Green Chemistry

Accepted Manuscript

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ARTICLE

Design and Operation of a Pilot-Scale Catalytic Biomass Pyrolysis Unit

dReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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RTI International is developing an advanced biofuels technology that integrates a catalytic biomass pyrolysis step and a hydroprocessing step to produce infrastructure-compatible biofuels. At the current stage of development, the catalytic biomass pyrolysis process is being scaled-up in a 1 tonne per day (1 TPD) pilot plant based on a single-loop transport reactor design with continuous catalyst circulation and regeneration. The chemistry of biomass pyrolysis is manipulated by the catalyst and by controlling the pyrolysis temperature, vapor residence time, and biomass-to-catalyst ratio. The pilot unit has been successfully operated with a novel catalyst that produces a bio-crude intermediate with 24 wt% oxygen. Product yields and composition in the pilot plant are consistent with results obtained in a laboratory-scale 2.54 cm diameter bubbling fluidized bed reactor. The overall mass balance was 93%, while the carbon closure was 83%.

Keywords: catalytic biomass pyrolysis, pilot scale, bio-crude, applied pyrolysis

Introduction

A variety of pyrolysis technologies are being investigated for producing liquid intermediates from biomass that can be upgraded into hydrocarbon fuels.[1-9] Traditional biomass flash pyrolysis processes have demonstrated a roughly 70% liquid product yield; however, this pyrolysis oil product has limited use without stabilization and upgrading.[10-13] The physical and chemical properties of fast biomass pyrolysis oils make them unsuitable for integrating into existing petroleum refineries.[14-16] Undesired properties of conventional pyrolysis oil include 1) thermal instability and high fouling tendency; 2) corrosiveness due to high organic acid content (pH 2.2–2.4, typically); 3) immiscibility with refinery feedstocks because of high water and oxygenates content; and 4) metals (K, Na, and Ca) and nitrogen content, which fouls or deactivates refinery catalysts.

Using catalysts to improve the physical and chemical properties of bio-oils is an active area of research, development, and demonstration.[3, 4, 17-40] A recent article by Venderbosch provides a comprehensive review of the recent catalytic biomass pyrolysis literature.[41] Catalysts can be used downstream of the pyrolysis reactor to upgrade the pyrolysis vapors, or they can be added in direct contact with the biomass in the primary pyrolysis reactor in a catalytic fast pyrolysis (CFP) process. The goal of these advanced biofuels processes is to produce hydrocarbon-rich liquid intermediates that can be upgraded using conventional refining technology to produce cost-competitive gasoline, diesel, and jet fuel that leverages the capital expenditures in the existing petroleum refining industry and distribution infrastructure.

The role of catalyst in direct biomass liquefaction processes is to control the chemistry of biomass pyrolysis to promote deoxygenation reactions such as dehydration (loss of H_2O), decarboxylation (loss of CO_2), and decarbonylation (loss of CO). However, the promotion of these oxygen removal pathways negatively impacts the organic liquid yield. For example, dehydration of the biomass during pyrolysis (with or without a catalyst) produces large amount of water (water of pyrolysis) which consequently is the most abundant component of the liquid phase product. Also, since biomass is inherently oxygen-rich and hydrogen-deficient, the pyrolysis products become even more hydrogen deficient as dehydration occurs. This increases the tendency for aromatic formation and ultimately leads to char/coke formation. Furthermore, deoxygenation by CO and CO_2 removal plus any carbon losses from coke formation on the catalyst result in lower hydrocarbon liquid yields and lower energy recovery in the bio-crude intermediate. Likewise, thermal or catalytic cracking tends to produce gas phase products and carbonaceous solids (char and coke) which affect the carbon efficiency. These are some of the major challenges in catalytic pyrolysis. Eventually, the identification of suitable catalysts and process conditions would be key to minimizing carbon loss to char, light gases, and coke.

Another challenge associated with catalytic biomass pyrolysis research is determining the extent of deactivation during fixed or fluidized bed experiments. In small-scale systems, catalysts

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are continuously deactivated as biomass is fed into the reactor so the bio-crude has an average composition based on the ratio of biomass fed to catalyst present. As the catalyst deactivates, deoxygenation activity decreases and organic liquid yield tends to increase. In this way, the oxygen content and yield of bio-crude can be overestimated in laboratory experiments.

Developing catalytic biomass pyrolysis reactor systems to provide accurate quantitative results is essential to guide scale-up for technology development. Ideally, continuous catalyst replacement[34] or regeneration is needed to expose the input biomass to fresh or regenerated catalyst to maintain an equilibrium bio-crude composition and production rate. In small laboratory-scale systems, it becomes challenging to circulate or transport solids and vapors in the relatively small-diameter reactors and tubing involved. Continuous regenerating, circulating fluidized bed, or transport reactor systems can be developed at a larger scale where it is easier to transport solids and vapors through larger diameter piping with fewer operational issues. The reactors in larger systems should be designed to minimize wall effects and heat loss while maintaining maximum system operability. With these criteria, the resulting reactor systems become quite large and are identified by feedrates on the order of tens of kilograms per hour instead of grams per hour and require catalyst loadings on the order of 10–100 kg instead of 100 g.

In this paper, we discuss the design and operation of a 1 tonne per day (1 TPD) reactor system based on a single-loop transport reactor design to support the scale-up and development of catalytic biomass pyrolysis technology. Only a few examples of catalytic biomass pyrolysis reactor systems at this scale for research and development are found in the literature.[36, 42] The design basis of the pilot-scale unit was developed from laboratory-scale solid, liquid, and vapor yields and experimental conditions (temperature, pressure, residence time, and catalyst-to-biomass ratio). The resulting pilot-scale unit design is intended to provide experimental results to guide future process scale-up and produce large enough quantities of bio-crude to support future upgrading technology development and validation.

