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Evaluation of the Different Products from Batch 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 by weight (wt. %). The heating value of the raw CGT was determined to be 16,600 kJ* kg^{-1}*. The CGT was pyrolyzed at the temperatures of 600, 700, and 800 °C. The maximum char yield of greater than 38% was determined at 700 °C and pyrolysis period of 45 min. The heating value of the char at that pyrolysis temperature was 22,500 kJ* kg^{-1}*. A gaseous product yield of greater than 40% was measured at 800 °C with 60 min retention time. The liquid condensate was 30% by weigh and a major portion (about 90%) was water. The amount of solid produced generally decreased as the pyrolysis time and temperature are increased. The yield of gas component increased as the pyrolysis time and temperature are increased. The yield of the liquid portion increased with temperature but not with pyrolysis time. These optimal gas, liquid and solids product from pyrolysis of cotton gin trash may be used as a basis for modeling liquid fuel production from this particular waste stream.*

Keywords. Cotton gin trash; Pyrolysis; Syngas: Liquid condensates; Char

Introduction

The world’s dependence on fossil fuel has increased because of rapid industrialization, economic development and population increase. Fossil fuel reserves will be depleted and renewable energy resource development should keep energy in a sustainable form (Qi et al., 2006).

Biomass resources such as forest and agricultural residues including municipal solid wastes are composed of organic raw materials that can be converted into energy (Caglar and Demirbas, 2000). Most biomass wastes have negligible contents of sulfur which give lower emissions of SO_2 compared with conventional fossil fuels. This will keep the environment and the public's health safe (Qi et al., 2006; Tsai et al., 2006a).

High agricultural productivity could provide considerable amount of energy from the waste stream if properly utilized (Williams and Nugranad, 2000). Some thermo-chemical conversion processes of biomass could produce fuels efficiently and economically as opposed burning the biomass directly to produce heat or power (Caglar and Demirbas, 2000). Pyrolysis is one promising thermo-chemical process to produce char, gas and bio-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 char, gas, or bio-oil production (Encinar et al., 1997; Williams and Nugranad, 2000).

Catalyzed pyrolysis is a popular thermo-chemical conversion process for lingo-cellulosic 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. In the presence of catalysts, it was observed that the char fraction has increased while the liquid portion 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. An increase in temperature led to a decreased solid yield and increased gas yield, the optimum temperature was determined at 600 °C. Putun et al. (2005) used catalyzed pyrolysis on air-dried cottonseed cake using natural zeolite while varying the pyrolytic temperature, zeolite content and sweeping gas flow rate. A stainless steel retort was used as a reactor heated by an electric furnace. Tar condensation was avoided by providing heat along the connecting pipes. The maximum liquid produced was about 31% using 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 reported that increasing the pyrolysis temperature would also increase the yield liquid while decreasing the yield of char.

Tsai et al. (2006b) used induction heating for the lab-scale pyrolysis system of rice husk and was 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 horizontal tubular reactor was used for the fixed-bed fast pyrolysis experiment. The heating rate used was 100–500 °C in the high-frequency generator. As in the previous studies, the char yield declines as the final pyrolysis temperature is increased while the oil yield is also increased. The optimum condensation temperature for effectively collecting gas products was found at - 10 °C. The optimal oil yield of about 40% was achieved at a pyrolysis temperature of about 500 °C, with a heating rate of about 200 °C per 2 min.

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 reported to be due to the slow pyrolysis process.

Texas produces over 1.5 million tons of cotton gin trash (CGT) annually (NASS, USDA 2006 Annual Report). Disposal of cotton gin trash is one of the main problems faced by large cotton gin facilities. Currently, the cost associated with cotton gin trash disposal is very high, amounting to more than $2 million every year. The potential of cotton gin trash for energy production is promising. It has unique characteristics (i.e. high cellulose content) compared with other types of biomass and, thus, further research is necessary 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 waste 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 for comparative purposes.

Methodology

Sample Preparation

Samples of cotton gin trash used for the experiment were obtained from Varisco Court Gin Company in Bryan, Texas.

