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ELUCIDATING THE SOLID, LIQUID AND GASEOUS PRODUCTS FROM PYROLYSIS OF COTTON GIN TRASH

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Abstract

Cotton gin trash (CGT) was pyrolyzed at different temperatures and reaction times in a programmable temperature-controlled furnace. The total amount of output products (solid, liquid condensate, and non-condensable gases) from the pyrolysis of cotton gin trash was determined. The CGT was air-dried to reduce the moisture content to approximately 20 weight percent (wt.%); the CGT was then milled, sieved and weighed (100 g per sample) prior to pyrolysis. The heating value of the raw CGT was determined to be 7146 Btu lb^{-1}. Air was evacuated in the pyrolysis reactor before the start of each run. The CGT was pyrolyzed at the temperatures of 600, 700, and 800 °C. The maximum char yield of 38.34 wt.% was determined at the temperature of 700 °C and pyrolysis period of 30 min, and it was based on the highest char heating value of 9460 Btu lb^{-1}. The highest gaseous product yield was 44.20 wt.% at 800 °C and 60 min combination. The liquid condensates reached as high as 36.33 wt.% but it was also noted that a major portion (ca. 90 wt.%) of the liquid is composed of water and the remaining portion is composed of different oils, alcohols and other volatile liquids. The amount of solid produced generally decreased as the pyrolysis time and temperature increased. Moreover, the amount of gas yield increased as the pyrolysis time and temperature increased, while the amount of liquid yield increased in parallel with temperature but not with pyrolysis time. By elucidating on the solid, liquid and gaseous products of CGT pyrolysis, the conversion process could be modeled for the optimal production of either char for the production of activated carbon or syngas for the production of synthetic petroleum via catalytic cracking and reforming processes.

Introduction

The world's dependence on fossil fuel as the main source of energy is continuously increasing through time because of the rapid industrial and economic development and increase in population. With the inevitable depletion of fossil fuel reserves, renewable energy development should be focused on to renovate the energy source structures and keep sustainable development safe (Qi et al., 2006).

Biomass resources such as forest residues, low-grade plants, agricultural residues, and municipal solid wastes are composed of organic raw materials that can be converted to energy (Caglar and Demirbas, 2000). In addition, biomass wastes have negligible contents of sulfur, nitrogen and ash which give lower emissions of SO_2, NO_x and soot compared to conventional fossil fuels, thus keeping the environment and the public's health safe (Qi et al., 2006; Tsai et al., 2006a).

The high production of agricultural wastes could provide considerable amount of energy recovery if properly utilized (Williams and Nugranad, 2000). With the application of thermochemical conversion processes on biomass, fuels with higher heating values could be produced efficiently and economically, rather than just burning the biomass directly to produce heat or power (Caglar and Demirbas, 2000). Pyrolysis is one of the most promising thermochemical processes, producing pyrolytic char, gas and oil, all of which have potential end uses. Certain factors determine the amount and variety of these output products so that pyrolysis conditions can be optimized for either char, gas, or oil production (Encinar et al., 1997; Williams and Nugranad, 2000).

Catalyzed pyrolysis is fast gaining popularity in the thermochemical conversion processes, especially for lignocellulosic biomass. Encinar et al. (1997) conducted a catalytic pyrolysis of grape and olive bagasse using sulfuric and phosphoric acids under different conditions. A cylindrical stainless steel reactor with a ceramic furnace was used to pyrolyze the raw materials under the temperatures of 400–800 °C. They observed that, in the presence of catalysts, char fraction was increased while the liquid decreased. However, the gases (i.e. H_2, CO, CO_2 and CH_4)

were unaffected except when Fe or Al was used. The influence of temperature was also determined such that when an increase in temperature led to decreased solid yield and increased gas yield, the optimum temperature was determined at 600 °C. In a parallel study, Putun et al. (2005) used catalyzed pyrolysis on air-dried cottonseed cake using natural zeolite content while varying the pyrolytic temperature, zeolite content and sweeping gas flow rate. A 316 stainless steel Heinze retort was used as a reactor heated by an electric furnace. The temperature in the bed was monitored using thermocouples. Tar condensation was avoided by providing heat along the connecting pipes. The maximum liquid produced was 30.84%, under a pyrolysis temperature of 550 °C, sweeping gas flow rate of 100 cm^3 min^{-1}, and in the presence of clinoptilolite molecular sieve. It was also found that increasing the pyrolysis temperature also increased the yield of conversion while decreasing the yield of char; on the other hand, increasing the zeolite content resulted in only a slight change in the pyrolysis conversion.