Experimental

Pilot-scale Scale Reactor System Design Basis

A nominal 1 TPD catalytic biomass pyrolysis system has been designed based on proof-of-concept studies performed in a 2.54 cm diameter bubbling fluidized bed system. The pilot-scale catalytic biomass pyrolysis reactor is a continuously circulating single-loop transport reactor design that is flexible enough to allow sensitivity studies around temperature, residence time, biomass feedrate, and catalyst-to-biomass ratio (*i.e.,* catalyst circulation rate) for process optimization. A process flow diagram for the system is shown in Figure 1.

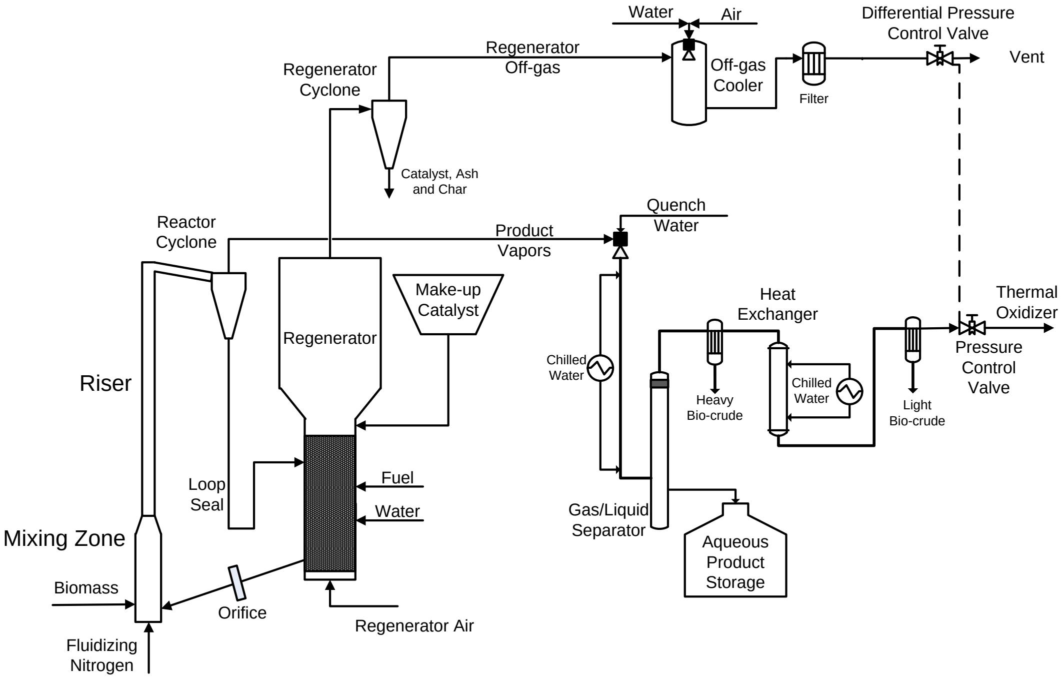

Figure 1: Process flow diagram of 1 TPD catalytic biomass pyrolysis unit.

Catalyst coke and char are oxidized in a bubbling fluidized bed regenerator to provide heat to drive the endothermic biomass pyrolysis process. The regenerator is 5.33 m tall with a 45.7 cm diameter reaction zone and 61 cm diameter disengagement zone. Air inlet flow rates are adjusted to maintain a minimum velocity of 0.3 m/s to maintain good mixing in the regenerator. Ideally, the heat of combustion balances the heat required for biomass pyrolysis and any heat losses in the system. Electrical heating is used for start-up and can be used to overcome minor heat losses during operation. Additional fuel (diesel) can also be added during start-up and to overcome excessive heat losses. Conversely, water can also be added to the regenerator to remove excess heat.

Biomass is injected into a 15 cm diameter dense-phase mixing zone using a screw feeder as shown in Figure 2. Nitrogen is added as fluidization gas to maintain a well-fluidized bed in this section. Biomass interacts and mixes with the hot catalyst and undergoes pyrolysis at the bottom of the mixing zone. Pyrolysis product gases and vapors flow upward from the mixing zone and entrain the catalyst and char particles into a 5 cm diameter by 4.3 m riser. Standard operating conditions establish a ~0.75 sec total residence time in the mixing zone.

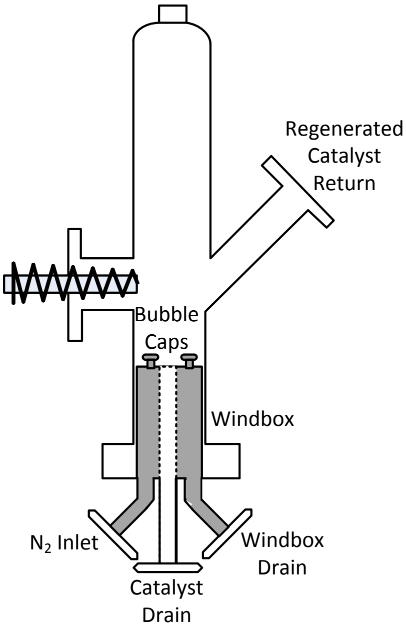

Figure 2: Schematic of the mixing zone detailing the biomass and nitrogen inlets with the regenerated catalsyt return.

The entrained char and catalyst are separated from the product vapors and gases in a cyclone separator. The separated solids (catalyst, char, and ash) are transferred through a loop seal to the regenerator. The product vapor stream exiting the top of the cyclone is condensed in a quench system. Water is atomized and mixed with the pyrolysis vapors to condense the bio-crude product (~100 °C) and scrub particulate and heavy oils. Remaining liquid is separated by two coalescing filters, one operated at ~100 °C and one operated at ~20 °C. Permanent gases are sent through a pressure control valve to a thermal oxidizer. The liquid products are collected in storage vessels and allowed to settle and phase separate over time. The aqueous and organic bio-crude fractions are collected in separate product drums.

