# CONTROLLED PYROLYSIS OF COTTON GIN TRASH

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## Abstract

Cotton-gin trash (CGT) was pyrolyzed at different temperatures (500, 600, 700, and 800°C) using an externally-heated batch reactor that was purged with nitrogen gas at 1000 $cm^3$ $min^{-1}$. The average yields of output products (solid/char, liquid/bio-oil, and gaseous) were determined. The heating value (HV) of CGT was measured to be around 15-16 MJ $kg^{1}$ (6500-7000 Btu $lb^{-1}$). Gas yield increased as temperature was increased while the effect was opposite on char yield. The maximum char yield of 38% by weight (wt.%) was determined at 500°C and 30 min. The char had the largest fraction in the energy output (70-83%) followed by gas (10-20%) and bio-oil (7- 9%). Maximum gas yield of 35 wt% was determined at 800°C. The average yield of CO, $H_2$ and total hydrocarbons (THC) generally increased with increased temperature but $CO_2$ production decreased. Methane, ethane, and propane dominated the THC. The bio-oil yield at 600°C was the highest at about 30 wt% among the temperature settings. The HV of bio-oil was low (2-5 MJ $kg^{-1}$) due to minimal non-hydrocarbon compounds and high moisture content (MC).

## Introduction

Biomass has received significant attention in the scientific community as a renewable source of energy since the oil crises in the early 1970s (Bridgewater, et al., 1991). Some processes must be evaluated to convert these resources into alternative fuels. Pyrolysis or destructive distillation is a direct thermal conversion process in the complete absence of an oxidant. It is the first step to thermo-chemical conversion that yields a wide variety of products such as condensable gases and tars (bio-oils), non-condensable gases (synthesis gas or syngas), and char (Boateng, et al., 2006).

Texas is one of the largest producers of cotton in the United States, yielding more than 1.5 million tons of cotton-gin trash (CGT) each year (NASS, 2006). One of the main problems faced by large cotton-gin facilities in Texas is the disposal of cotton-gin trash. The potential of cotton-gin trash for energy production is promising. Cotton-gin trash has different characteristics compared to other types of biomass commonly used in pyrolysis and, therefore, further research is needed on its composition to attain optimum energy conversion (Zabaniotou, et al., 2000).

## Objectives

The study was designed to determine the different products (solid, liquid, and gas) from batch pyrolysis of CGT. The specific objectives were as follows:

a. To determine the effect of pyrolysis temperature on the solid, liquid, and gaseous product yield from CGT pyrolysis;
b. To evaluate the quality of the solid, liquid, and gaseous products using proximate analysis, gas analysis/gas chromatography (GC) and heating value analysis;
c. To identify the conditions to maximize the solid (char), liquid, and gaseous products from CGT pyrolysis;

## Methods

The following are the experimental procedures implemented for this study:

### Sample Preparation

Materials were gathered from the Farmers Co-Operative of El Campo located at El Campo, Texas. The CGT was air-dried for three (3) days and the moisture content (MC) of the air-dried CGT was determined following ASTM method E1756-95. The average MC (as-received, a.r.) was about 10% by weight (wt.%, dry basis). After drying, the CGT was ground in a laboratory mill with 6.0-mm (diameter of holes) sieve to achieve close to uniform particle sizes.

## Pyrolysis Runs

Approximately 50 g fresh CGT was used for every run. Figure 1 shows the schematic of the set-up. The reactor was purged with nitrogen ($N_2$) during each run. The reactor was then heated from room temperature (approx. 25°C) until the desired temperature settings (500, 600, 700, and 800°C) using a fixed ramp rate of 1.5°C $s^{-1}$ and was held at that temperature for the required reaction time. After pyrolysis, the solid products (char and ash) were collected and weighed as well as the condensed gases (bio-oil); the non-condensable gases were calculated by difference. The pyrolysis tests were done in triplicate and the average values were reported in this paper.

## Char Analysis

The products of pyrolysis were collected, quantified, and analyzed after each test run. Proximate analysis was done to characterize the solid products (char and ash) and was performed according to ASTM standards. The heating values were determined using the Parr isoperibol bomb calorimeter.