Tsai et al. (2006b), on the other hand, used induction heating for the lab-scale pyrolysis system of rice husk and were able to produce pyrolytic oils and chars. The process parameters that were examined include pyrolysis temperature, heating rate, holding time, nitrogen gas flow rate, condensation temperature, and particle size on the pyrolysis' product yields and their chemical compositions. A horizontally tubular reactor was used for the fixed-bed fast pyrolysis experiment. The heating rate used was 100–500 °C in the high-frequency generator. Like in the previous studies, the char yield had a decline trend as the final pyrolysis temperature is increased while the oil yield also increased. The optimum condensation temperature for effectively collecting gas products was found at - 10 °C. The optimal oil yield of > 40% was achieved at a pyrolysis temperature of > 500 °C, heating rate of > 200 °C, holding time of > 2 min, condensation temperature of < - 10 °C and particle size of < 0.5 mm.

A laboratory study of cotton gin waste pyrolysis was conducted by Zabaniotou et al. in 2000. The effect of temperature (350–800 °C) on the product yields was determined using a captive sample batch reactor heated at a rate of 80–100 °C s^{-1}. It was found that high temperature favored gas production (i.e. CO, CH_4, CO_2, H_2, and C_2H_4) while it gave very low yields of tar and liquid (almost negligible) which, the authors say, was probably due to the slow pyrolysis process.

Texas is one of the largest producers of cotton in the United States, producing over 1.5 million tons of cotton gin trash (CGT) annually (NASS, USDA 2006 Annual Report). One of the main problems faced by large cotton gin facilities in Texas is with the gin trash disposal. Currently, the cost associated with cotton gin trash disposal is very high, amounting to more than $2 million every year. The typical methods of CGT disposal include the following: (1) composting or mulching; (2) feed roughage additive; (3) land filling; and (4) incineration. Among the most commonly utilized methods of gin trash disposal, incineration can be considered the fastest but it also imposes several health hazards. The potential of cotton gin trash for energy production is promising. It has different characteristics (i.e. high cellulose content) compared to the other types of biomass commonly used in pyrolysis and, therefore, further research on its composition is needed in order to attain optimum energy conversion (Zabaniotou et al., 2000).

This study aims to characterize the different pyrolysis products (solid, liquid and gas) of cotton gin trash in a batch pyrolysis process by varying the temperature (furnace) settings and pyrolysis time. The optimum conditions to maximize the solid (char), liquid and gaseous products from the pyrolysis of CGT will be determined. The heating values of the raw cotton gin trash and the collected solid products (char) will be determined using a bomb calorimeter for the purpose of simple energy comparison between the two.

Methodology

Sample preparation

Samples of cotton gin trash used for the experiment were obtained from the Varisco Court Gin Company located at Bryan, Texas. The cotton gin trash used was a mixture of small pieces of ground cotton pods, leaves, and stalks in various shapes and sizes. A considerable portion (approx. 50 %) of lint from the harvested cotton was also present in the samples. Because of this wide variability in the composition of cotton gin trash, it was impossible to study particle size variation in this experiment.

The moisture content of the air-dried cotton gin trash was determined by oven drying with the temperature set at 105 °C overnight (24 h). The calculated average moisture content was 20 weight percent (wt.%, dry basis). Values for the ultimate analysis of cotton gin trash from the present study and from the literature are listed in Table 1. After oven drying, the cotton gin trash was ground in a hammer mill and was allowed to pass a screen with 6.0-mm-diameter holes to achieve close to uniform particle sizes. A part of the dried and ground cotton gin trash sample was used for the heating value determination in the Parr Bomb Calorimeter (Parr Model No. 6200).

Table 1. Proximate and ultimate analyses (wt.%, dry basis) and other characteristics of cotton gin trash.