For a nominal 45 kg/h feedrate of dry biomass, the products include ~11 kg/h char, ~9 kg/h permanent gases, and ~ 25 kg/h condensable vapors. Pyrolysis temperatures are typically between 450 and 600 °C, and the system is operated close to ambient pressure but high enough to overcome the pressure drop across the system and control gas flow through the process.

Pilot-scale System Unit Operations

Biomass Feed System. The biomass feed system consists of a conveyer to deliver biomass from the ground level to the top of a dual-lock hopper biomass feeder. The feed conveyer is a Flexicon Bulk Bag Discharge unit. The hopper on the bulk bag discharger unit has a capacity of 0.51 m^3 (18 ft^3) and contains a mechanical agitator and air actuated vibrator to continuously move biomass to the feed conveyer screw. A long, flexible screw is inserted through a 10 cm diameter polyethylene tube and is attached to the shaft of a motor that is mounted above the inlet of the biomass feeder. Biomass is continuously drawn up the tube and into the top bin on the biomass feeder. The biomass feeder consists of three sections separated by air actuated ball valves. The top bin of the biomass feeder is open to the atmosphere and has a capacity of 0.028 m^3. When this bin is full, the first ball valve is opened and the biomass charge is dropped into the second (purge) bin. The purge bin also has a capacity of 0.028 m^3 but can be isolated and purged with nitrogen and pressurized to match the system pressure before it is dropped into the bottom, main feeder section. The main feeder section has a capacity of 0.085 m^3. The biomass in the main feeder section is dropped onto a set of four dosing screws that feed the biomass to the primary feed screw. The biomass is then conveyed into the mixing zone of the reactor by the primary feed screw. The design of the primary feed screw is such that the biomass near the end of the screw completely fills the inlet to the pyrolysis reactor by forming a plug that helps seal against the system pressure in the mixing zone. The translational velocity of the biomass plug in the reactor feed screw is designed to be greater than the theoretical permeating velocity of the hot gases through the biomass plug at the system pressure in the mixing zone of the reactor. The reactor feed screw is water cooled to restrict heat transfer from the mixing zone along the length of the screw to avoid premature pyrolysis of biomass material prior to its discharge into the mixing zone.

The speed of the dosing screws and the primary feed screw is adjusted to achieve the desired biomass feedrate. The biomass feed system is effectively a volumetric feed system so the actual feedrate on a weight basis is a function of the bulk density of the prepared biomass. High- and low-level sensors in each section of the biomass feeder are used to coordinate continuous biomass feeding.

Prepared biomass is size reduced to less than 6 mm top size and dried to approximately 10 wt% moisture. The ultimate and proximate analyses of the loblolly pine feedstock are presented in Table 1. The loblolly pine has low ash content. The nitroge and sulphur content is also quite low. This composition is typical of woody biomass feedstocks.[43, 44]

Table 1: Loblolly Pine Feedstock Composition

Volatiles	82.5 wt%
Fixed Carbon	17.2 wt%
Ash	0.6 wt%
C	46.0 wt%, dry
H	6.0 wt%, dry
O (by difference)	47.0 wt%, dry
N	0.5 wt%, dry
S	0.027 wt%, dry
Higher Heating Value	19.98 MJ/kg
Moisture (as received)	10.6 wt%

The biomass feedrate was calibrated for 3 mm top-size loblolly pine sawdust. The bulk density of this material is 257 kg/m^3 (16 lb/ft^3) with a moisture content of 10 wt%. This material flows very freely in the system. With this material, the speed of the primary feed screw actually controls the feedrate, and the dosing screws mainly provide mechanical agitation to maintain solids flow. The calibrated biomass feedrate with various speeds for the dosing screws and the primary feed screw is shown in Figure 3. The speed of the dosing screws is always less than or equal to the main feed screw speed.

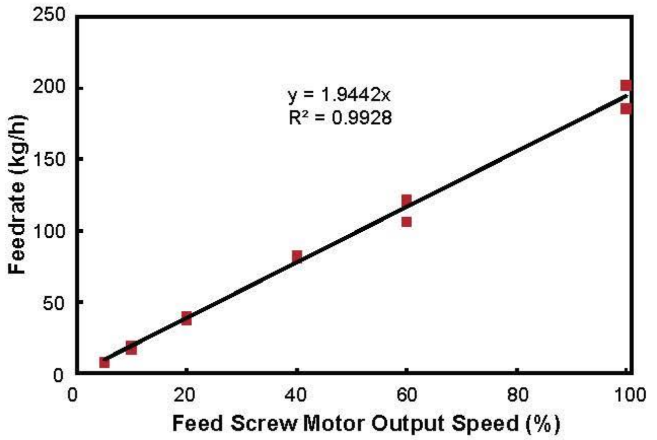

Figure 3: Biomass feeder calibration for 3 mm top-size loblolly pine sawdust. The dosing screw speed and primary feed screw speed can be adjusted independently, but the primary feed screw speed is always greater than the dosing screw speed. Motor speed is represented as a percentage of the maximum current delivered by the variable frequency drives.

Biomass Pyrolysis Section. Sized biomass at ambient temperature is fed horizontally into the side of the biomass/catalyst mixing zone (see Figure 2). Hot catalyst at 600–700 °C from the regenerator is recirculated through the regenerator catalyst transfer orifice into the biomass/catalyst mixing zone to provide the heat necessary to 1) raise the temperature of the biomass, vaporize its associated moisture, and heat the fluidizing nitrogen to the desired reaction temperature of 500–600 °C; 2) offset the endothermic heat demand for the biomass pyrolysis reactions; and 3) offset heat losses. The catalyst also assists in controlling the pyrolysis reactions. Fluidizing nitrogen is metered through bubble caps at the bottom of the mixing zone to maintain solids fluidization in the pyrolysis reactor.