The moisture content of the air-dried cotton gin trash was determined following the American Society for Testing and Materials (ASTM) method E1756-95. The sample materials were oven-dried with the temperature setting of 105 °C overnight (24 h). The calculated average moisture content was about 20% by weight (wt%, dry basis). The ash content was found to be 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	0.0	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

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

Pyrolysis Time (mins)	Heating Values (kJ kg^{-1}) 600 ºC	700 ºC	800 ºC	Raw CGT
30	16 895	21 956	18 304	
45	16 869	22 423	16 263	16 580
60	16 728	20 290	17 825	

Pyrolysis and Pyrolysis Reactor

The prepared cotton gin trash was pyrolyzed in a batch-type reactor made from a schedule 80 steel pipe, 0.9 m (3 ft) long with 7.62 (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), 55 cm (21.50 in.) in length and with a maximum of 7.62 cm (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 10.16 cm (4.0 in.)-diameter coils (0.5-in.-internal diameter copper tube) and a total height of 46 cm (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.

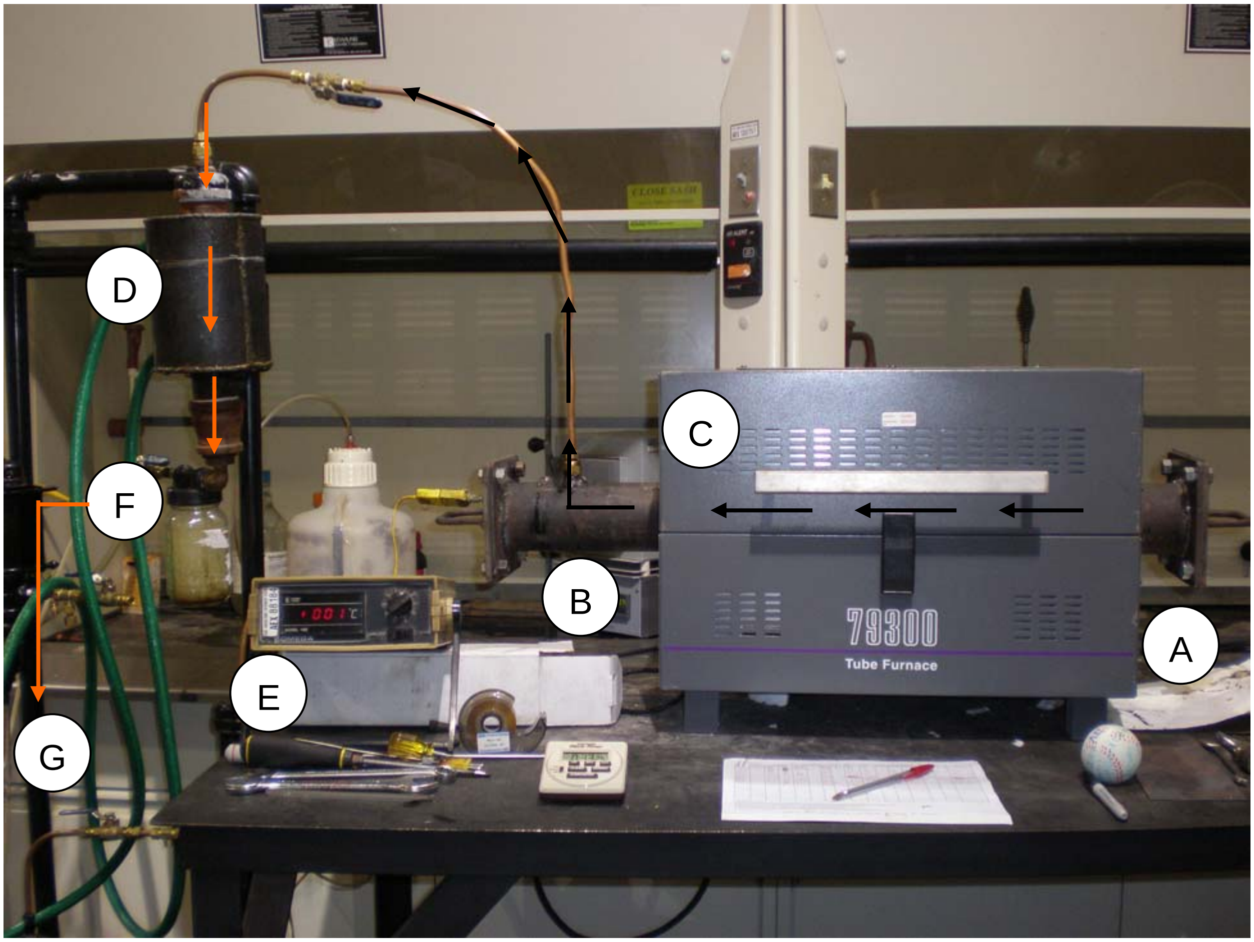

Fig. 1. Pyrolysis setup used in the experiment showing the following parts: (A) steel container, (B) horizontal tube reactor, (C) horizontal tube furnace, (D) condenser, (E) thermocouple reader, (F) liquid collector/cold trap, and (G) displacement tanks.

