

## **ADVANCES IN GASIFICATION AND PYROLYSIS RESEARCH USING VARIOUS BIOMASS FEEDSTOCK**

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### **Abstract**

This paper discusses recent advances in gasification and pyrolysis research utilizing various biomass wastes including cotton gin trash. Texas A&M University (TAMU) has recently filed a provisional patent for a modular fluidized bed gasification and pyrolysis system (Serial No. 61/302,001, February 2010). Discussions on the capabilities of both systems are explained. In addition, recent research accomplishments were identified. These research advances include the following: development of new control systems, gasification and pyrolysis of multiple feedstocks, the development of a modular system on a trailer and investigating other co-products of the systems. More interesting research studies have recently been focused on pyrolysis technologies for the production of bio-crude oil from various biomass feedstock. Compounds present in the bio-oil were identified; various extraction, fractionation and catalytic procedures were outlined to generate transport fuels such as JP8, gasoline and diesel fractions. Finally, the concept on the development of mobile fast pyrolysis system for the sustainable production of bio-oil at the cotton gins was illustrated using geographic information system (GIS) mapping tools.

### **Introduction**

The two most important thermal conversion systems applicable to biomass resources and including cotton gin wastes are pyrolysis and gasification. Pyrolysis is a thermal conversion process in a complete absence of oxidant (Pandey, 2009). Products include synthesis gas (CO, H<sub>2</sub>, CH<sub>4</sub> and other low molecular weights hydrocarbons), liquid bio-oil and bio-char. The most important product of pyrolysis is bio-oil, similar to crude-oil in physical appearance but very different in chemical composition. If acids, moisture and oxygen are removed from the bio-oil, the resulting product is compatible with crude oil and may be refined and fractionated to generate transport fuels such as gasoline, diesel and aviation fuel (JP-8). Gasification on the other hand is a thermal conversion process using limited amounts of oxygen. Products include low calorific value synthesis gas (LCV gas) and bio-char. The synthesis gas may be used in internal combustion engines and when these engines are coupled with generators, electrical power is produced. A new provisional patent for this system has been submitted on February of 2010 with Serial No. 61/302,001 (Capareda, et al., 2010). These technologies are ready for commercialization and licensing is being handled by the Office of Technology and Commercialization at Texas A&M University. This paper discusses the research efforts that lead to the development of the gasification and pyrolysis technologies at Texas A&M University using various biomass resources.

### **Objectives**

The main goal of this paper is to report on the most recent advances in gasification and pyrolysis research being conducted at Texas A&M University. The focus will be on the production of bio-oil for liquid transport fuel production.

The specific objectives are as follows:

- (a) Compare gasification and pyrolysis technology,
- (b) Discuss the advantages and disadvantages of each conversion processes,
- (c) Present current and future directions for advanced processes, and
- (d) Identify various products and by-products of the technologies.

### **Materials and Methods**

#### **The TAMU Fluidized Bed Gasifier**

The newly designed fluidized bed gasifier was used to convert various biomass resources into LCV gas. Aside from cotton gin trash (CGT), the other biomass resources gasified are as follows: wood chips, sorghum biomass, switchgrass, poultry litter, peat, wheat and rice straw and dairy manure have been tested for gasification. A new computer control system for the gasifier utilizing various biomass resources has been developed and a new unit has

been fabricated and installed on top of a flat bed trailer. The 1-foot diameter unit can handle between 2-4 tons per day of biomass. The advantages of a fluidized bed gasification system are as follows:

- (a) High throughput,
- (b) High thermal inertia for continuous operation,
- (c) Can handle wide range of feed stocks and
- (d) Mobile systems are possible.

The mobile gasifier needs to be pre-heated only during start-up and would require electrical power to run the blowers and feed motors. The TAMU fluidized bed gasifier was licensed by SDL Citadel Global (Dallas, Texas) for the conversion of municipal solid wastes (MSW) into electrical power. Other companies are in the process of securing licenses for the technology using other biomass resources (and field of use) such as animal manure (e.g. Global Restoration, Inc, Seabeck, WA).

### **The TAMU Fluidized Bed Pyrolyzer**

Texas A&M University has also developed the fluidized bed pyrolyzer technology. This pyrolyzer can convert various biomass resources including cotton gin trash (CGT) into high energy content bio-oil, bio-char, medium to high calorific value synthesis gas (HCV). The TAMU continuous pilot pyrolyzer can handle biomass feed rates of between 10-80 kg/hr for various biomass. Note that a gasifier may be operated in the pyrolysis mode if inert gas is used for fluidization. The unit is scalable and may be able to handle several tons of biomass each day. The advantages of pyrolysis processes are as follows:

- (a) Higher value products are produced,
- (b) Mobile portable systems are available and
- (c) Various other biomass products may be processed.