The pyrolysis reactions primarily occur in the mixing zone and are completed as the gases and solids rise through the pyrolysis reactor. The pyrolysis reactor is externally heated with electrical heat tracing if necessary to overcome any heat losses. The system is designed to nominally operate at a pyrolysis reactor outlet temperature of 500 °C. The pyrolysis reactor temperature can be controlled by adjusting the following parameters: 1) catalyst-to-biomass ratio, 2) regenerator operating temperature, and 3) external reactor heat tracing.

As the pyrolysis reactions proceed, the biomass solids are converted to gases (hydrogen, CO, CO_2, methane, and ethane), bio-crude and water vapors, char, and ash. The fluidizing nitrogen and pyrolysis gases formed are sufficient to pneumatically transport the catalyst solids and residual char and ash up through the riser section of the pyrolysis reactor. The riser zone is designed to operate with a solids flow rate nominally at 7.32 m/s with a residence time of 0.35 seconds. During operation, the velocity and residence time in the riser can be adjusted by metering nitrogen into the pyrolysis reactor above the mixing zone. Additionally, nitrogen can be metered into the mixing zone during start-up and turn-down conditions. The gaseous pyrolysis products and transported solids from the riser are separated with a cyclone. The majority of the solids in the pyrolysis gas are removed in the reactor cyclone and pass through the solids transfer loop seal to be returned to the regenerator bed. The solids are maintained in a fluidized state by adding a small flow of nitrogen in the upstream and downstream legs of the loop seal. The particle-free pyrolysis gas from the reactor cyclone is then sent to a downstream liquid recovery quench system.

Quench System. The quench system is designed to use ambient-temperature water for direct contact cooling of the pyrolysis vapor products. Pyrolysis vapors are contacted with a co-current spray of water at 25 °C to cool the incoming vapors to about 100 °C. The partially cooled product vapors and gases enter a gas-liquid separator where most of the aqueous fraction is collected and any fine solids that are not separated by the reactor cyclone are trapped. The quench water and any bio-crude liquid products that are collected at the bottom of the gas-liquid separator vessel are drained into a storage tank. Any organic bio-crude in the liquid product is collected after it phase separates.

The quenched product vapors and gases pass through a coalescing filter downstream of the gas-liquid separator. The inlet gas temperature is maintained at 90–100 °C, and a heavy bio-crude fraction is collected at this point. The remaining product vapors and gases are then cooled to ~7 °C in a shell and tube heat exchanger with circulating chilled water in the shell. The condensed light products, including any remaining water, are collected with a second coalescing filter downstream of the heat exchanger. Finally, the product gas flows through a pressure control valve that is used to control the pressure in the pyrolysis reactor before it is directed into an electrically heated catalytic thermal oxidizer. A slip stream of the product gas is analyzed with an online gas chromatograph (GC).

Catalyst Regenerator. Compressed air is metered into the windbox at the bottom of the regenerator and passes through a number of bubble caps (air distribution nozzles). The compressed air maintains fluidization of the catalyst solids in the regenerator and serves as combustion air for oxidation of the char returned with the solids from the pyrolysis reactor and coke deposits on the catalyst. The combustion air can be preheated for more rapid and trouble-free start-up from cold conditions in addition to providing flexibility in regenerator temperature control. The depth of the fluidized bed provides 1) the hydrodynamic driving force for the catalyst recirculation to the pyrolysis reactor through the regenerator catalyst transfer orifice and 2) the gas residence time required for char and coke oxidation reactions in the fluid bed zone. The catalyst recirculation rate is directly controlled by adjusting the purge nitrogen upstream of the critical flow orifice and the differential pressure across the system.

The regenerator is initially charged with catalyst solids loaded into the catalyst make-up bin. The regenerator is designed to nominally operate at a fluid bed depth of 1.5 m. During operation, catalyst solids may be lost from the regenerator as catalyst fines become entrained in the flue gas and exit the regenerator. A decrease in catalyst solids inventory is measured as a decrease in the pressure drop between the freeboard and the lowest pressure tap in the regenerator (located 0.3 m above the constriction plate). Solids are replaced by periodically loading fresh catalyst from the make-up bin.

Recirculating catalyst solids and residual char and ash are fed into the regenerator bed from the reactor solids transfer loop seal. Char and coke combustion in the regenerator reheats the catalyst solids before they are recirculated back into the pyrolysis reactor. The regenerator is externally heated to maintain a constant wall temperature and overcome heat losses. The system is designed to nominally operate at a regenerator temperature of 600–700 °C. Control of the regenerator temperature can be achieved by adjusting the following parameters: 1) regenerator external heater power, 2) in-bed addition of fuel oil, 3) in-bed addition of water quench, 4) catalyst solids recirculating flow rate, and 5) preheating the combustion air.

The regenerator flue gas along with entrained catalyst fines and ash solids exit the top of the regenerator through a cyclone separator. The entrained solids are collected in a pot at the bottom of the cyclone dipleg, and the flue gas from the regenerator cyclone is sent to the flue gas cooler. Filtered water is sprayed into the flue gas cooler through a dual-fluid (air/water) nozzle that produces very fine droplet sizes over a varying range of water flow rates. The rate of water addition is controlled based on the desired temperature at the outlet of the flue gas cooler. Any remaining solids (fines or soot) entrained in the flue gas are filtered downstream of the flue gas cooler. The cooled, particle-free flue gas flow rate is controlled to maintain a constant differential pressure between the pyrolysis and regenerator sections. An online, continuous, nondispersive infrared analyzer is used to measure the CO_2 and CO concentrations in the flue gas before it is vented.

