

# TRANSPORTABLE FAST-PYROLYSIS PROCESS FOR DISTRIBUTED CONVERSION OF WASTE BIOMASS TO RENEWABLE LIQUID FUELS

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## Abstract

In Florida alone, sugarcane bagasse, orange residue from juicing, and logging/mill residues are produced at a rate exceeding 16,000 dry tons per day. However, these agricultural residues are often spread over large areas and are difficult to access, particularly the logging residues. Rather than trucking large quantities of low-density biomass to a massive centralized biofuel production plant, the distributed conversion of agricultural residues into bio-oil is an attractive alternative for sustainable biofuel production. Opportunities also exist for the conversion of mixed waste to biofuel at forward-deployed military outposts, where the true delivered cost of fuel often exceeds \$15 per gallon. Mainstream Engineering (MEC) recently commissioned a highly instrumented fast-pyrolysis pilot plant (1 ton/day) to demonstrate small-scale conversion of waste organic material to bio-oil. The pilot reactor was designed for flexibility and tight process control, as we explore the product yield and quality for a variety of feedstocks. Testing to date has used pine sawdust or a granulated mixed-waste surrogate consisting of corrugated cardboard, office paper, and several plastics.

MEC is working to commercialize the portable process at a 10 ton/day scale for commercial applications and at the <1 ton/day scale for military applications. Our efforts have focused on improving the reactor yield by minimizing secondary cracking and improving the energetics with tight heat integration. Both improvements are geared towards achieving viable process economics at a small throughput. We have also experimentally investigated feedstock pre-processing (size reduction and drying) and end-use utilization of raw bio-oil in a burner/boiler. Results are presented on our pilot reactor testing and techno-economic analysis of the portable reactor approach.

## Introduction

While MEC's implementation of fast pyrolysis includes innovations that address several key roadblocks, the underlying fast pyrolysis technology benefits from at least 25 years of development and refinement by the global scientific and engineering community. As evidence, progress in biomass fast pyrolysis has recently been reviewed by Bridgwater and Peakcocke [1] and Mohan, Pittman and Steele [2]. Bridgwater and coworkers [3] performed a techno-economic analysis of pyrolysis, gasification and combustion that showed economic advantages for pyrolysis, especially at the small scale. Czernik and Bridgwater [4] reviewed end-use utilization of bio-oil. Solantausta et al. [5] describe a recent (2011) ongoing pilot-scale fast-pyrolysis demonstration in Europe.

Our focus has been on circumventing several technical barriers that have prevented biomass fast pyrolysis from taking hold commercially. The key technical barriers to small-scale thermochemical biomass conversion are: 1) keeping the unit production costs low while shrinking the process capacity (i.e., overcoming the "six-tenths" rule), and 2) finding a viable offtake route for bio-oil. Options for bio-oil end-use include using raw bio-oil for industrial heat and power in modified burners or hydrotreating the bio-oil to produce a transportation fuel.

## Experimental Methods

Initially thermogravimetry was used to measure pyrolysis kinetics for a variety of waste biomass feedstocks. That information was then used to design a continuous, bench-scale reactor (1 kg/hr). Bench-scale reactor data and process simulations were used to scale up the process to the pilot scale (45 kg/hr, nominally 1 ton/day). Results from the pilot-scale testing were used to design a full-scale 10 ton/day (tpd) system.

### *Thermogravimetric Analysis*

The organic fraction of landfill waste is comprised of a variety of lignocellulosic and plastic materials. Thermogravimetric analysis (TGA) was used to gather kinetic data for pyrolysis of organic landfill constituents. TGA works by heating a small mass of material at a constant rate and tracking the weight loss with a microbalance over the specified temperature range. The residue left after the experiment is designated as char (the inorganic ash present in the residue is negligible). The weight lost during the experiment is a combination of the amount of liquid product (condensable gases that would produce pyrolysis bio-oil) and non-condensable gases produced via thermal depolymerization reactions.

