

Batch pyrolysis of cotton stalks for evaluation of biochar energy potential

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Abstract. The thermal cracking of cotton stalks (CS) via pyrolysis was performed using a laboratory scale batch pyrolysis reactor. The effects of the final pyrolysis temperature varying from 300 to 800°C on the pyrolysis products distribution has been investigated. The maximum biochar yield of 46.5% was obtained at 400°C. As the pyrolysis process temperature increased, the solid char product yield decreased. The lowest biochar yield of 28% was obtained at 800°C. The largest higher heating value (HHV, 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.

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 around 29.136 million tons in 2017/2018 [2], therefore, CS constitutes a significant source of waste biomass [3] with roughly 80 million tons globally each year. The traditional method of disposal for waste biomass in less developed regions is usage as a fuel in simple cooking stoves or direct incineration on farm-land. These methods are associated with high local air pollution [4]. Therefore, exploring alternative methods for environmentally friendly disposal of CS is important. Furthermore, these significant quantities of CS waste from agricultural production are a potential source of revenue. Other risks associated with cotton waste such as farm hygiene by pesticide remnants and soil-borne pathogens can also be addressed. In summary, utilizing CS has the potential to be a significant source of energy and an opportunity to reduce the environmental issues and financial costs associated with disposal [5].

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Several studies have encouraged the conversion of agricultural residues into useful products as a method of carbon sequestration rather than their direct combustion. Some of these useful products include paper, boards, biofuels [6–10], and biochar, which is a solid carbon-rich residue left after pyrolysis of carbonaceous biomass. 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 [11, 12]. Utilization of cotton waste as an energy feedstock has become a subject of many studies in recent years [13–16]. Researchers have generally focused on the production of biogas, ethanol and the production of fuel pellets or briquettes. Past pyrolysis experimentation of CS has been performed for the coproduction of char, oil, and gas [17, 18]. The liquid bio-oil and synthetic 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 [19]. 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 [20]. However, since pyrolysis of CS is still in its developing stage, many challenges such as the energy evaluation of biochar stand in the way of substantial implementation of the process. Therefore, in the present work, we investigate the conversion of CS into pyrolysis char and heat energy with the purpose of assessing the effect of different temperatures on the energy production via pyrolysis end products with focus on the biochar.

2 Materials and methods

2.1 Material

Cotton stalk 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 (see Fig. 1). It was ground and sieved to produce a granular powder with a particle size of 1–3 mm. The cotton stalk employed herein 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. The ultimate and proximate analysis of composition and HHV of the raw CS feedstock and of each pyrolysis char was determined in accordance with ASTM standards [21].



Fig. 1. Air dried cotton stalk samples.

2.2 Experimental procedure

CS pyrolysis experiments were conducted using a laboratory batch pyrolysis reactor. The stainless-steel reactor was a batch design which was cylindrical and airtight. 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 N₂ to create an O₂ 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 in the steel reactor for each run. After loading the CS and before the start of each run, N₂ was purged into the reactor at a rate of roughly 0.5 litres min⁻¹ for fifteen minutes. Following the initiation of each run, N₂ input into the reactor continued until the furnace reached the desired temperature. At the desired temperature N₂ 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 13 K 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 are 2% or lower, duplicate experiments were deemed satisfactory as suggested by Louwes et al [22]. Each sample at its respective pyrolysis temperature was given a sample ID as designated in Table 1.

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

*Sample ID	Initial Mass (g)	Nitrogen Flow (liters min ⁻¹)	Temperature (°C)	Replication
C1	20	0.5	300	3
C2	20	0.5	400	3
C3	20	0.5	500	3
C4	20	0.5	600	2
C5	20	0.5	700	2
C6	20	0.5	800	2

*Sample ID's are denoted by C for CS char and subsequently identified numerically from 1–6. C1: 300°C, C2: 400°C, C3: 500°C, C4: 600°C, C5: 700°C, C6: 800°C.

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 [23]:

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

Oil yield (Y_{oil}) was determined from experiments and the gas yield (Y_{gas}) has been calculated according to equation 2 where Y_{oil} and Y_{gas} are defined analogous to equation 1.

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

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

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

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

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

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.

$$E_{Chem} = Y_{Char} \cdot LHV \quad (5)$$

The bio-oil and syngas chemical energy were estimated from the energy simulation heat balance

3 Results and discussions

3.1 Products distribution

Pyrolysis yields (wt%) of CS at different temperatures are shown in Fig. 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 sample C1 at 300°C, decreasing with increase of the pyrolysis temperature to the lowest char yield in sample C6 at 800°C. It has to mentioned that at 300°C it is rather torrefaction than pyrolysis and this leads to a minimum of volatiles being released. 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 [24].