Results and Discussion

In a recent experimental campaign, over 500 kg of loblolly pine sawdust were fed in 15 h, with 10 h of steady-state operation. A commercially available spray dried, non-zeolitic, alumina-based catalyst has been identified as a promising catalyst with excellent deoxygenation activity for bio-crude production. The measured BET surface of the catalyst is 114.6 m^2/g. Catalyst acidity was evaluated by ammonia temperature programmed desorption. The quantity and strength of acid sites can be measured by the amount of ammonia that absorbs onto the surface of the catalyst as well as the temperature required to desorb it from the surface. Ammonia TPD was conducted by treating the catalyst with ammonia (10% NH_3 in He) at 30°C for two hours followed by ramping the sample to 700°C in helium. The peak desorption temperature was 200.2 °C and 400.75 µmoles/g of ammonia was adsorbed by the catalyst. The solid acid catalyst has a mean particle size of approximately 70 µm and was selected from a wide variety of materials because it has demonstrated suitable deoxygenation activity for producing a thermally stable, low-oxygen-content bio-crude and is available in large enough quantities for pilot plant testing.

System Start-Up

The pyrolysis unit requires 110–140 kg of fluidizable catalyst for a full charge. The catalyst is loaded in the catalyst make-up bin and added to the regenerator. Before the system is heated, ambient-temperature air is added to the regenerator to fluidize the catalyst. Fluidization is continued until the catalyst fines ejected from the regenerator are minimized based on the solids collected in the ash pot as a function of time.

The system is electrically heated at a rate of about 1 °C/min until the system temperatures (reactors, vessels, and piping) reach 300 °C. At this point, the nitrogen flow to the mixing zone and the air flow to the regenerator are increased, while the control valves on the pyrolysis and regeneration sides of the loop are controlled to initiate solids circulation. The control valves at the pyrolysis and regenerator outlets are then automatically controlled to maintain a constant total system pressure and differential pressure between the pyrolysis and regenerator sides of the loop, respectively. The total system pressure and differential pressure during start-up and catalytic biomass pyrolysis are plotted in Figure 4. System pressure is measured in psig and differential pressure is measured in inches of water column (in. H_2O). Pressure measurements have been converted to SI units in the figures for consistency.

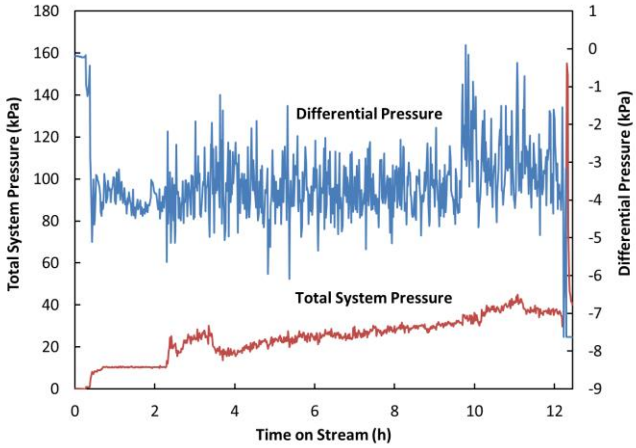

Figure 4: Total system pressure (psig) and differential pressure (kPa) between the pyrolysis and regenerator sides of the loop.

Once solids circulation has stabilized and the differential pressures across the system have equilibrated, the temperature of the system is increased by injecting diesel fuel into the bubbling catalyst bed in the regenerator. Figure 5 displays the temperatures measured in the mixing zone and in the regenerator as a function of time during system start-up and steady-state catalytic biomass pyrolysis. Diesel injection started at 0.33 h time on stream and continued for approximately 2 h. During that period, the system pressure was maintained at 10.3 kPa with the differential pressure controlled at 3 kPa. The rate of diesel injection is controlled to maintain a ~1 °C/min temperature increase in the system. Diesel injection continues until the temperature in the mixing zone reaches at least 525 °C.

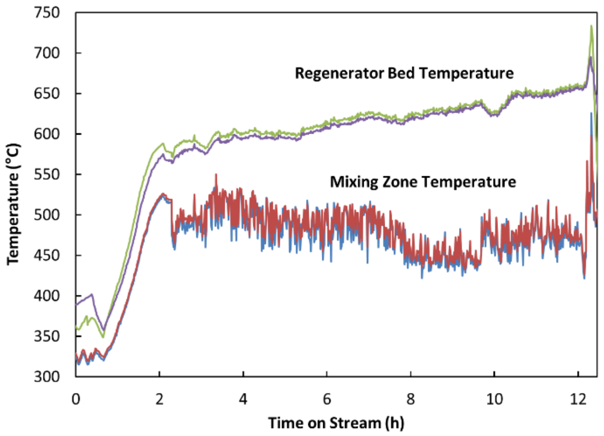

Figure 5: Biomass pyrolysis system temperatures during start-up and steady-state catalytic biomass pyrolysis.

When the mixing zone temperature reaches the desired biomass pyrolysis temperature, the diesel injection is terminated and biomass feeding is initiated. This occurs at 2.5 h time on stream in Figure 4 and Figure 5. As biomass is fed into the mixing zone, the mixing zone temperature decreases because of injection of cold biomass and the endothermic biomass pyrolysis process. Biomass char and spent catalyst are circulated through the system to the regenerator providing fuel for combustion to reheat and regenerate the catalyst.

As pyrolysis begins, the nitrogen flow rate is decreased to compensate for the product gases and vapors generated during biomass pyrolysis and maintains a constant velocity through the riser. The product gas flow rates measured at the outlet of the pyrolysis reactor and regenerator are plotted in Figure 6. The system pressure also increases as the pressure drop across the coalescing filters increases when the more viscous pyrolysis vapors and gases flow through the system. During catalytic biomass pyrolysis, the system pressure is controlled at 24 kPa, while the differential pressure control set point is not changed.