## Gas Analysis

The gaseous product composed mainly of $H_2$, CO, and $CO_2$, also known as synthesis gas (syngas) and total hydrocarbons (THCs), was analyzed by the Horiba on-line gas analyzer mentioned earlier. The composition of the low–molecular weight hydrocarbons ($C_1$ to $C_6$) was determined using an SRI gas chromatograph (GC) (Model 8610C, SRI Instruments, Torrance, CA) equipped with an on-column injection system and two detectors: flame ionization detector (FID) and photo-ionization detector (PID). The calibration gas standard mixture used was composed of $C_1$ to $C_6$ paraffins (Scott Specialty Gases, Plumsteadville, PA) with analytical accuracy of ±5 %. Hydrogen and helium were used as carrier gas.

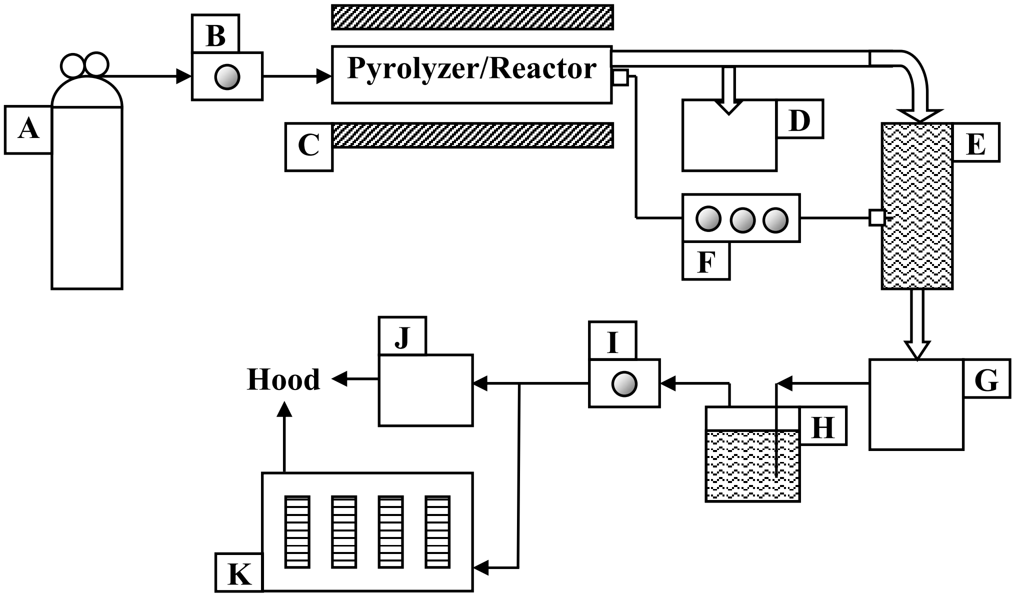

Fig. 1. The modified pyrolysis setup used for cotton-gin trash: (A) Purge gas ($N_2$), (B) Gas flow meter 1, (C) Digitally-controlled furnace, (D) tar/moisture trap, (E) Condenser, (F) Thermocouple reader, (G) Liquid collector, (H) moisture trap, (I) Gas flow meter 2, (J) Sampling/exhaust port, and (K) Gas analyzer.

## Pyrolytic Oil Analysis

The liquid product (bio-oil) was collected in a glass bottle and the filter paper soaked in dichloromethane and used as a tar trap was slowly evaporated at ambient temperature. The liquid product yield was determined by weighing the tarred glass bottle and filter paper. The pH of the bio-oil was measured using Fisher Scientific (Accumet Model 25) pH/ion meter to determine its corrosion properties. The bio-oil was decanted, vacuum-filtered through a 0.4-µm filter paper, and was centrifuged for 15 min to separate the solids and some impurities from the bio-oil. The heating value of the prepared bio-oil was determined using the Parr isoperibol bomb calorimeter (Model 6200).

## Results and Discussion

### Product Yields

Table 1 shows the product yields at different pyrolysis conversion temperatures. The highest yields of solid, liquid and solid products with the corresponding temperatures are as follows: Solid, 38% at 500°C; Liquid, 30% at 600°C and Gas, 35% at 800°C. High temperature favors the formation of gaseous products while low temperature favors the generation of solid products.