Ten landfill waste constituents were tested at two heating rates (5 °C/min and 200 °C/min) in a TGA (TA Instruments, New Castle, DE). Grønli, Antal, and Várhegyi [6] demonstrated the suitability of TGA for measuring biomass pyrolysis kinetics by conducting a round-robin comparison of eight laboratories performing the same TGA measurement on Avicel PH-105 cellulose. To ensure that our TGA experiment was accurate, experiments were also conducted with the same cellulose standard. The TGA mass loss data was fit to a first-order rate equation and Arrhenius parameters,  $A$  and  $E_a$ , were determined for each feedstock at each heating rate. The measured Arrhenius parameters for the Avicel PH-105 cellulose fell within the accepted range reported by Grønli, Antal, and Várhegyi [6].

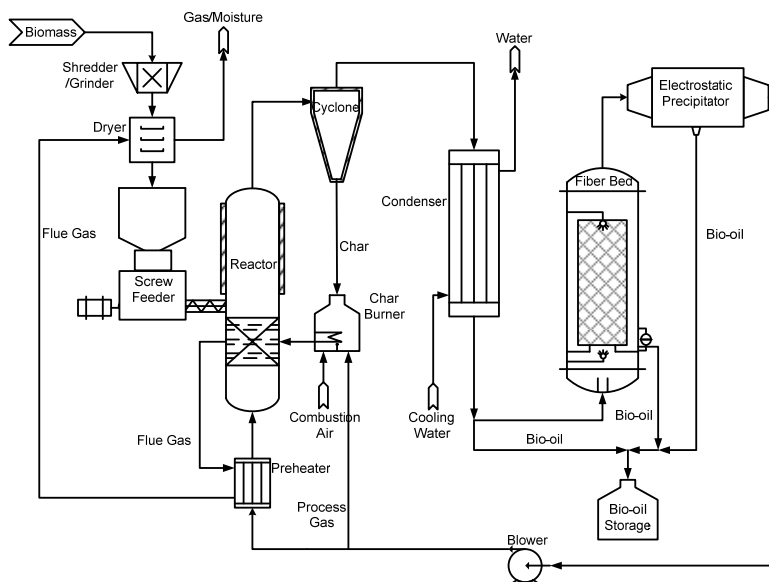
### *Process Design*

A chemical process model was constructed to design the small-scale fast-pyrolysis process using CHEMCAD (Chemstations, Houston, TX). The major unit operations were specified according to the process flow diagram shown in Figure 1. Biomass enters the process where it is first pre-processed (dried and ground) and then fed to the fluidized-bed reactor through a screw feeder. Oxygen-free fluidizing gas flows up through the reactor, which is held at approximately 500 °C, giving a vapor residence time of approximately 1 s. The biomass material is depolymerized to form condensable bio-oil vapors, non-condensable gases, and solid char. The products exit the reactor at the top and flow into a cyclone which removes the char. The vapors and gases then flow through a condenser that produces mostly aerosolized bio-oil liquid droplets entrained in the non-condensable gases at the outlet. A fiber bed and electrostatic precipitator are used to collect the bio-oil aerosol. The non-condensable gases are then recycled to the process. A portion of the non-condensable gases are used as the fluidizing gas, and the remainder is burned to provide process heat for the reactor and for drying.

Pyrolysis bio-oil is a complex mixture of hydrocarbons, oxygenated hydrocarbons (e.g., phenols, aldehydes, guaiacols, and carboxylic acids), and emulsified water. A 70-component bio-oil surrogate was formulated based on major classes of compounds found in bio-oil. The non-condensable gases were simulated as a mixture of N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and other small hydrocarbons. Thermodynamic properties for these compounds were calculated using the CHEMCAD property database. The fluidized-bed reactor was treated as a stoichiometric reactor with a fixed yield. The condenser was modeled as having a fixed outlet temperature. A vapor-liquid equilibrium (VLE) calculation was performed on the condenser effluent to predict the liquid fraction. The cyclone, fiber bed, and electrostatic precipitator were modeled using prescribed separation efficiencies.

More detailed spreadsheet models of the fluidized bed reactor, condenser, cyclone, and

electrostatic precipitator were also created to design and size those components. Capital and operating costs were estimated based on established methods described by Ulrich [7]. Process models, including component sizing and costing, were created at both the 1 ton/day (tpd) and 10 tpd scales.