Reference	*C*	*H*	*N*	*S*	*O*	*Ash*	*Moisture*	HV (kJ kg^{-1})
Present study	–	–	–	–	–	11.3	20.0	16,580
Zabaniotou et al. (2000)	41.23	5.03	2.63	~0	34.0	13.3	6.0	15,780
Lepori and Parnell (1989)	43.82–45.97	4.62–4.85	2.95–2.04	0.43–0.45	32.61–34.23	11.88–12.46	0.0	15,480

HV = heating value

Pyrolysis and pyrolysis reactor

The prepared cotton gin trash was pyrolyzed in a batch-type reactor made from a schedule 80 steel pipe, 3 ft long with 3 in. internal diameter. Two steel trays/containers (A) were made to fit the interior of the tubular reactor (B). The trays can hold a maximum load of approximately 200 g ground cotton gin trash inside the reactor during pyrolysis. The horizontal Thermolyte™ tube furnace (C) (Thermolyte Model No. 79300), 21.50 in. in length and with a maximum of 3.0 in. in internal furnace diameter, provided the different temperature settings for pyrolysis, i.e., 600 °C, 700 °C or 800 °C.

Fig. 1 shows the schematic diagram of the pyrolysis setup used in the experiment. The time period for the pyrolysis of each cotton gin trash sample was also varied (30, 45 and 60 min) along with the varying temperature. Approximately 100 g (± 0.5 g) of the prepared cotton gin trash was loaded in the steel tray container for each run. The gaseous products produced during pyrolysis were directed to pass through a condenser (D), with 4.0-in.-diameter coils (0.5-in.-internal diameter copper tube) and a total height of 18.0 in. The cooling water flow rate at the condenser was maintained at 1.875 L min^{-1} while the temperature was maintained at approximately 17 °C. The liquid condensates (oil and water) were collected in a glass cold trap (F) that uses crushed ice to maintain the temperature at around 0 °C. The non-condensable gases were then collected and measured using the water displacement tanks (G). After pyrolysis, the chars were collected, weighed and stored in individual polyethylene (PET) bags. The amounts of liquid condensates and non-condensable gases were measured by volume. The heating values of the collected pyrolysis chars from each run were also determined using the bomb calorimeter described earlier. The summary of the heating values of char is shown in Table 2.

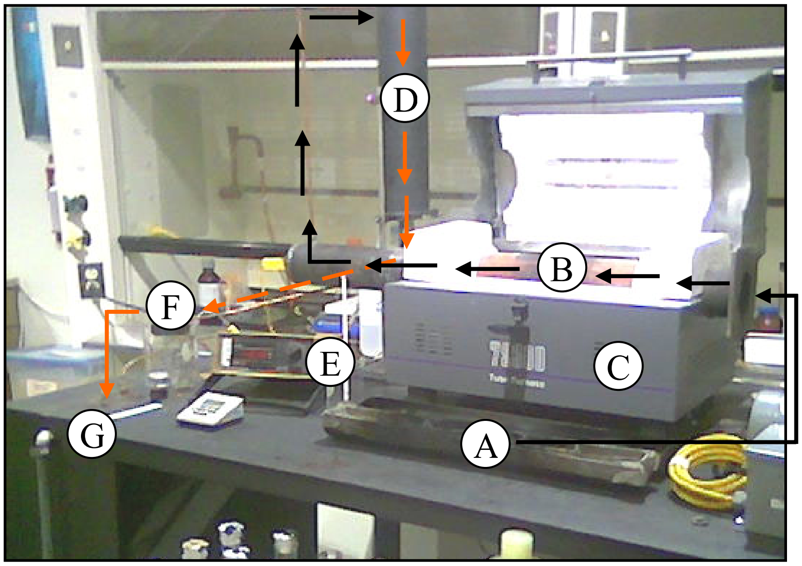

Figure 1. Pyrolysis setup used in the experiment showing the following parts: (A) steel container, (B) horizontal tube reactor, (C) horizontal tube furnace, (D) condenser, (E) thermocouple reader, (F) liquid collector/cold trap, and (G) displacement tanks.