Table 1. Product yield from the pyrolysis of cotton-gin trash (wt. %).

| Temperature (°C) | Solid | Liquid | Gas[a] | Gas[b] | Losses[c] |
|---|---|---|---|---|---|
| 500 | 38.25 | 27.38 | 34.37 | 27.65 | 6.91 |
| 600 | 37.40 | 30.65 | 31.95 | 25.56 | 6.39 |
| 700 | 36.32 | 29.69 | 33.99 | 27.19 | 6.80 |
| 800 | 35.08 | 29.65 | 35.27 | 28.22 | 7.05 |

[a] Determined by difference (no losses).

[b] Wt. % of gas assuming 20 wt. % losses.

[c] Losses fixed at 20 wt. %

### Char Analysis

Based on the proximate analysis, it was observed that the volatile matter significantly decreased along with char production while the ash content significantly increased as temperature is increased. The volatile matter decreased by about 72 wt.% and the ash increased by about 30.5 wt.% from 500 to 800°C. The ash content of char is rather high (28–38 wt.%) which is much higher than coal. Both data were statistically tested at $\alpha = 0.05$. The heating value of the char at different temperatures was also measured and determined to be not significantly different ($\alpha = 0.05$) from each other, although the highest heating value (ca. 22 MJ $kg^{-1}$) was recorded at 700°C and the lowest (ca. 20 MJ $kg^{-1}$) was at 500°C. On the other hand, the moisture content of the char was not measured and assumed to be negligible. The complete results of the proximate analyses for char can be found in a thesis by Aquino (2007).

### Gaseous Product Analysis

Table 2 shows the major composition of the gaseous products from the pyrolysis of cotton-gin trash at different temperatures. The data reported were based on the collected gas under a nitrogen-rich atmosphere. The highest percentage of hydrogen production was recorded at 7.4% (mol%) at conversion temperature of 700°C. The total hydrocarbon was also highest at this temperature. Figure 2 shows the trend in the production of solid, liquid and gaseous products while Figure 3 summarizes the different composition of total hydrocarbons produced at different temperatures.

Table 2. Major composition of the pyrolysis gas at different temperatures (mol%).

| Temperature (°C) | CO | $CO_2$ | THC | $O_2$ | $H_2$ | $N_2$ |
|---|---|---|---|---|---|---|
| 500 | 2.60 | 8.54 | 3.00 | 1.46 | 0.24 | 84.16 |
| 600 | 2.29 | 7.52 | 6.60 | 1.67 | 2.62 | 79.30 |
| 700 | 2.58 | 5.74 | 8.55 | 0.31 | 7.36 | 75.45 |
| 800 | 4.63 | 3.66 | 4.76 | 0.03 | 7.07 | 79.85 |

THC = total hydrocarbon. Purge gas ($N_2$) was measured by difference, $H_2O$ ~ 0.