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).

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. The heating values of the char at the pyrolysis temperature of 600 °C were considerably lower (approx less than 6000 kJ kg^{-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 16600 kJ kg^{-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).

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.

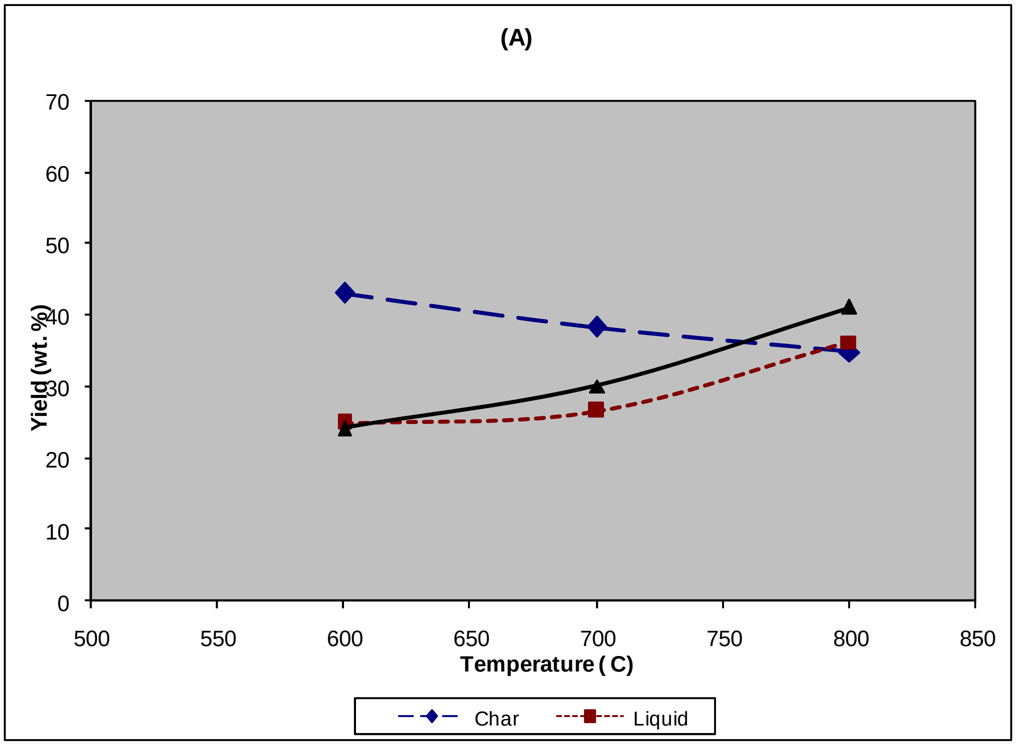

Fig. 2. Product yields at different temperatures with pyrolysis time of 30 min.