Table 2. Heating values (HVs) of raw and pyrolyzed cotton gin trash

Pyrolysis time (min)	HVs char (Btu lb^{-1})			
	600 °C	700 °C	800 °C	Raw CGT
30	7278.61	9458.63	7885.32	7146.00
45	7267.17	9660.21	7006.16	
60	7206.59	8741.15	7679.31	

Results and Discussion

Figs. 2, 3 and 4 show the effects of the different temperature settings on the product yields at pyrolysis periods of 30, 45, and 60 min, respectively, for the pyrolysis of cotton gin trash with the horizontal tube batch reactor. All of the yields were expressed in weight percentage based on the original sample and were obtained from the average yields from duplicate experiments. Fig. 2 shows that the char production has decreased by almost 10 wt.% as the pyrolysis temperature increased from 600 to 800 °C. On the other hand, the liquid production has increased by more than 12 wt.% while the gas production also increased by more than 13 wt.%. The increasing or decreasing trends of the solid, liquid and gaseous products of pyrolyzed cotton gin trash were consistent with the trends of other pyrolyzed biomass reported on the literature (Putun et al., 1999; Caglar and Demirbas, 2000; Boateng et al., 2006; Tsai et al., 2006B).

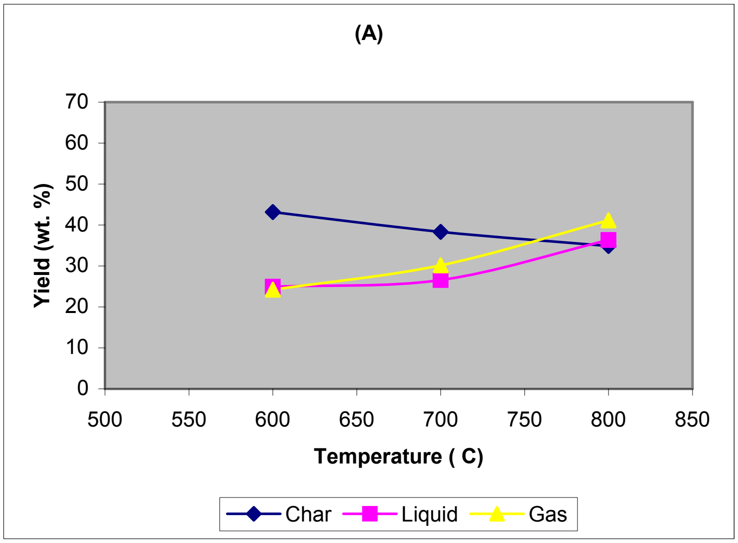

Figure 2. Product yields at different temperatures with pyrolysis time of 30 min.

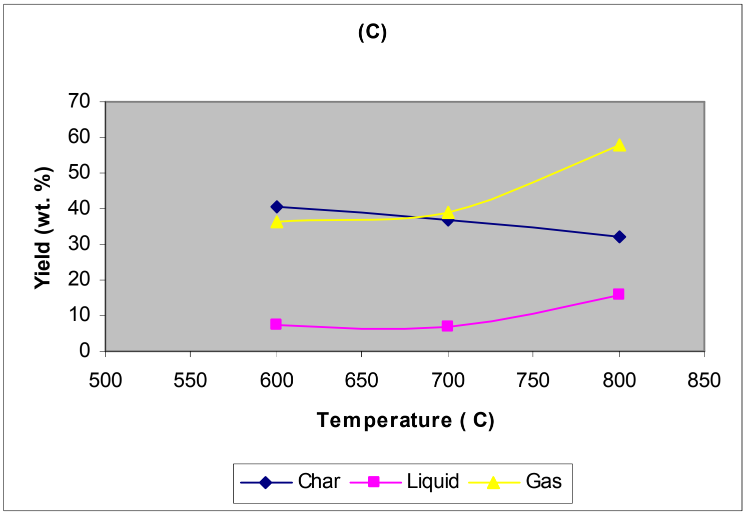

Figure 3. Product yields at different temperatures with pyrolysis time of 45 min.