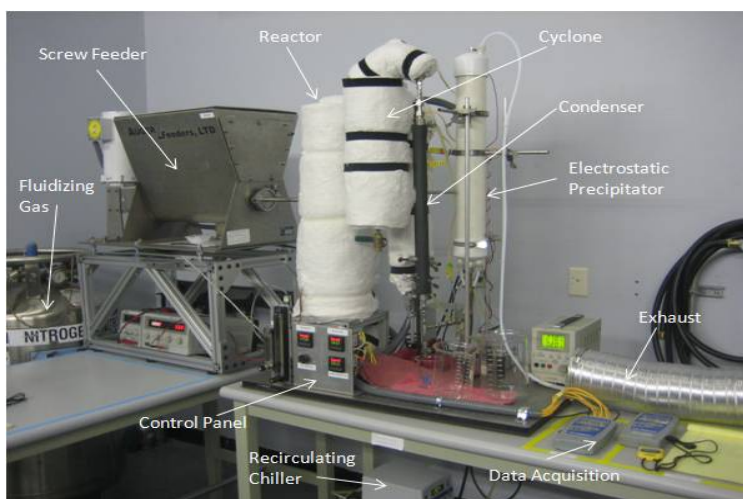


**Figure 1. Process flow diagram for the small-scale pyrolysis process**

### ***Bench-Scale Reactor Development***

A bench-scale fast pyrolysis reactor was designed based on the TGA results and process simulations. The bench-scale reactor shown in Figure 2 has a throughput of approximately 1 kg/hr. The reactor has the majority of the unit operations shown Figure 1 except that the non-condensable gases were not recycled and burned; instead the reactor was electrically heated. Also, the preprocessing was performed off-line.

The bench-scale reactor was designed for flexibility such that components could be swapped out easily. The reactor has an internal diameter of approximately 5.1 cm (2 in). The fluidized sand bed is supported on a porous frit to distribute the flow and provide uniform fluidization. Several iterations of the cyclone, electrostatic precipitator, condenser, and fiber bed were experimentally tested. Experiments were also performed with a spray tower added to the bio-oil separation and collection train.



**Figure 2. Bench-scale, continuous fast-pyrolysis reactor (1 kg/hr)**

### ***Pilot-Scale Reactor Development***

Following the bench-scale testing, the fast-pyrolysis process was scaled up to 45 kg/hr (100 lb/hr). The pilot reactor implements the process shown in Figure 1, with the exception that the reactor is electrically heated and the non-condensable gases are flared. Also, the pre-processing was again performed off-line using a knife mill. The reactor skid is shown in Figure 3. Also shown is the fluidized-bed reactor (41 cm inside diameter) before it was encased in insulation. The pilot reactor was designed for flexibility and performance testing. As such, it is heavily instrumented with thermocouples, pressure transducers, and flow meters. The reactor alone was outfitted with 26 thermocouples to provide comprehensive thermal data and to quantify the temperature uniformity in the sand bed. A PLC-based controller maintains process set points and logs sensor data. A touchscreen interface allows monitoring of process conditions and inputting set points. The controller includes programmed sequences for startup, shutdown, and cleaning cycles.



**Figure 3. Pilot-scale fast-pyrolysis reactor (45 kg/hr)**

## **Results and Discussion**

### ***Pyrolysis Kinetics***

All organic feedstocks were analyzed with the TGA at two heating rates, and the pyrolysis kinetics of each sample was determined. Grønli and coworkers [6] found that the organic decomposition by pyrolysis follows a first-order rate equation for  $\alpha = 1 - (m(t) - m_c)/(m_0 - m_c)$  with  $k = A \exp(-E_a/RT)$ ,

$$\frac{d\alpha}{dt} = k(1 - \alpha)$$

where  $m(t)$  is the sample mass at any specific time,  $m_0$  is the initial sample mass (dried),  $m_c$  is the final sample mass,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature of the sample at time,  $t$ . A MATLAB program was written to determine the Arrhenius parameters,  $A$  and  $E_a$ , from the TGA data. The results for the 10 feedstocks are shown in Table 1. The fitting error for each experiment was less than 1% suggesting the proposed rate equation accurately described the pyrolysis decomposition kinetics. The 9 lignocellulosic feedstocks tested all demonstrated similar reactivity. The plastic (PET) was less reactive and the depolymerization occurred at a temperature approximately 100 °C higher than that observed for the lignocellulosic material. The

