

4 Conclusions

Our pyrolysis study has shown that CS can be effectively used as a raw material for the preparation of biochar rather than integration into or incineration in the field. This would prevent CS from serving as an overwintering site for insects such as the pink bollworm. The biochar could be used as soil amendment fertilizer to close nutrient cycles. Alternatively, the biochar can be used as activated charcoal. However, the material, as intended here, offers the ideal composition for use as a form of energy storage to overcome storage and transportation issues throughout inclement seasons of the year.

Temperature has a major influence on the mass and energy yield from pyrolysis for CS. As the pyrolysis process temperature increased, solid char product yield decreased. Although the highest char yield was obtained at 300°C, the HHV was determined to be close to that of the unpyrolyzed CS feedstock and therefore the char at this temperature underwent torrefaction rather than pyrolysis. Therefore, the yield at 400°C was deemed as the optimal pyrolysis temperature for char production. Char samples between 500° and 700°C had higher mass-energy density than the initial feedstock. The char with the highest measured HHV was determined at 600°C, due to its high fixed carbon content. Furthermore, according to placement on the Van Krevelen diagram, the molar H/C and O/C ratios from this experiment suggest that the CS chars at and above 400°C are suitable for substituting coal.

According to the syngas and bio-oil estimations, more syngas and bio-oil were produced at higher temperatures. The quantities of bio-oil produced by the pyrolysis experiments were lower than those of the gas yields at the same respective temperatures.

The energy simulation of CS pyrolysis reveals that the process is self-sustaining at all temperatures at and above 400°C through combustion of all of the syngas in conjunction with a portion of the produced bio-oil. If the pyrolysis process technology is used to produce energy, then the total global energy from CS is 380 PJ yr^{-1} which is under 0.1% of global TPES. The energy potential from the pyrolysis process was the same across temperatures, however the energy distribution varied across products at different temperatures. In general, our results show that a higher temperature process yielded more energy from the bio-oil while a lower temperature process yielded more energy from the char. More specifically, a temperature of 800°C would be most optimal for deriving energy from the bio-oil, because its share of energy is higher than that of the char or gas share. A temperature of 400°C would be optimal for deriving energy from the char because its share of energy is higher than that of the bio-oil or gas share. Meanwhile, temperatures of 600°, 700°, and 800°C produce the largest share of energy from gas out of all the temperatures, although the shares are lower than the char and bio-oil shares. Therefore, a determination of appropriate pyrolysis

temperature would likely be dependent on prioritization of higher char or bio-oil yield. Considerations contributing to preferentially selecting a higher char or bio-oil yield are transportation and storage costs, end-use of products, the price of utilizing each product, as well as others. Therefore, in-depth studies of the techno-economic challenges of pyrolysis CS at the pilot/demonstration scale are highly recommended.

Acknowledgement

References

[1] R. Mythili, P. Venkatachalam, Briquetting of Agro-residues. J Sci Ind Res **72**, 1, pp 58–61 (2013)

[2] J. Johnson, S. MacDonald, L. Meyer, L. Stone, The world and United States cotton outlook, Agricultural Outlook Forum. U.S. Department of Agriculture (2018)

[3] M.A. Egbuta, S. McIntosh, D.L.E. Waters, T. Vancov, L. Liu. Molecules, **22**, 1, pp 1–25 (2017)

[4] P. Fu, S. Hu, J. Xiang, L. Sun, S. Su, S. An. Journal of Analytical and Applied Pyrolysis, **97,** pp. 130-136 (2012)

[5] A.G. Olabi, Energy, 181, Pages 450-454 (2019)

[6] R. Al Afif, C. Pfeifer, T. Pröll. IntechOpen, DOI: 10.5772/intechopen.88005 (2019)

[7] Y. Fahmy, T.Y.A. Fahmy, F. Mobarak, M. El-Sakhawy, M.H. Fadl. International Journal of ChemTech Research, **2**, pp. 424-448 (2017)

[8] D. Kaur, N. K. Bhardwaj, R. K. Lohchab. Waste Management, **60**, pp. 127-139 (2017)

[9] T.Y.A. Fahmy, F. Mobarak. Cellulose, **20**, 3, pp. 1453-1457 (2013)

[10] R. Al Afif, B. Linke. Energy, **171**, 1046-1052 (2019)

[11] R. Al Afif, T. Amon. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, **10**, 1080 (2018)

[12] L. Lonappan, T. Rouissi, R.K. Das, S.K. Brar, A.A. Ramirez, M. Verma, R.Y. Surampalli, J.R. Valero, Waste Manage., 49, pp. 537-544 (2016)

[13] A. A. Azni, W.A. W. A. K. Ghani, A. Idris, M. F. Z. Ja'afar, M. A. M. Salleh, N. S. Ishak, Renewable Energy, 142, Pages 123-129 (2019)

[14] S. Seyedsadr, R. Al Afif, C. Pfeifer, Carbon Resources Conversion 1, Issue 1, Pages 81-85(2018)

[15] D. Czajczy ́nska, L. Anguilanoc, H. Ghazald, R. Krzy ̇zy ́nsk, A.J. Reynold, N.Spencer, H. Jouhara, Therm. Sci. Eng. Prog. 2017, 3, 171–197.