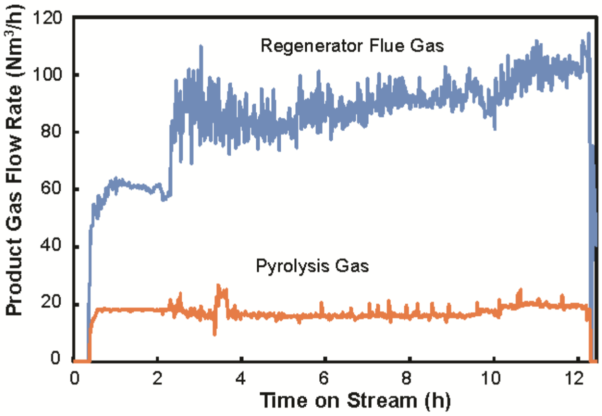

Figure 6: Product gas flow rates (Nm^3/h).

Continuous Catalytic Biomass Pyrolysis

Loblolly pine sawdust was continuously fed into the mixing zone at an average rate of 57.2 kg/h. Approximately 14 kg/h of nitrogen were added to the mixing zone to fluidize the hot, regenerated catalyst, and approximately 70 kg/h of air were added to the regenerator to oxidize char and coke in the bubbling fluidized bed. Nitrogen and air were also added to a number of purge taps throughout the system, but these flows make up less than 10% of the total flow in the system. Water and air were added to the regenerator off-gas cooler to quench the flue gas from the regenerator. Water was also added at a rate of approximately 49 L/h in the quench system to condense the bio-crude product.

In total, 508 kg of biomass were fed into the system and 42 kg of bio-crude were collected. The overall material balance, on a nitrogen-free basis, is shown in Table 2. The water was input through the quench system, and the oxygen input was from the air introduced into the regenerator. The organic product was collected from the coalescing filters and the aqueous liquid product was the effluent from the gas-liquid separator. The flow rate of the pyrolysis gases was continuously measured and the gas composition determined from the online GC. The flow rate of the regenerator off-gas is also continuously measured and the composition determined from an online gas analyser. Cha was collected from the standpipe of the regenerator cyclone.

Table 2: Overall Material Balance for Loblolly Pine Catalytic Pyrolysis. Inputs: Biomass (508 kg), Water (644 kg), and Oxygen from air (195 kg).

Organic Liquid Product (Bio-crude)	3%
Aqueous Liquid Product	62%
Pyrolysis Off-Gas	3%
Regeneration Off-Gas	23%
Char	2%
Total	*93%*

The carbon balance during the loblolly pine catalytic pyrolysis is shown in Table 3. Half of the carbon exits out of the regenerator as either solid char or CO and CO_2 from char combustion. The aqueous fraction also contains a significant amount of carbon. The missing carbon is likely uncollected bio-crude product that saturated the coalescing filters, light hydrocarbons that escape the collection system and are sent to the thermal oxidizer, and unaccounted for carbon dissolved in the aqueous fraction remaining in the system.

Table 3: Overall Carbon Balance for Loblolly Pine Catalytic Pyrolysis. Input biomass carbon is 226.8 kg.

Organic Liquid Product (Bio-crude)	10%
Aqueous Liquid Product	18%
Pyrolysis Off-Gas	7%
Regeneration Off-Gas	42%
Char	8%
Total	*85%*

The product gas measured at the outlet of the pyrolysis side of the system as a function of time on stream during biomass feeding is shown in Figure 7 on a dry, nitrogen-free basis. The primary gas-phase pyrolysis products are CO_2 and CO, as expected with lesser amounts of hydrogen, methane, and other hydrocarbons. The sum of C2-C5 hydrocarbons (ethane, ethylene, propane, propylene, butane, butenes, pentane, and pentenes) is combined into C_2+. The average pyrolysis gas composition on a nitrogen-free basis is presented in Table 4.

Table 4: Average Gas Phase Pyrolysis Product Composition (vol%, N_2 Free)

Product	Volume %, N_2 free
CO	23
CO_2	62
H_2	3
CH_4	6
C_2+	2

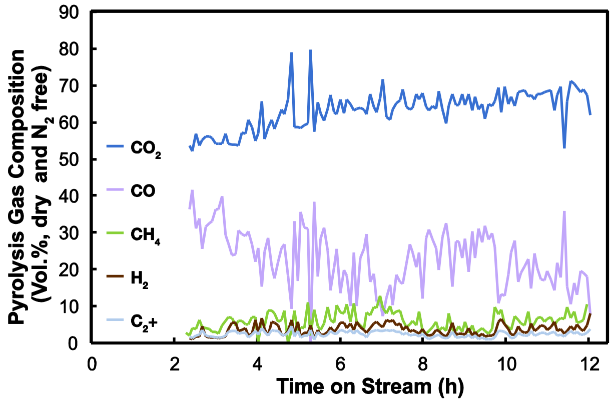

Figure 7: Pyrolysis product gas composition, volume % on a dry, nitrogen-free basis

As the system reaches equilibrium, the char concentration in the regenerator begins to increase. At first, all of the char is burned to provide process heat. An excess of char builds up in the regenerator as the rate of char accumulation becomes greater than the rate of char consumption. The char that is not consumed is entrained by the flue gas and collected in the standpipe of the regenerator cyclone. Figure 8 shows the solids collection rate as a function of time on stream. A sample of the total amount of solids collected at a given time is put in an oven and heated to combust any char or coke in the sample. The loss of weight after combustion is the percentage of char in the sample. The ash content of the loblolly pine is 0.6 wt%, so ash accumulation during this relatively short experiment is negligible.