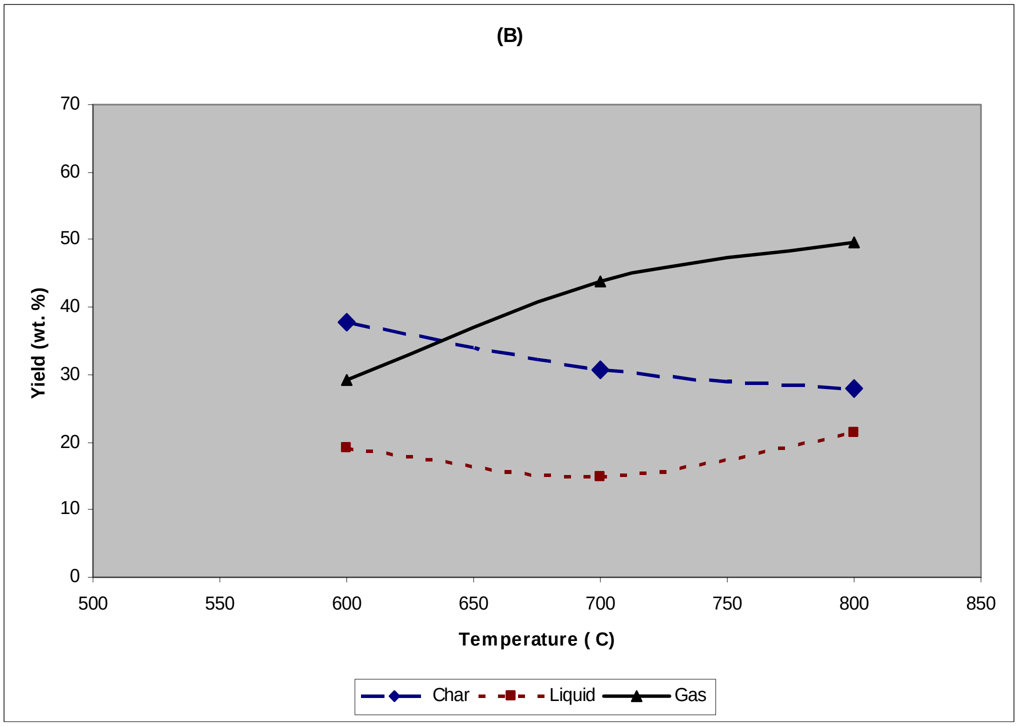

Fig. 3. Product yields at different temperatures with pyrolysis time of 45 min.