The primary disadvantage of using a pyrolyzer is that external heat is required for the pyrolysis process. Thus, the combination of having a fluidized bed gasifier to supply the necessary heat for the continuous operation of the pyrolyzer will be a sustainable process option. Excess synthesis gas may be used to pre-heat the system as well.

## **Results and Discussion**

### **Gasification of Multiple Feedstock**

One critical advantage of a fluidized bed gasification system (as opposed to downdraft or fixed bed system) is the use of multiple feed stocks without experiencing downtime. Figure 1 shows an example using various feed stocks without shutting down the system. In this case cotton gin trash may be gasified for 30 minutes followed by switchgrass for approximately 25 minutes and woodchips for the remaining 35 minutes for the demonstration activity. Reaction temperatures are maintained between 700°C to 800°C by appropriate control of air to fuel ratios.

Another important characteristic of the fluidized bed system is the ability to operate at various throughputs without having to use a larger diameter unit. This is accomplished by changing the appropriate bed material. By using a larger bed material, more air flow rate is required for fluidization and thus more biomass may need to be fed at higher rates to maintain the same fuel to air ratio as before. The reactor free-board must then be high enough so that bed materials are not blown out of the system.

For the efficient use of the synthesis gas, the char particulates must be cleaned prior to use. This can be achieved by the proper design of series cyclones to effectively remove larger particulate matter on the first stage and a more efficient cyclone to remove smaller particulates on the second stage.

The TAMU fluidized bed gasifier may be used to generate continuous production of heat or electrical power by the combustion of synthesis gas. Synthesis gas may be burned effectively in a staged-combustion system (to limit NO<sub>x</sub> emissions) and generate heat. If the synthesis gas is combusted in a gas engine or an internal combustion engine that is coupled with a generator, electrical power will be produced continuously. The gasifier may also be used to provide supplemental heat for the operation of a fluidized bed pyrolyzer.

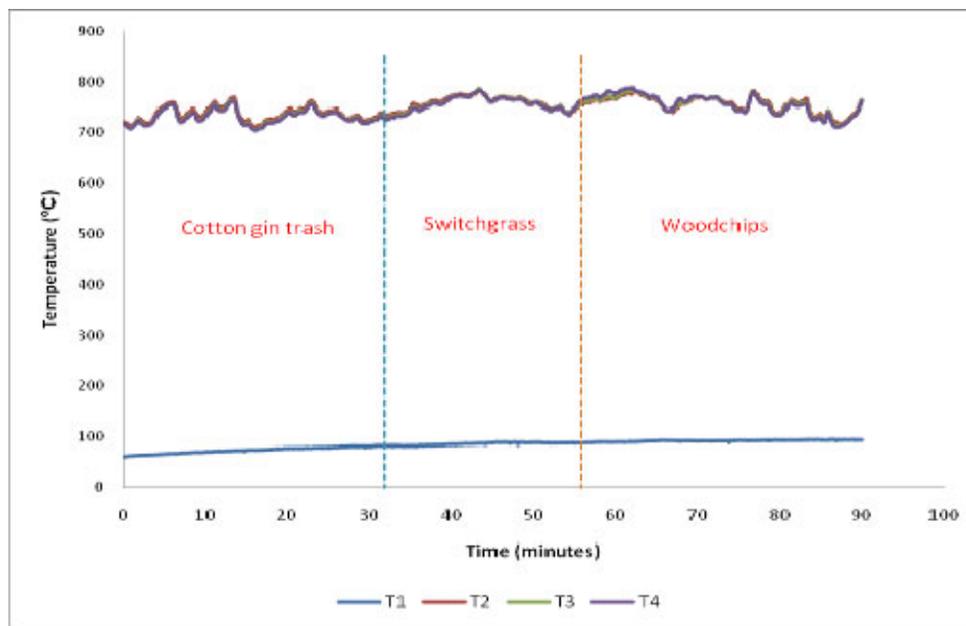


Figure 1. Temperature profile during gasification of multiple feed stocks

#### Pyrolysis of Various Biomass Feedstock

One of the most interesting thermal conversion processes is the production of bio-oil from various biomass resources. Bio-oil is the main product of fast pyrolysis process if the synthesis gas is quenched quickly in a specially-designed condenser (Bridgewater and Peacocke, 2000). Bio-oil has the same physical appearance as crude oil but quite different chemically. There are three parameters that must be removed from the bio-oil as follows: moisture, acids and oxygen. Moisture is easily removed via the use of molecular sieve or appropriate separation processes, the acids must be neutralized and separated from the oil fractions and the oxygen must be removed via de-oxygenation processes. De-oxygenation involves hydrogenation (addition of hydrogen) and catalytic conversion (removal of oxygen). Table 1 shows the range of compounds identified in bio-oil samples upon simple extraction using various solvents such as chloroform or dichloromethane. Except for the acid groups, most other compounds may be easily upgraded into hydrocarbon fuels found in gasoline, diesel or aviation fuels (Garcia-Perez, et al, 2007).