[16] S. Schaffer, T. Pröll, R. Al Afif, C. Pfeifer. Biomass and Bioenergy, **120**, (2018)

[17] M. Ertas, B. Acemioglub, M. H. Alma, M. Usta. J. Hazardous Mater, **183**: 421-427 (2010)

[18] G. Allesina, S. Pedrazzi, F. Allegretti, N. Morselli, M. Puglia, G. Santunione, P, Tartarini, Applied Thermal Engineering, 139, Pages 387-394 (2018)

[19] X. Yua, L. Ma, B. Wen, D. Zhou, M. Kuang, W. Yang, Z. Cui. Bioresource Technology, **207**, Pages 293-301 (2016)

[20] M. Adl, K. Sheng, A. Gharibi. Applied Energy, 93, Pages 251-260 (2012)

[21]Y. Xie, K. Zeng, G. Flamant, H. Yang, N. Liu, X. He, X. Yang, A. Nzihou, H. Chen,. Energy, 179, Pages 1124-1132 (2019)

 [22] S.A.Y. Shah, ,M. Zeeshan, M. Z. Farooq, N. Ahmed, N. Iqbal, Renewable Energ, 130, Pages 238-244 (2019)

 [23] T. Pröll, R. Al Afif, S. Schaffer, C. Pfeifer. Energy Procedia, **114**, 6057-6066, (2017)

[24] X. Xianjun, L. Hui, M. Peiyong, S. Yadong, H. Yunlong, L. Tao. Energy Procedia, **66**, 297 – 300 (2015)

 [25] G. Venkatesh, B. Venkateswarlu, K.A. Gopinath et al. Indian J. Dryland Agric. Res. & Dev., **28,** 1, pp. 48-57 (2013)

[26] ASTM D4442-16. 2016. Standard Test Methods for Direct Moisture Content Measurement of Wood and Wood-Base Materials. ASTM International, West Conshohocken, PA. DOI: 10.1520/D4442-16.

[27] ASTM E1755-01. 2015. Standard Test Method for Ash in Biomass. ASTM International, West Conshohocken, PA. DOI: 10.1520/E1755-01R15.

[28] ASTM E872-82. 2013. Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels. ASTM International, West Conshohocken, PA. DOI: 10.1520/E0872-82R13. 93

 [29] ASTM D5865-13. ASTM International, West Conshohocken, **10**, 1520 (2013)

[30] A. C. Louwes, L. Basile, R. Yukananto, J. C. Bhagwandas, E. A. Bramer, G. Brem. Biomass and Bioenergy, **105**, Pages 116-126 (2017)

[31] T. G. Bridgeman, J. M. Jones, I. Shield, P. T. Williams. Fuel, **87**, Issue 6, Pages 844-856 (2008)

[32] Klass, D.L. Biomass for Renewable Energy, Fuels, and Chemicals, Academic Press, Pages 137-158, ISBN 9780124109506 (1998)

[33] Z. He, H. Zhang, H. Tewolde, M. Shankle. Chemical Characterization of Cotton Plant Parts for Multiple Uses. Agric. Environ. Lett., **10**, 2134 (2017)

[34] F. L. Aquino, F.L. Office of Graduate Studies of Texas A&M University (2007)

[35] A. E. Pütün, N. Özbay, E. P. Önal, E. Pütün. Fuel Processing Technology, **86**, Issue 11, Pages 1207-1219 (2005)

[36] Mohan, Dinesh & Pittman, Charles & Steele, Philip, 2006. Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review. Energy. 20. 848-. 10.1021/ef0502397.

[37] Tripathi, A.K., Iyer, P.V.R., Kandpal, T.C., Singh, K.K. Energy Conversion and Management. **39**, Issue 15, Pages 1611-1618, (1998)

[38] Fantini, M. Biorefineries, Targeting Energy, High Value Products and Waste Valorization. Springer International Publishing. ISBN 978-3-319-48288-0 (2017)

[39] He, X., Liu, Z., Niu, W., Yang, L., Zhou, T., Qin, D., Niu, Z., Yuan, Q. Energy, **143**, Pages 746-756, ISSN 0360-5442, (2018)

[40] Chen, Y., Yang, H., Wang, X., Zhang, S., Chen, H. Bioresource Technology, **107**, Pages 411-418, ISSN 0960-8524 (2012)

[41] J. Poudel, T. Ohm, S. C. Oh. Fuel, **140**, Pages 275-281 (2015)

[42] Crombie, K., Mašek, O. Bioresource Technology, **162**, Pages 148-156, ISSN 0960-8524 (2014)

[43] Xu, R., Ferrante, L., Hall, K., Briens, C., Berruti, F. Journal of Analytical and Applied Pyrolysis, **91**, Issue 1, Pages 55-66, ISSN 0165-2370 (2011)

[44] Bridgwater, A.V. Biomass and Bioenergy, **38**, Pages 68-94, ISSN 0961-9534 (2012)

[45] Mythili, R., Venkatachalam, P., Subramanian, P., Uma, D. Bioresource Technology, **138**, Pages 71-78, ISSN 0960-8524 (2013)

[46] Renewable Energy Policy Network for the 21st Century (REN21). REN21 Secretariat (2018)

[47] Bentsen, N.S., Felby, C., Thorsen, B.J. Progress in Energy and Combustion Science, **40**, Pages 59-73, ISSN 0360-1285 (2014)

Highlights

- Biochar yields decrease and syngas yields increase with temperature increase from 300 to 800°C.
- The largest higher heating value (25.8 MJ kg^{-1}) of biochar was obtained at 600°C
- Process simulation showed that the pyrolysis process is energetically self-sustaining at 400°C and above.
- A temperature of 400°C is optimal for deriving energy from the biochar
- global energy potential from pyrolysis CS could contribute to 0.1% of the actual global total energy supply