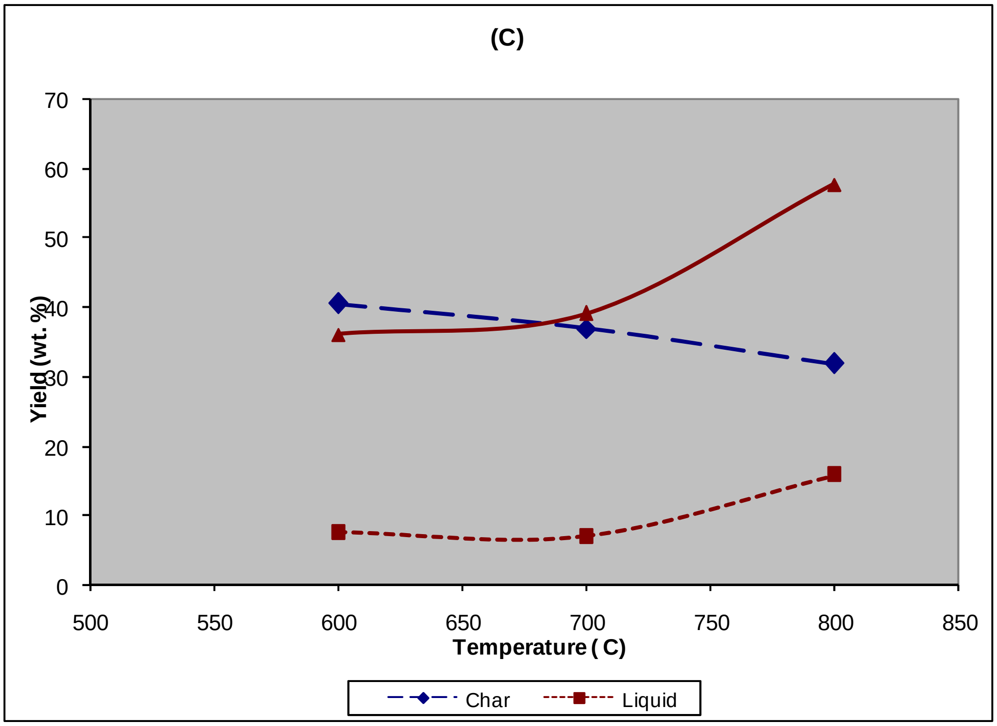

Fig. 4. Product yields at different temperatures with pyrolysis time of 60 min

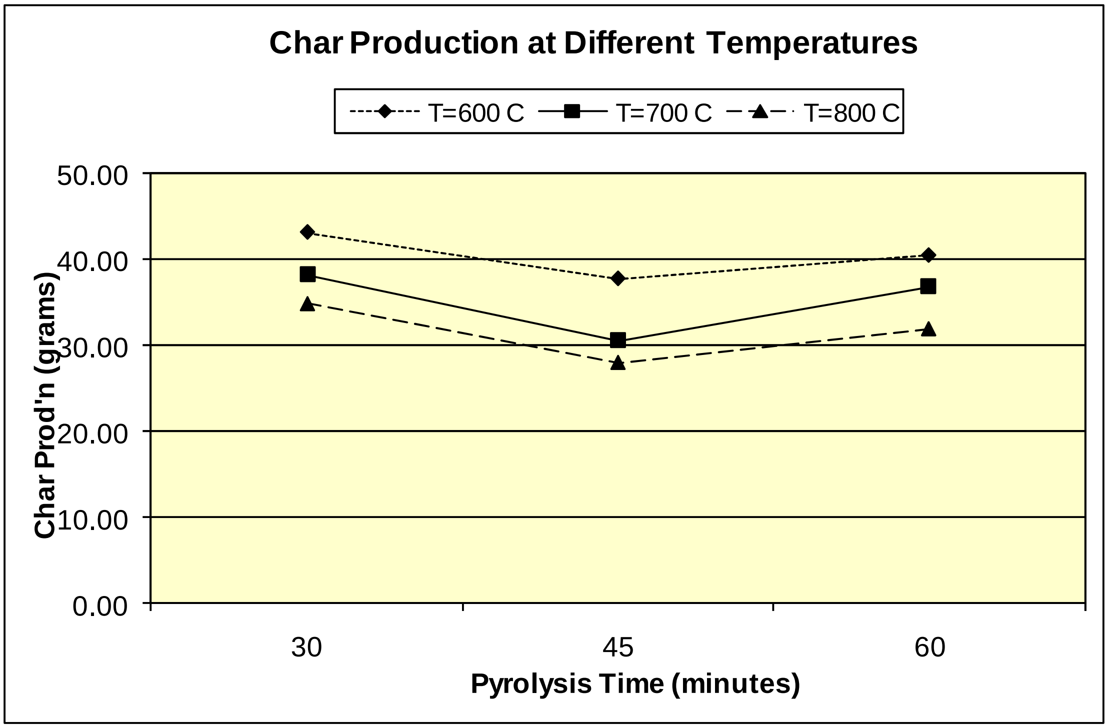

Fig. 5. Solid (char) production at different temperatures with increasing pyrolysis time.