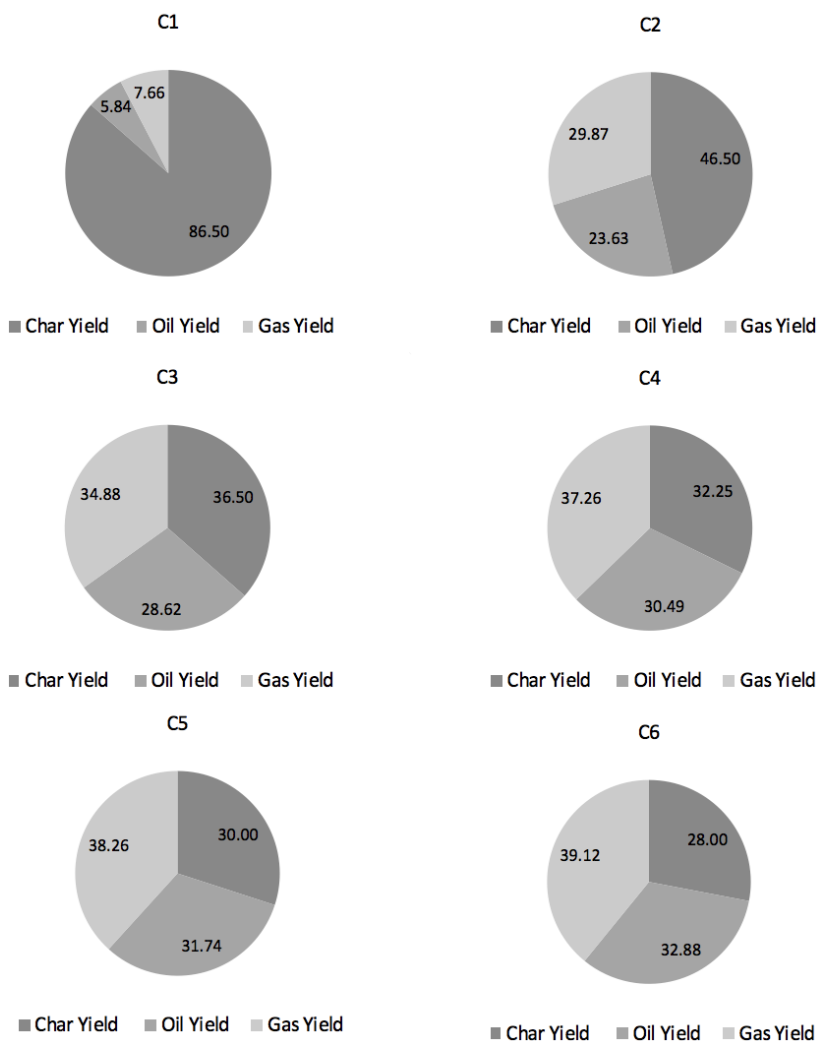


Fig. 2. Yields of pyrolysis products at each temperature.

The lowest bio-oil and syngas yield occurred at 300°C with 5.84% and 7.66%, respectively were estimated on previous experiments as well as on literature. This can be attributed to the fact that sample C1 at 300°C 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 decreasing 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 [25, 26]. 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 Solids Energy Yield, and Mass Energy Density

The char energy yield of the samples is displayed in Table 2. It is a comparison of the energy retained after pyrolysis with the energy content of the initial biomass feedstock.

Table 2. Mass and Energy yields of CS and char samples.

Sample ID	Solids Mass Yield (%)	Solids Energy Content (HHV) (MJ kg ⁻¹)	Solids Energy Yield (%)	Energy Densification Ratio
CS	100	18.32	-	1
C1	86.5	19.63	92.68	1.07
C2	46.5	25.40	64.48	1.39
C3	36.5	25.765	51.31	1.41
C4	32.25	25.855	45.50	1.41
C5	30	25.80	42.24	1.41
C6	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 sample C1 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 sample C2 at 64.48% which underwent pyrolysis at 400°C, while the lowest was found in sample C6 at 39.14% which underwent pyrolysis at 800°C. 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, samples C3, C4, and C5 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 sample C2 at 400°C, while selection based on the energy densification ratio would be the samples C3, C4, and C5 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 [27].

4 Conclusions

Temperature has an influence on the mass and energy yield from pyrolysis for cotton stalks. The largest char yield was obtained at 300°C, whereas the highest yields of gas and oil were estimated at 800°C. The char with the highest measured HHV was determined at 600°C and char samples between 500 and 700°C had a significantly higher mass-energy density (1.41) than the initial feedstock. However, the evaluation showed that the 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 most 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. Factors 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.

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