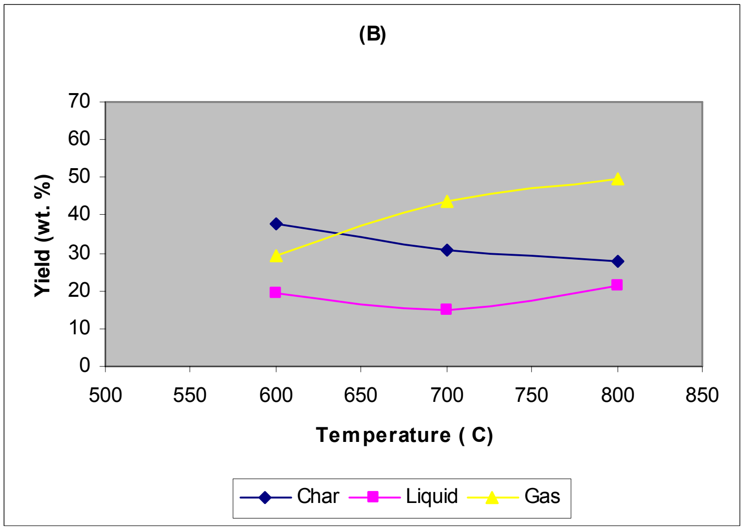

Figure 4. Product yields at different temperatures with pyrolysis time of 60 min.

According to Boateng et al. (2006), char yield is a function of pyrolysis temperature and this explains the decline in char production with increased temperature that were observed in all of the samples after pyrolysis. The increasing yields of liquid and gaseous products with increasing temperature could be attributed to the conversion of biomass to volatile materials at high temperatures (Putun et al., 1999). It was also expected that at very high pyrolysis temperature, liquid production will decrease while gas production will increase. This could be explained by the rapid devolatilization of the cellulosic and hemicellulosic materials at very high temperature according to Putun et al. (1999).

The effects of increasing pyrolysis time on the solid or char, liquid and gas productions were also observed during the experiment. Fig. 5 shows the solid production against the pyrolysis time at different temperature settings (600, 700 and 800 °C). It can be noted that while the pyrolysis time was increased from 30 to 60 min, the solid production was almost constant but had a slight decrease at time equal to 45 min for all the temperature settings. The maximum solid yield was observed at the temperature equal to 600 °C, followed by 700 °C; the temperature setting of 800 °C had the least solid production. One possible reason for having a higher solid production with the 600 °C setting is that the lower temperature and time (30 min) settings were not enough to completely pyrolyze all the cotton gin trash input, especially those in the middle portion of the sample. This was further supported by the observed heating values of the char collected from each sample (Table 2). The heating values of the char at the pyrolysis temperature of 600 °C were considerably lower (approx. less than 2000 Btu lb^{-1}) compared to the heating values of char at 700 °C and were closer to the heating values of the "unpyrolyzed" (raw) cotton gin trash which was around 7146 Btu lb^{-1} (Fig. 8). On the other hand, with the highest temperature setting at 800 °C, the solid production started to decline. This could be because, at increasing temperature, coupled with longer pyrolysis time, most of the char is further decomposed and converted to volatile gases (Putun et al., 2005). The final solid product would then be composed of char with a high ash content. This could also explain why the char collected at 800 °C have lower heating values than those collected at 700 °C (Fig. 8).