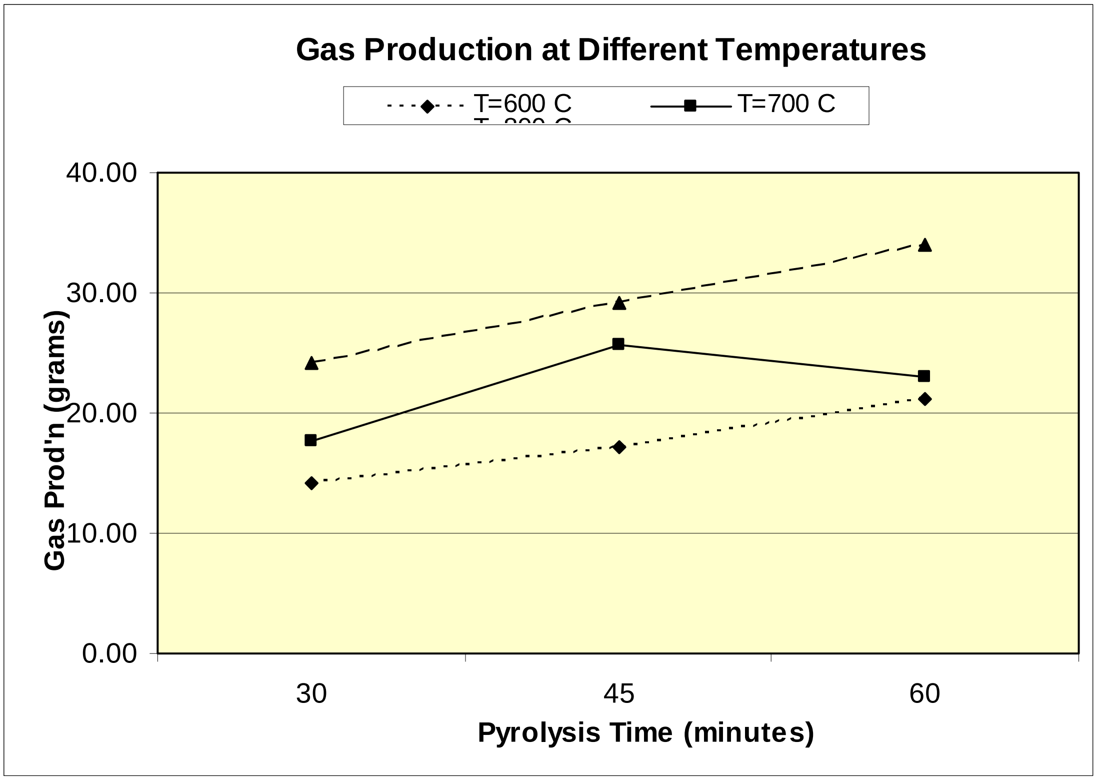

Fig. 6. Gas production at different temperatures with increasing pyrolysis time.

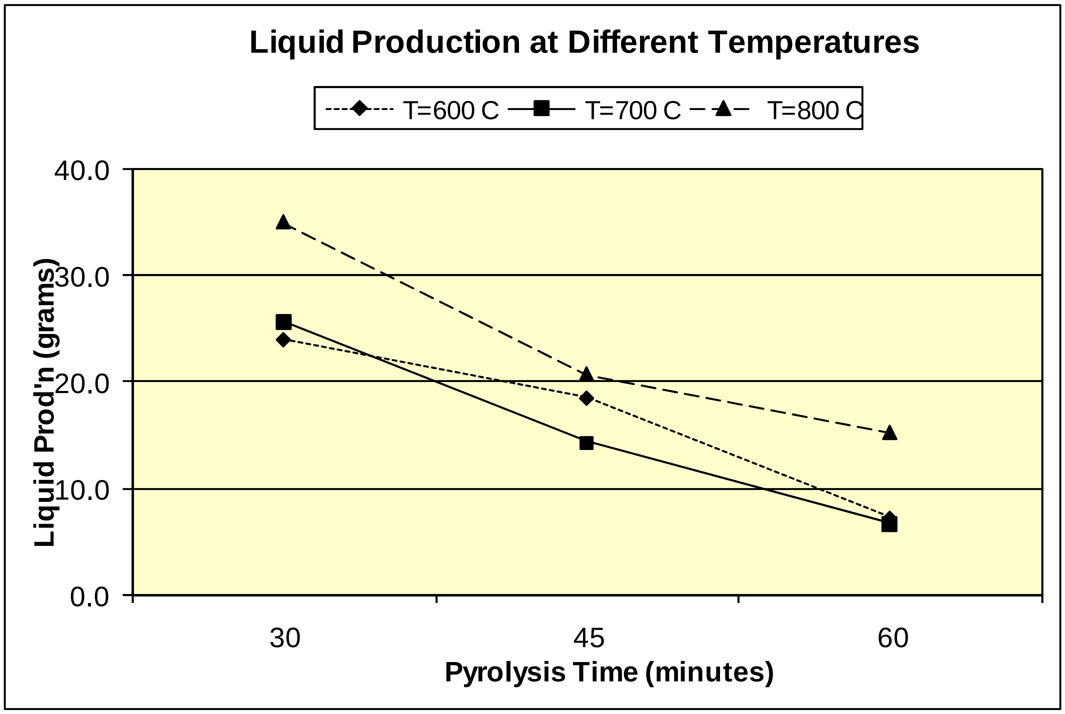

Fig. 7. Liquid production at different temperatures with increasing pyrolysis time.