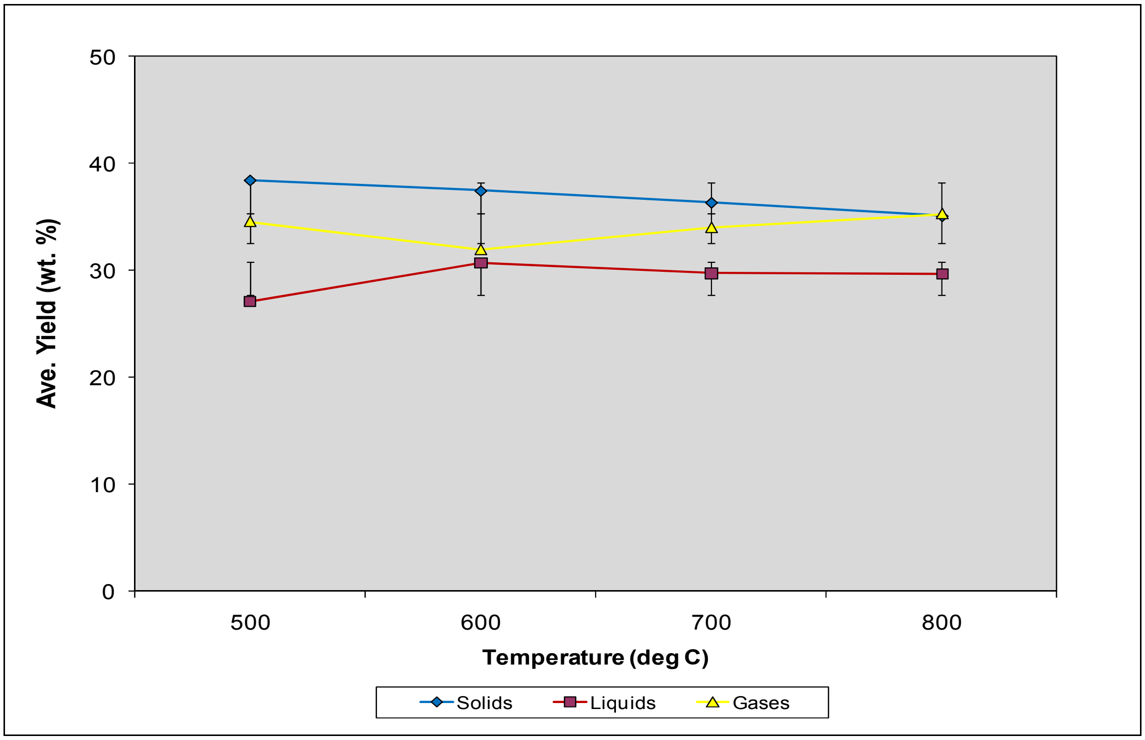

Figure 2. The distribution of the different products of pyrolysis (solid, liquid and gas) from CGT at different reaction temperatures.

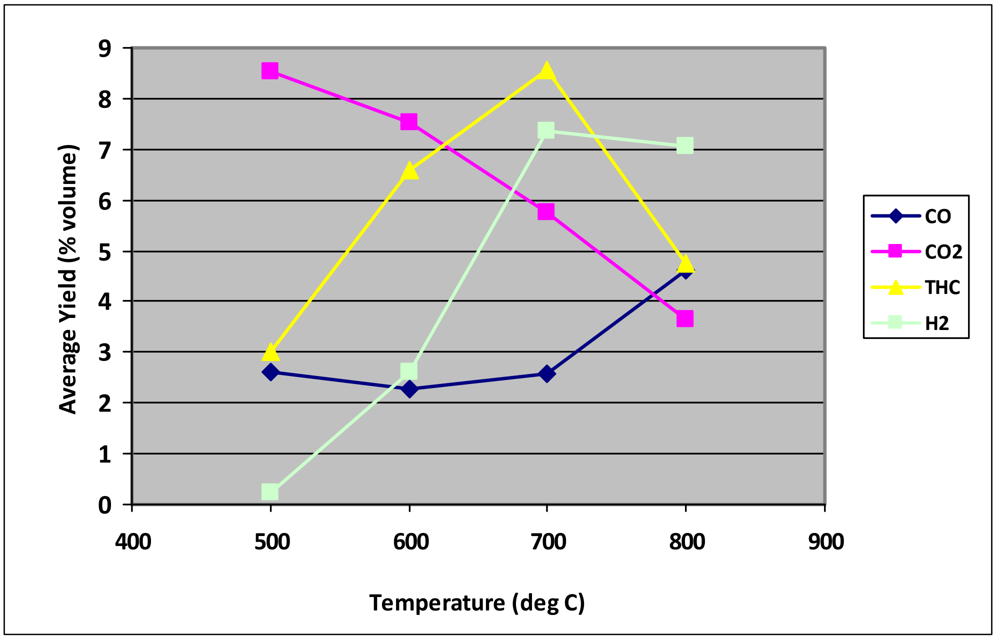

Figure 3. Average production of synthesis gas as affected by temperature.

### Liquid (Bio-oil) Analysis

The liquid product (bio-oil) was composed of the collected condensable gases (including moisture), tar and some solid products like ash and char that were carried through by the moving gases.