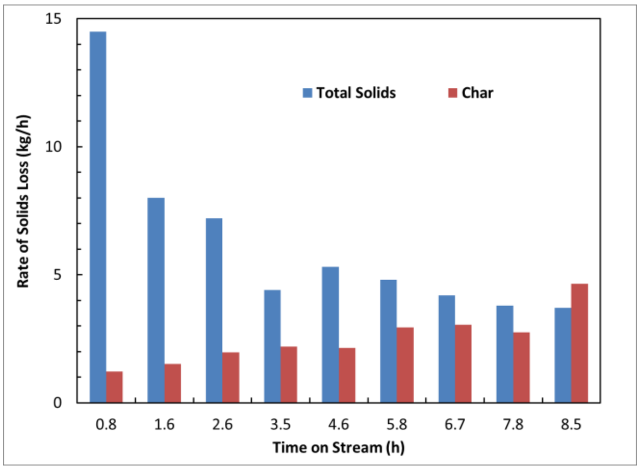

Figure 8: Distribution of catalyst fines and biomass char collected with the regenerator cyclone as a function of time during catalytic biomass pyrolysis. Char content is determined from the residual losses after the sample is heated in air to oxidize the carbon.

The first sample collected was almost entirely fine catalyst solids. Analysis of the particle sizes indicated that the material entrained out of the regenerator in the first sample was primarily smaller than 40 µm. The relative amount of catalyst fines collected during this trial decreased as the relative amount of char increased. The particle size distribution was measured for each of the solid samples collected after the char was burned off. These are presented in Figure 9 along with the particle size distributions for the fresh catalyst (dashed red line) and a sample of the catalyst remaining in the regenerator after the experiment was completed (black line). The first solid samples contained a high fraction of very fine material (less than 40 µm). As the catalyst fines were removed from the system, the mean particle size of the collected samples increased. Later samples also contained an increased number of very small particulate likely from the ash remaining after char combustion because these samples mainly contain char. The final bed material had a mean particle diameter of nearly 100 µm compared with 61 µm for the fresh catalyst.

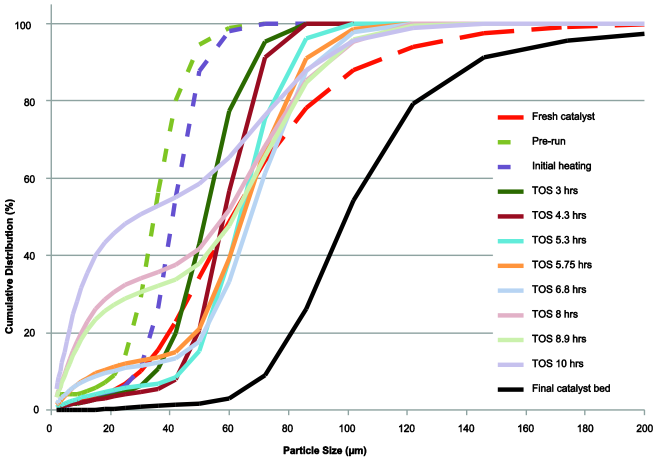

Figure 9: Particle size distribution of solids collected with the regenerator cyclone over time during catalytic biomass pyrolysis.

To be consistent with the literature[36, 42], the total liquid pyrolysis product yield determined from the material balance reported in Table 2 is 45 wt% of the input biomass feed. This includes 42 kg of organic bio-crude and 186 kg of aqueous phase liquid (total aqueous product less input water for quench).

The bio-crude sample is a combination of the organic liquids collected from the two coalescing filters. The aqueous fraction collected includes both the water of pyrolysis and water added for quench. The elemental analysis of the liquid samples, bio-crude and aqueous fraction, are shown in Table 5.

On a carbon basis, 28% of the input biomass carbon is recovered in the liquid product with 10% of the carbon recovered in the organic phase and 18% of the carbon lost to the aqueous phase. The continuous addition of water to the system through the quench section enhances the loss of the water soluble products to the aqueous phase. Consequently, the carbon loss to the aqueous fraction is much higher compared to the results from our laboratory scale reactor system and compared to other pilot scale results presented in the literature.[42] The overall carbon balance indicates that 15% of the input carbon is not accounted for and could easily be uncollected organic product or additional carbon lost to the aqueous phase.

From a process perspective, only the organic bio-crude product can be considered for upgrading and any carbon in the aqueous phase is lost. The overall yield of organic bio-crude fraction is 8 wt% of the total biomass fed into the system. This represents 14% of the energy recovered in the bio-crude compared to the input biomass feed (see equation 4 in reference 41). The bio-crude oxygen content was 24 wt% and, as expected, the sulfur and nitrogen contents of the bio-crude were quite low and reflected the low concentrations of sulfur and nitrogen in the starting pine material.

The overall bio-crude yield presented in this study appears to be 2-3 times lower than yields presented from other pilot scale catalytic biomass pyrolysis studies.[36, 42] However, this yield represents a cumulative average for the entire duration of biomass feeding and it takes several hours for the entire system to reach equilibrium. The pyrolysis gas production rate and composition equilibrate very quickly after biomass feeding is started. This is not the case with the liquid and solid production rates. As biomass is fed into the system, the water added for quench and the water produced from dehydration during pyrolysis become saturated with water-soluble organic hydrocarbons as the pyrolysis vapors pass through the system. The coalescing filters also saturate with bio-crude downstream of the gas-liquid separator. Consequently, very little bio-crude is collected during the first 2–3 h of operation. The bio-crude collection rate increases over time and during the last 2 h of the experimental campaign, approximately 17 L of bio-crude were collected, accounting for ~18 wt% of the material balance during that time period.

The chemical compositions of the bio-crude organic and aqueous fractions were determined using gas chromatography with mass spectrometric detection (GC/MS). An HP-5MS column (30 m x 0.25 mm, 0.25 µm film thickness) was used for the separation of the components. The National Institute of Standards and Technology (NIST) mass spectral library was used for the initial identification of the most abundant compounds. The identity of the major components were confirmed and the mass spectral responses were quantified using calibration standards prepared from mixtures of over 60 major compounds (purchased from Sigma-Aldrich). The analytical standards for the calibration were prepared in accordance to ASTM method D4307. For each compound, a linear calibration curve was established for concentrations of 1000, 2000, and 3000 µg/mL. The calibration curves had R^2 value greater than 0.97. Calibration curves were not generated for all compounds. For these compounds, the response factor of a closely related compound was used. For example, the response factor of 1-Hydroxy-2-propanone was used in estimating the amount of 1-Hydroxy-2-Butanone and likewise the response factor of 2(5H)-Furanone was used for 3-methyl-2(5H)-Furanone. The quantified compounds were then grouped into chemical classes based on their functionality as shown in Table 5.