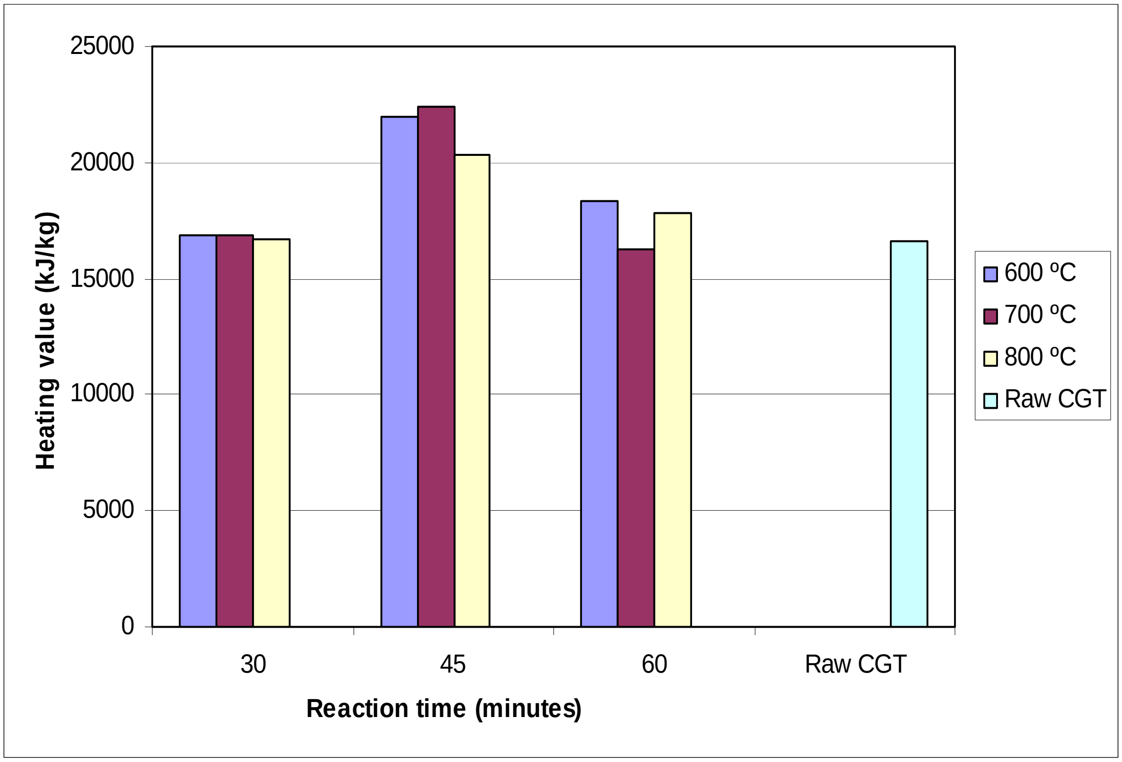

Fig. 8. The measured heating values of the raw and pyrolyzed cotton gin trash samples.

Conclusion

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 >40 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 approximately 40 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 (ca. 45 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 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 char, gas or biooil production plant.

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References

Boateng, A.A., Jung, H.G., Adler, P.R., 2006. Pyrolysis of energy crops including alfalfa stems, reed canary grass, and eastern gamagrass. Fuel 85, 2450–2457.

Caglar, A., Demirbas A., 2000. Conversion of cotton cocoon shell to liquid products by pyrolysis. Energy Convers. Manage. 41, 1749–1756.

Dominguez, A., Menendez, J.A., Inguanzo, M., Bernad, P.L., Pis, J.J., 2003. Gas chromatographic-mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges. J. Chromatogr. A, 1012: 193-206.

Encinar, J.M., F. J. Beltran, A. Ramiro, and J.F. Gonzalez, 1997. Catalyzed pyrolysis of grape and bagasse. Influence of catalyst type and chemical treatment. Ind. Eng. Chem. Res. 36, 4176–4183.

Lepori, W.A., C. Parnell, 1989. System and process for conversion of biomass into usable energy. Texas A&M University Syst (US). US Patent 4 848 249.

National Agricultural Statistics Service (NASS), USDA 2006 Annual Report.

Putun, A.E., Ozcan, A., Putun, E., 1999. Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: yields and structural analysis of bio-oil. J. Anal. Appl. Pyrolysis 52, 33–49.

Putun, E., Uzun, B.B., Putun, A.E., 2005. Fixed-bed catalytic pyrolysis of cotton-seed cake: effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate. Bioresour. Technol. 97, 701–710.

Qi, Z., Jie, C., Teijun, W., Ying, X., 2006. Review of biomass pyrolysis oil properties and upgrading research. Energy Convers. Manage. 48, 87–92.

Tsai, W.T., Lee, M.K., Chang, Y.M., 2006a. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. J. Anal. Appl. Pyrolysis 76, 230–237.

Tsai, W.T., Lee, M.K., Chang, Y.M., 2006b. Fast Pyrolysis of rice husk: product yields and compositions. Bioresour. Technol. 98, 22–28.

Williams, P.T., Nugranad, N., 2000. Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy 25, 493–513.

Zabaniotou, A.A., Roussos, A.I., Koroneos, C.J., 2000. A laboratory study of cotton gin waste pyrolysis. J. Anal. Appl. Pyrolysis 56, 47–59.