The liquid was red-brown to dark brown in color with some black portion at the bottom which is believed to be tar and char. The bio-oil has a strong, irritable odor that is common to all pyrolysis liquid from biomass (Tsai, et al, 2006). The liquid fraction was measured by weight. Encinar, et al., (2000) stated that the small amount of liquids that is lost due to condensation and that high gas flow is impossible to prevent and was supplemented by means of weight difference. Table 3 shows some of the properties of the liquid product. The pH level increased significantly (*p*-value = 0.0012) as the pyrolysis temperature was increased. One possible reason for this could be that the amount of water present in the bio-oil increased as temperature is increased. The secondary tar degradation at high temperatures (800°C) could have lead to the production of more $H_2$, CO, and several light HC and it is also possible to have an increased $H_2O$ production (Williams and Nugranad, 2000; Zabaniotou, et al, 2000; and Tsai, et al, 2006). The high water content in the bio-oil could also be the reason why the heating values are considerably lower than most commercial oil and petroleum products. There could also be high amounts of non-hydrocarbons present in the bio-oil such as $O_2$-rich compounds and ash. The bio-oils are commonly made of polar and non-polar organic components such as methanol, acetic acid, furfurals, and phenols. These organic components that are highly oxygenated are chemically bound with water and would need to be separated first and upgraded using either hydrocracking-hydrotreating or catalysis (i.e., zeolite synthesis) to increase the heating value and reduce corrosiveness when used as alternate fuel (Bridgewater et al., 1991 and Tsai, et al, 2006).

Table 3. Some properties of the liquid product.

| Temperature (°C) | $\rho_{ave}$[a] (g cm$^{-3}$) | Average pH | HV (MJ kg$^{-1}$) |
|---|---|---|---|
| 500 | 0.982 | 4.7 | 2.430 |
| 600 | 0.992 | 5.7 | 2.336 |
| 700 | 1.015 | 6.6 | 2.011 |
| 800 | 1.009 | 7.6 | 2.020 |

[a] $\rho_{ave}$ = average density (including water and tar).

## Conclusions

Pyrolysis of cotton-gin trash under different temperature 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 char yield of about 38 wt.% was determined at 500°C while the lowest char yield of about 35 wt.% was determined at 800°C, both at the 30-min reaction time. The pyrolysis temperature required to completely pyrolyze CGT into char at a fixed reaction time depends on the amount of biomass. After proximate analysis of the char, an increase in the ash and fixed carbon percentages was observed as the temperature was increased while there was a decrease in volatile matter. The quality of char improved at higher temperature. It was also determined in the energy analysis that the heating value of char increased with increased temperature and comprises 70% to 83% of the total energy output in the modified test.

More gaseous products were generated at a higher temperature and longer pyrolysis time due to the rapid devolatilization and decomposition of biomass and char. The gas produced was determined to be highly combustible, which could be due to the presence of producer or synthesis gas (CO, $H_2$, and THC).The highest gaseous product yield of about 35 wt.% was determined at 800°C and the lowest (32 wt.%) was observed at 600°C. The gas yield trend was also consistent with the literature. The concentrations of CO, THC, and $H_2$ in the gas generally increased as the temperature was increased from 500 to 800°C but $CO_2$ showed otherwise. The concentration of $CO_2$ has decreased by almost 60% (mol) from 500 to 800°C. The high fraction of flammable gases (CO, $H_2$, and THC) in the gaseous product has contributed to its energy content that was 10–20% of the total energy output.

The amount of liquid (bio-oil) produced was lower compared to the char and gas production. The liquid bio-oil produced contained appreciable amounts of water as verified by its density and heating value. The yield of bio-oil increased significantly from 500 to 600°C but decreased slightly from 600 to 800°C. The production of bio-oil is greatly favored by rapid heating at lower pyrolysis temperatures (400–500°C) and shorter residence time. The conventional pyrolysis mode used in the experiment gave higher char yield and lower bio-oil yield. The energy content of bio-oil was determined to be very low (2–3 MJ $kg^{-1}$) because it was highly oxygenated and contains large portion of chemically bound water and non-HC compounds.

## Acknowledgement

The authors would like to thank the Cotton Foundation, Texas AgriLife Research, and TAMU Cotton Chair (Dr. Parnell) for the financial support. Thanks also to the *Varisco Court Gin Co.* at Bryan, TX and to *El Campo Gin Co.* through Mr. Jimmy Roppolo at El Campo, TX for providing the cotton-gin trash.

## Disclaimer

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