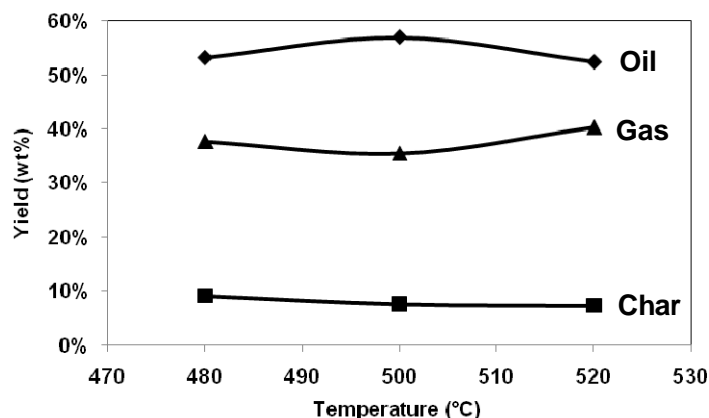
similarity in reactivity, at least for the lignocellulosic feedstocks, suggests that the process would be tolerant of a mixed feedstock typical of landfill waste.

**Table 1. Pyrolysis Kinetic Parameters for Various Organic Materials**

FeedStock	5 °C/min		200 °C/min	
	$E_a$ (kJ/mol)	$\log A$ ( $\log s^{-1}$ )	$E_a$ (kJ/mol)	$\log A$ ( $\log s^{-1}$ )
Pine	92.9	6.17	77.1	4.92
Office Paper	137.9	10.3	110.5	7.74
Sawdust	86.1	5.52	68.1	4.25
Treated Wood	63.6	3.56	62.8	3.78
Magazine	97.8	6.65	81.6	5.33
Cardboard	99.7	6.95	86.2	5.85
Cloth	94.0	6.18	108.2	7.29
Newspaper	83.8	8.30	79.3	5.03
Yard Trimmings	82.8	2.79	45.5	2.59
Plastic, PET	254.1	17.9	249.9	16.01

### Product Yields

Three main products are produced by the fast-pyrolysis reaction: bio-oil, gas, and char. The bench-scale reactor was run continuously with pine sawdust, and the yield was measured gravimetrically. Prior to feeding the sawdust to the reactor, it was dried to 10 wt% moisture and milled to approximately 1 mm particle size. Care was taken to recover as much of the bio-oil as possible from the downstream separation and collection components. The measured yield (wet basis) is shown in Figure 4 as a function of reactor temperature. A reactor temperature of 500 °C was shown to maximize the yield of bio-oil, the desired product. These data were collected for a vapor residence time of 0.8 s, which was determined to be the optimal value in this reactor. This optimal reactor temperature and residence time are characteristic of other studies of fast pyrolysis [8]. The dependence of bio-oil yield on reactor temperature was weak, at least over the range of temperature explored, suggesting that some variability in reactor temperature is tolerable. The fluidized bed temperature in the *pilot-scale* reactor was shown to be uniform to within 10 °C suggesting that the reaction was occurring at close to the optimal conditions. The pilot-scale reactor has only been run for short-duration tests, not long enough for reliable yield measurements to be made.



**Figure 4. Effect of reactor temperature on bench-scale product yields (0.8 s residence time)**

### **Product Quality**

Sufficient bio-oil has been collected with both the bench-scale and pilot-scale reactors to determine the quality of the bio-oil product. Results are shown in Table 2 for the bench-scale reactor operated with pine sawdust feedstock. Also shown are results for the pilot-scale reactor with a pine sawdust feedstock and a mixed-waste surrogate feedstock. The mixed-waste feedstock contained granulated paper, corrugated cardboard, and several plastics (polystyrene, PET, and HDPE). As a point of comparison, the requirements for pyrolysis bio-oil established by the ASTM D7544 standard are also shown. The pine bio-oil from the bench-scale reactor was fully characterized and found to meet all the ASTM 7544 requirements except ash content, which was slightly higher than the acceptable value. The high ash content may have been due to entrainment of solid ash/char particles in the bio-oil. The pine bio-oil collected from the pilot-scale reactor was slightly higher in moisture content and lower in heating value compared to the bench-scale reactor. With further refinement of the pilot-scale bio-oil collection equipment, the pilot reactor is expected to produce bio-oil similar to the bench-scale reactor.