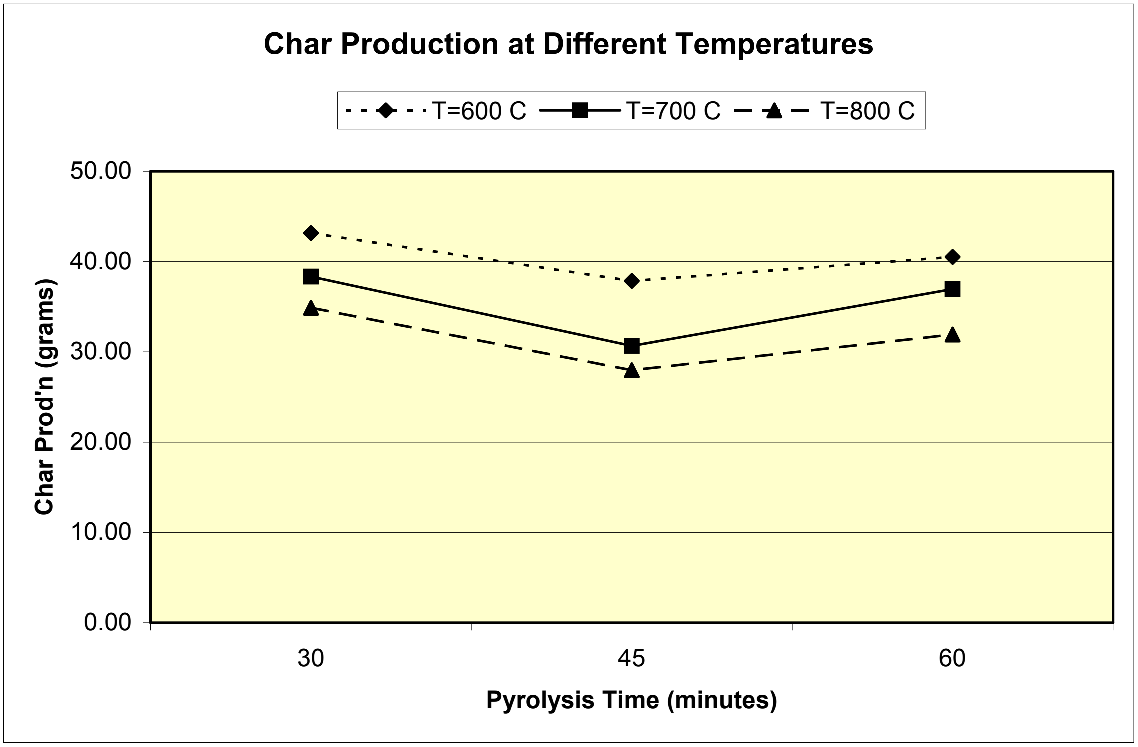

Figure 5. Solid (char) production at different temperatures with increasing pyrolysis time.

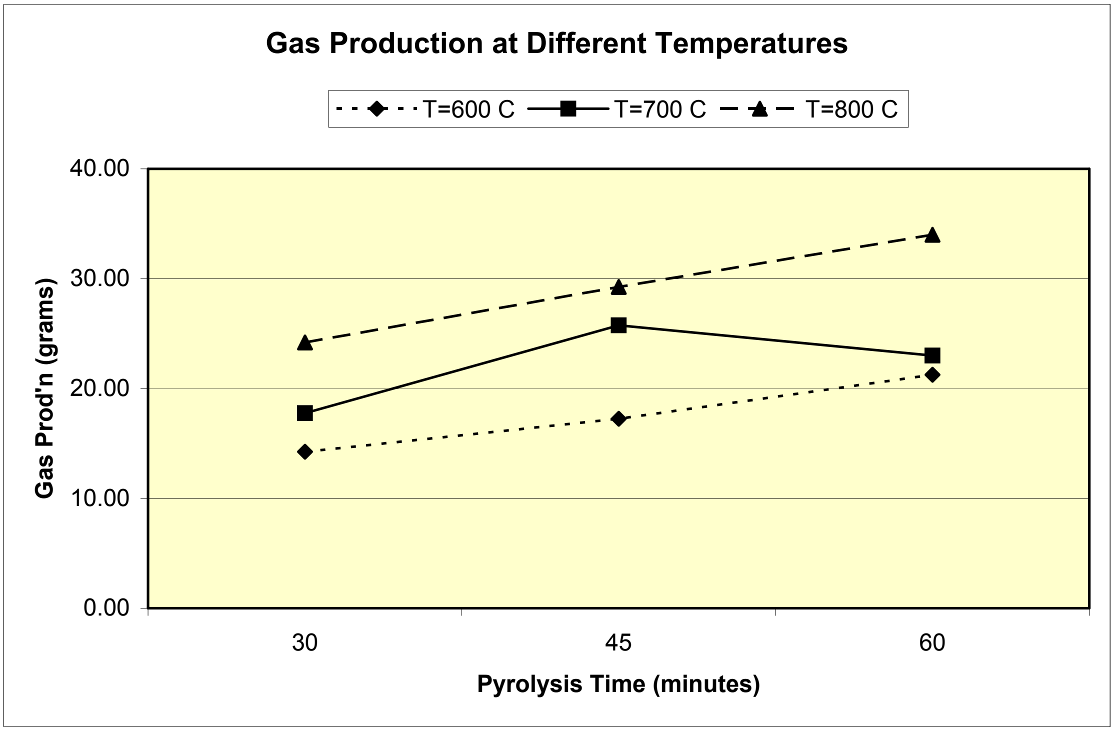

Figure 6. Gas production at different temperatures with increasing pyrolysis time.