Table 1. Groups of compounds found from extraction of biooil samples using various solvents.

<u>Biooil extracted in chloroform</u>				<u>Biooil extracted in dichloromethane</u>			
<u>Group</u>	<u>%</u>	<u>Group</u>	<u>%</u>	<u>Group</u>	<u>%</u>	<u>Group</u>	<u>%</u>
<u>Alkane</u>	<u>36.2</u>	<u>Furan</u>	<u>3.5</u>	<u>Alkane</u>	<u>9.1</u>	<u>Xylene</u>	<u>3.5</u>
<u>Phenol</u>	<u>20.5</u>	<u>Ester</u>	<u>2.4</u>	<u>Phenol</u>	<u>29.9</u>	<u>Pyrazole</u>	<u>2.4</u>
<u>Alkene</u>	<u>8.8</u>	<u>Benzene</u>	<u>2.2</u>	<u>Alkene</u>	<u>5.0</u>	<u>Benzene</u>	<u>2.2</u>
<u>Acids</u>	<u>8.7</u>	<u>Naphthalene</u>	<u>1.7</u>	<u>Acids</u>	<u>9.8</u>	<u>Naphthalene</u>	<u>1.7</u>
<u>Alcohol</u>	<u>7.4</u>	<u>Amide</u>	<u>1.5</u>	<u>Alcohol</u>	<u>3.1</u>	<u>Amide</u>	<u>1.5</u>
<u>Ketone</u>	<u>5.1</u>	<u>Others</u>	<u>2.1</u>	<u>Ketone</u>	<u>8.3</u>	<u>Others</u>	<u>2.1</u>

#### Catalytic Upgrade of Bio-Oil Samples Into Hydrocarbon Fuels

The list of compounds found in Table 1 may be easily upgraded into hydrocarbon fuels using various catalysts listed in Table 2. Varying the operating conditions for various catalysts will also change the product outputs as shown. The important fuels found in aviation fuel (JP-8) are benzene and cyclo-hexane and the estimated yields are shown in

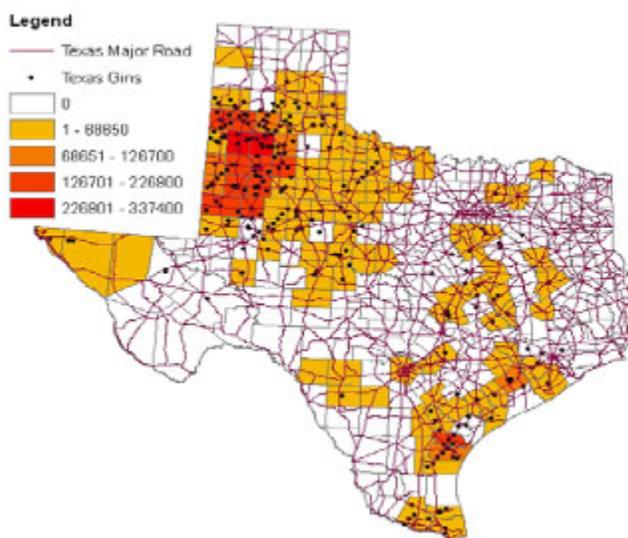
Table 2 as well. Future research are now directed at producing large quantities of bio-oil from biomass and converting those into hydrocarbon fuels and fractionated into transport fuels such as gasoline, diesel or JP-8 (French and Czernik, 2010).

**Table 2. Various catalysts used to produce hydrocarbon fuels via catalytic conversion of bio-oils.**

<u>Catalysts</u>	<u>Product</u>	<u>Amount of Product (%)</u>
<u>Sulfided CoMo @400°C</u>	<u>Benzene</u>	<u>33.8</u>
	<u>Cyclohexane</u>	<u>3.6</u>
<u>Ni</u>	<u>Benzene</u>	<u>16.9</u>
	<u>Cyclohexane</u>	<u>7.6</u>
<u>Sulfided Ni</u>	<u>Benzene</u>	<u>0.4</u>
	<u>Cyclohexane</u>	<u>8.0</u>
<u>Pd @ 400°C</u>	<u>Benzene</u>	<u>7.8</u>
	<u>Cyclohexane</u>	<u>2.7</u>
	<u>Cyclohexanone</u>	<u>5.5</u>
<u>Pd @ 300°C</u>	<u>Benzene</u>	<u>2.0</u>
	<u>Cyclohexane</u>	<u>2.5</u>
	<u>Cyclohexanone</u>	<u>8.1</u>

### **A New Paradigm in Biomass Fuel Conversion**

One main disadvantage concerning large-scale utilization of biomass resources for energy purposes is the high cost of transport associated with moving low energy density biomass into bio-refineries. Thus, an emerging concept is the establishment of mobile fast pyrolysis systems and stationed where abundant biomass resources could be gathered. This is an advantage in cotton gin operation since CGT is already brought to a centrally located site: the cotton gin. Figure 2 shows the location of all active gins in Texas.