The water content was lower for the mixed-waste bio-oil compared to the pine bio-oil and the heating value was considerably higher. The oxygen content of the bio-oil produced from mixed waste was also considerably lower than the pine bio-oil. The lower oxygen content observed with the mixed waste is due to lower oxygen content in the feedstock, which included some oxygen-free plastics. The lower oxygen content lends itself to better bio-oil stability (less aging) and improved upgrading potential (lower hydrogen requirement for deoxygenation). Although not measured, we did observe that the mixed-waste bio-oil was considerably more viscous than the pine bio-oil.

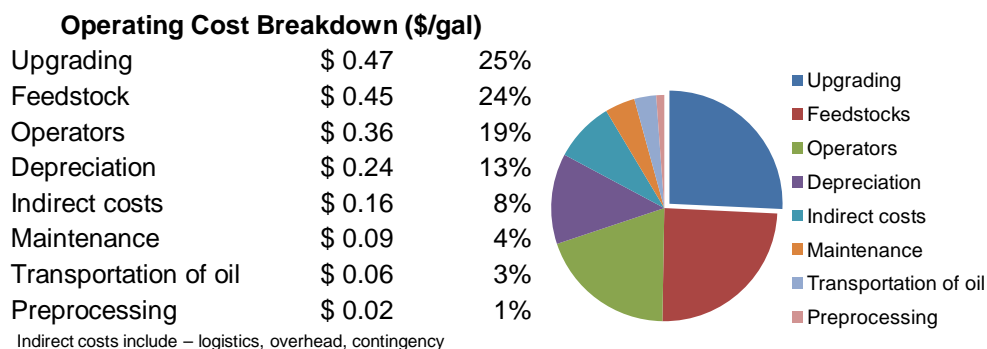
**Table 2. Pyrolysis Bio-Oil Properties**

<b>Property</b>	<b>ASTM D7544 Bio-Oil Std</b>	<b>Bench-Scale / Pine Sawdust</b>	<b>Pilot-Scale / Pine Sawdust</b>	<b>Pilot-Scale / Mixed Waste</b>
Higher Heating Value (MJ/kg)	15 min	19.0	14.1	28.6
Water Content (mass %)	30 max	30.0	33.1	14.5
Kin. Viscosity at 40°C (mm <sup>2</sup> /s)	125 max	76	—	—
Density (g/mL)	1.1–1.3	1.2	1.07	1.10
Sulfur Content (mass %)	0.05 max	0.013	—	—
Solids Content (mass %)	2.5 max	0.5	—	—
Ash Content (mass %)	0.25 max	0.30	—	—
Flash Point (°C)	45 min	57	—	—
Pour Point (°C)	−9 max	<−10	—	—
pH	report	3.0	3.8	—
TAN (mg KOH/g)	—	161	76.1	86.0
Elemental Analysis, wet basis (mass %)				
C	—	41.2	38.2	64.1
H	—	7.3	8.5	6.7
O	—	51.6	53.3	29.2
Elemental Analysis, dry basis (mass %)				
C	—	58.9	57.0	75.0
H	—	5.6	7.2	6.0
O	—	35.6	35.8	19.0

### **Techno-Economic Analysis**

A techno-economic assessment of the portable pyrolysis business model was also performed. We conservatively estimated that the capital cost for each 10-tpd processing unit is \$1,250,000 for pioneer systems. The normalized capital cost is \$3.70 per annual gallon of capacity assuming a utilization of 250 days/year. The operating cost to produce renewable fuel oil is estimated at \$1.85 per gallon of No. 6 fuel

oil equivalent (takes into consideration difference in heating value) assuming four 10-tpd units operating in parallel with a \$40/ton feedstock price. The current sales price (2013) for low-sulfur No. 6 residual fuel oil is \$2.77/gallon indicating a viable margin. Figure 5 shows a breakdown of the major contributions to the operating costs. Bio-oil upgrading, feedstocks, and operators account for roughly 70% of the operating costs. If the bio-oil were sold raw, the upgrading costs (\$0.47/gal) would not be incurred. The cost of upgrading to a refinery-ready intermediate is expected to be comparable in magnitude to the upgrading cost to produce a renewable No. 6 fuel oil replacement. The upgrading costs are the most uncertain contribution to the cost model.



**Figure 5. Estimated breakdown of operating costs for 10-tpd mobile pyrolysis reactor**

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