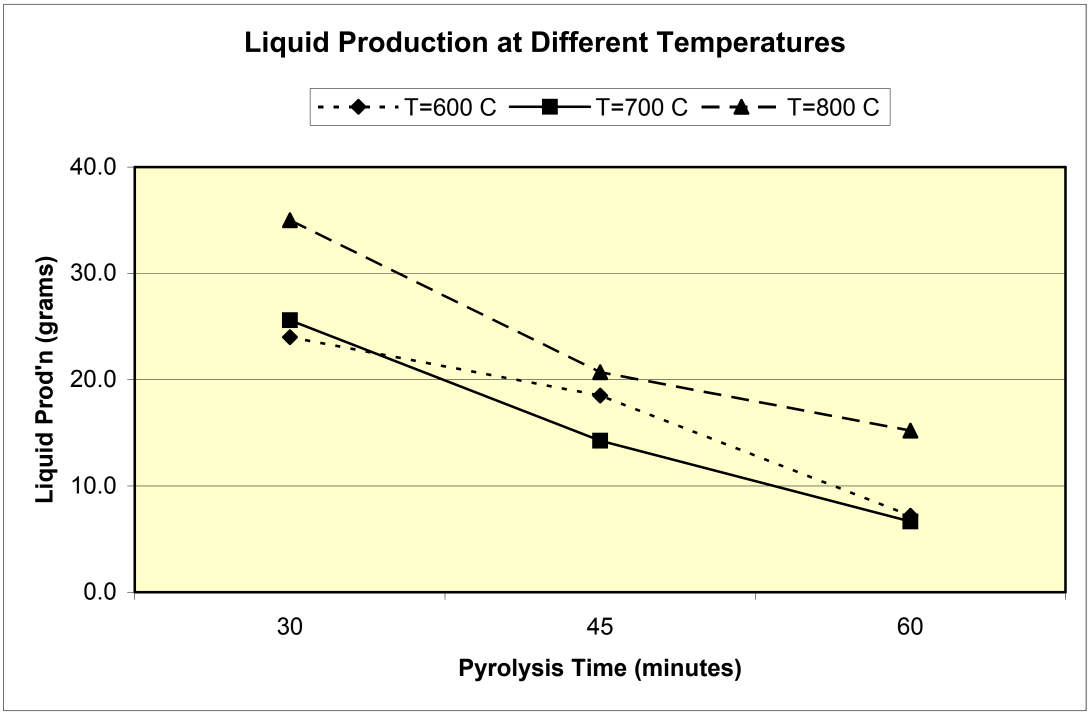

Figure 7. Liquid production at different temperatures with increasing pyrolysis time.