Table 5: Loblolly Pine Liquid (Bio-crude and Aqueous Fraction) Elemental and Chemical Compositions

Elemental Composition	Bio-crude	Aqueous Fraction	Chemical Classification	GC/MS (wt%)		GC/MS (%, C)	
				Bio-crude	Aqueous Fraction	Bio-crude	Aqueous Fraction
C, wt%	61.5	5.1	*Aliphatic*	-	-	-	-
H, wt%	6.96	10.8	*Aldehyde/Ketone*	13.07	30.12	11.34	34.56
O, wt%	29	83.6	*Acid*	2.18	10.64	1.24	8.15
S, wt ppm	278	---	*Aromatic*	19.77	0.86	21.40	1.19
N, wt ppm	1,700	*4200*	*Sugars (Levoglucosan)*	11.40	-	7.23	-
H_2O, wt%	9.3	80.7	*Other oxygenates*	0.48	5.14	0.32	4.92
C, wt% (dry basis)	70	27	*Total*	46.90*	46.76**	41.54*	48.82**
H, wt% (dry basis)	7	10	* Represents 70.8% of the total ion chromatogram area.				
O, wt% (dry basis)	24	62	** Represents 60.1% of the total ion chromatogram area				

The results in Table 5 indicate that the loblolly pine bio-crude contained at least 20 wt% aromatic compounds (phenols, PAHs, and benzene derivatives) of which phenolics constituted the highest fraction (over 90%). The bio-crude also had reasonable amount of aldehydes, ketones and levoglucosan. The acid contents were lower compared with non-CFP bio-oil compositions.[10, 12] The water soluble compounds identified and quantified in the aqueous-phase were aldehydes (e.g., furfurals), ketones (e.g., hydroxy-2-propanone, and cyclopentanones) and acids (e.g., acetic acid). The concentration of phenolics and other aromatic compounds were very low in the aqueous fraction.

Overall, about 50 wt% of the components in both fractions were quantified; this represent 70.8% of the area under the total ion chromatogram (TIC) for the bio-crude and 60.1% of the area under the TIC for the aqueous fraction.

Based on the quantified GC/MS results, 41.5% of the carbon in the bio-crude and 48.8% of the carbon in the aqueous fraction was accounted. Considering that not all of the components in the TIC were quantified, it was estimated that 59% of the carbon in the bio-crude and 81% of the carbon in the aqueous fraction could be accounted for by GC/MS method. This suggests that the bio-crude contains higher molecular weight compounds or other non-volatiles components that cannot be measured by GC/MS.

Conclusions

A nominal 1 TPD catalytic biomass pyrolysis unit was designed based on the material balances and product compositions measured in a 2.54 cm diameter bubbling fluidized bed laboratory reactor system. The pilot plant is based on a single-loop transport reactor design with a nominal 45 kg/h biomass feedrate. The catalyst continuously circulates from the mixing zone, up the riser section, through a loop seal, and into the regenerator. The catalyst circulation rate is on the order of 450 kg/h at the target biomass feedrate such that the catalyst-to-biomass ratio is approximately 10:1. Catalytic biomass pyrolysis temperatures in the mixing zone are between 450 and 600 °C, and the catalyst is regenerated with air below 700 °C. Typical residence time in the pyrolysis zone is approximately 0.75 sec.

The pilot unit has been successfully operated to produce a low-oxygen content bio-crude intermediate compared to non-catalytic fast pyrolysis. Product yields and quality in the pilot plant are consistent with results obtained in a laboratory-scale 2.54 cm diameter bubbling fluidized bed reactor. The collection efficiency of the quench system has been improved by separately collecting heavy and light bio-crude fractions in two coalescing filters separated by a heat exchanger but carbon loss to the aqueous phase is excessive due to the large quantity of water added to the system for quenching the vapour phase products. The overall mass balance was 93%, while the carbon closure was 85%. Most of the excess carbon was likely uncollected bio-crude product that saturated the coalescing filters and unaccounted for carbon dissolved in the aqueous fraction remaining in the system. The combined bio-crude product had 24 wt% oxygen on a dry basis. The bio-crude contained aromatic hydrocarbons that were predominantly phenolic. Future work will focus on improving carbon closure and extending the continuous, steady-state operation of the system. Improving the collection efficiency of the quench system by optimizing temperatures and minimizing water input to reduce losses to the aqueous phase are other strategies for increasing bio-crude yield. Process conditions (temperature, residence time, and catalyst circulation rate) will be optimized to increase the carbon efficiency of the bio-crude product by enhancing deoxygenation while reducing char formation.

A key objective is to produce large enough volumes of bio-crude for validating upgrading technology being developed for advanced biofuel production. The effect of bio-crude properties on the upgrading process can be evaluated in the future for bio-crude samples produced at different process conditions, with different catalysts, and with different feedstocks.

Acknowledgments

The authors would like to acknowledge the financial support from the U.S. Department of Energy, Advanced Research Projects Agency–Energy (DOE/ARPA-E) under contract DE-AR000021 (Catalytic Bio-crude Production in a Novel, Short Residence Time Reactor) and the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies Office under contract EE-0005358 (Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons). The authors would also like to acknowledge the analytical support of Mr. Ernest Johnson for providing sample analyses and the technical contributions of Dr. Kaige Wang in reviewing this manuscript.

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Pilot-scale catalytic biomass pyrolysis unit for producing low oxygen content, thermally stable bio-crude for upgrading into advanced biofuels.