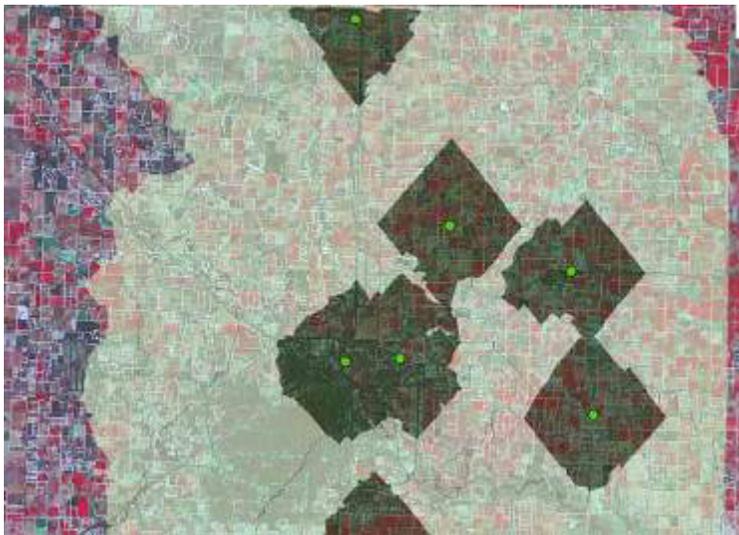


**Figure 2. Geographic information system (GIS) map showing location of active cotton gins in Texas.**

These gins are potential sites where mobile fast pyrolysis systems could be deployed, convert all CGT into bio-oil, sell the bio-char as activated carbon or as soil amendment and sell the bio-oil to the nearest refinery for fractionation into transport fuels.

Figure 3 below shows the location of cotton gins in a county in Texas where a mobile fast pyrolysis system may be deployed year-round. For this site, the pyrolyzer owner may move from one gin to another to process all of the CGT

at the site. The process is repeated every year. One cotton gin may own the facility or they may be purchased through cooperative agreement with all gin owners in this county. The advantage of using a fluidized bed system is that, the capacity may be adjusted depending upon the quantity of CGT available at each gin by simply changing the size of the bed material to adjust the throughput at a given gin. The pyrolyzer owner may opt to operate at the highest throughput as possible and take advantage of economies of scale and thus improve his economic returns. In this case, the operator will have to expand his service area to have a full year of operation.



**Figure 3. Location of six active cotton gins in a county in Texas that may be designated as one service area for a mobile fast pyrolysis system.**

Currently, the only remaining researchable area concerning the bio-oil production route is the technical barrier in removing the moisture, acids and oxygen in the bio-oil. Once these technical barriers have been overcome, this country will have a sustainable source of heat, electrical power and transport fuels. Thus, more research dollars should be available to upgrade the quality of bio-oil from fast pyrolysis processes.

### **Conclusions**

The two most popular thermal conversion systems, namely, gasification and pyrolysis applicable to converting cotton gin trash into heat, fuel and power were discussed. Fluidized bed gasifier may be used to convert cotton gin trash into heat and electrical power or simply to convert CGT wastes into value bio-char. The gasification unit may be scaled to fit the requirements of cotton gins or may be used to process even large-scale systems by simply changing the bed material sizes. Fluidized bed gasification technologies may be a ubiquitous facility in many bio-refineries in the future.

Mobile fast pyrolyzers on the other hand are beneficial for converting low energy density biomass into high energy density bio-oil that may be upgraded into crude oil. The bio-crude oil may then be delivered to various commercial refineries in the US for fractionation into gasoline, diesel and aviation fuel. The bio-char may be recycled as soil amendment or as material for producing activated carbon. Mobile pyrolysis systems may be deployed to various cotton gins in the country to process the CGT wastes year round. .

Future research should be directed at upgrading the quality of bio-oil produced from various biomass resources. These include removal of moisture and acids and the extraction of valuable compounds that will be converted via hydrogenation and catalytic processes into transport fuels such as gasoline, diesel and aviation fuel (JP-8). There is a potential possibility that cotton gin facilities may be producing their own diesel or gasoline fuel in the future.

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- (e) Sungrant South Central Region
- (f) Texas Agri-Life Research
- (g) Texas Engineering Experiment Station (TEES)

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