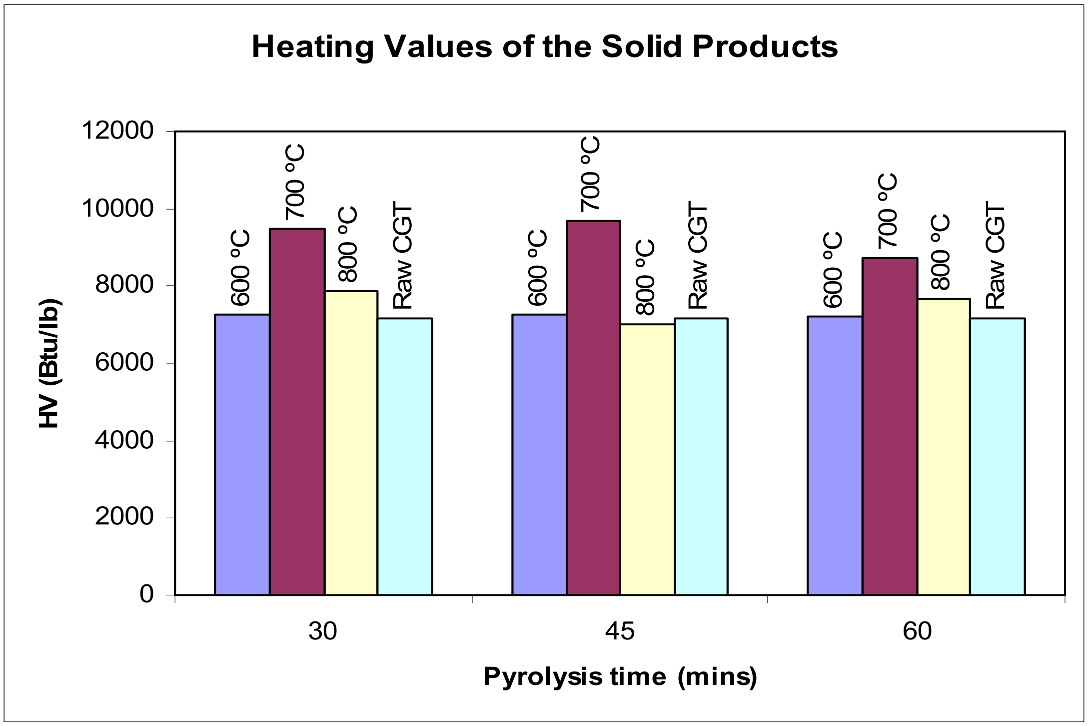

Figure 8. The measured heating values of the raw and pyrolyzed cotton gin trash samples.

In Fig. 6, a longer pyrolysis time resulted to higher gas product yield for almost all the temperature settings. The highest gas yield (44.20 wt.%) was observed at 800 °C and 60 min settings followed by 700 °C settings and the least (18.53 wt.%) was from the 600 °C setting. As stated earlier, longer pyrolysis time and higher temperature favors gas production due to further conversion of biomass to volatile gases. Moreover, the gaseous products produced were determined to be highly combustible and could be readily used or stored in canisters. The gaseous products contain high concentrations of producer gas (syngas) composed of CO, H_2 and other low-molecular-weight hydrocarbons which could be used as primary fuels for direct combustion according to Boateng et al. (2006). The amounts of liquid products from the pyrolysis of cotton gin trash were almost negligible, although Fig. 7 still shows an inverse relation with increasing time for all the temperature settings. It was also determined that a major portion (ca. 90 wt.%) of the condensed liquid products from each sample is composed of water because its density (1.038 g ml^{-1}) was very close to that of water (1.00 g ml^{-1}) and it also has a negative heating value which was comparable to water.

Formation of a thick, black tar stuck on the walls inside the tubular reactor was observed after every run while some portions of the tar can also be seen mixing with the condensed liquid products. No other procedure was done to minimize the tar build up and any amount of tar produced was just treated as errors or losses.

Conclusions

Pyrolysis of cotton gin trash under different temperatures and time settings have produced different amounts of pyrolytic products, i.e., in solid, liquid and gaseous forms. In general, as the pyrolysis temperature increases, the char or solid production decreases and vice versa. The maximum solid yield after pyrolysis was 43.16 wt.% at the pyrolysis temperature of 600 °C and pyrolysis period of 30 min, but after considering the heating values of the char, the optimum value of 38.34 wt.% was established at conditions equal to 700 °C and 30 min.

More gaseous products could be generated at a higher temperature and longer pyrolysis time. The optimum gaseous product yields (44.20 wt.%) were observed when the pyrolyzer was operated at the highest temperature of 800 °C as what was described in the literature, while the least gas yields were observed at the lowest temperature setting of 600 °C. The gas produced was also highly combustible, which could be due to the presence of producer or synthesis gas (CO and H_2). Much more work is needed to determine the amounts and compositions of the gaseous products from CGT. The use of a gas chromatograph coupled with mass spectrometer (GC–MS) with appropriate accessories is recommended for better compound identification and quantification. Furthermore, the heating value of gas could be estimated by computing the individual heating values of each identified compound.

The amount of liquid produced was almost negligible as compared to the char and gas production and there was also a high possibility that the liquid produced contains large amounts of water. Although small amounts of liquids were produced, an obvious trend was still established from the data collected. As the temperature increases, the liquid production increases; on the other hand, there was an inverse relationship between the liquid and the pyrolysis time. GC–MS is also suggested to be used to accurately characterize the different compounds present on the liquid products (Dominguez et al., 2003). The use of a catalyst is suggested to optimize liquid production while the techniques of liquid fractionation such as the Fisher–Tropsch process and adsorption chromatography are recommended to get better separation of the highly valued liquids.

A more detailed study of the energy and mass balance for the entire pyrolysis process of cotton gin trash is underway to evaluate and justify the feasibility of constructing a large-scale production plant.

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