

Production of Primary Pyrolysis Oils in a Vortex Reactor

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ABSTRACT

A vortex tube has certain advantages as a chemical reactor, especially if the reactions are endothermic, the reaction pathways are temperature dependent, and the products are temperature sensitive. With low temperature differences, the vortex reactor can transmit enormous heat fluxes to a process stream containing entrained solids. This reactor has nearly plug flow and is ideally suited for the production of pyrolysis oils from biomass at low pressures and residence times to produce about 10 wt % char, 13% water, 7% gas, and 70% oxygenated primary oil vapors based on mass balances. This product distribution was verified by carbon, hydrogen, and oxygen elemental balances. The oil production appears to form by fragmenting all of the major constituents of the biomass.

INTRODUCTION

The pyrolysis of biomass follows a complex set of different chemical pathways, which have thus far not been well established. However, several global pathways have been established, which explain most of the observed phenomena. As shown in Figure 1, the first reaction in fast pyrolysis of biomass is the depolymerization of the lignocellulose macropolymers to form viscous primary oil precursors. These precursors are formed with almost no by-products, and consequently their elemental composition is very similar to the original biomass. With low heating rates, much of the primary oil precursors can repolymerize to thermally stable polymers through the elimination of mostly water to eventually form the material known as char. Physical evidence for a liquid or plastic phase intermediate in the formation of char is the physical shrinkage of the macrodimensions of wood, which takes place during charring (1) in a manner analogous to heat shrinkable polyethylene tubing. If the heating of the biomass proceeds very quickly to temperatures above 450°C, most of the primary oil precursors can crack and vaporize before they form char. In the vapor state, the primary oil molecules are quite dilute, which slows possible second-order polymerization reactions. This dilution allows any unstable primary oil vapors to be converted by first-order reactions to more stable compounds, which can be collected from a reactor designed to have a short gaseous residence time followed by rapid quenching. Thermal stability is relative, however, and these stabilized primary oil vapors readily crack to gases following a global first-order reaction (2). The cracking of the primary oil vapors proceeds with a 10% loss in 36 ms at 700°C and extrapolated 10% losses in 6 ms at 900°C and 591 ms at 500°C.

Obviously, the lower the temperature of the primary vapors in the reactor, the greater the yield of primary vapors which can survive passing through the reactor to the quench zone. Minimizing the time required to travel from the vapor formation zone in the reactor to a lower temperature quench zone also helps to maximize the primary oil vapor yields. The ideal reactor would thus provide large heat fluxes preferentially to the pyrolyzing biomass particle, while not overheating the surface of the particle to cause cracking of the primary vapors to gases as the vapors escape the surface of the particle. The ideal reactor would allow the vapors to be immediately swept away by a colder carrier gas stream out of the reactor to a cold quench zone in order to preserve as much of the vapors as possible. The residence

time of the biomass particles in the ideal reactor must be long enough to ensure complete pyrolysis, but the accumulation of dead char in the reactor is undesirable. It would also be advantageous if the reactor could selectively remove dead char and recycle partially pyrolyzed particles.

The use of thermal radiation for fast pyrolysis has been explored, as this approach preferentially heats the solid with potentially high heat fluxes. However, heating the particle with a high temperature heat source can drive the surface temperature of the particle too high and some vapor cracking would be expected. The use of hot flue gases or hot solids as a heat transfer medium requires that they be at very high temperatures to lessen the amount of the medium which must be generated or recycled; flue gases or hot sand at 900° to 1000°C have been used for fast pyrolysis, but tend to produce higher yields of noncondensable gases from cracking the primary pyrolysis oil vapors to gases as described above. The ideal reactor for the pyrolysis of biomass to primary oils would achieve high heat transfer rates through the use of a mechanism which has an inherently high heat-transfer coefficient, rather than through the use of a high-temperature source. Such a heat transfer mechanism is attained by the conduction of heat from a moderately hot reactor wall directly to the biomass particle.

It can be readily demonstrated that when a stainless steel wire at 500° to 900°C is contacted with a monolithic piece of biomass, the biomass surface is ablatively pyrolyzed and converted to a liquid which allows passage of the wire and to vapors which condense to form smoke. If the stored energy in the wire is transferred to the biomass by sliding the wire across the biomass, pyrolysis rates over 3 cm/sec are observed (3). This method of heat transfer has been studied by pushing a wooden rod into a heated, stainless steel disk, and the pyrolysis rate has been found to be proportional to the pressure exerted and to the temperature difference, where the biomass surface was calculated to be pyrolyzing at 466°C. Heat transfer coefficients as high as 8 W/cm² were reported, which is over 300 times higher than for thermal radiation from a wall at 900°C having an emissivity of one (4).

Although a reactor can be designed to push wooden rods into a hot surface for research purposes (4, 5), most practical biomass feedstocks are expected to be in the form of sawdust or chips. A modified entrained-bed reactor was selected in which the entrained particles enter the reactor tangentially so that centrifugal forces push the feedstock particles onto the externally heated cylindrical wall. Drag forces induced on the particle by the entraining gas stream serve to keep the particles moving on the wall. Since the particles are on or very nearly on the wall, they tend to intercept preferentially the heat, which is conducted through the reactor wall. With nonreacting solid particles in a heat exchanger made from a cyclone separator, the total heat transferred to the process stream was relatively independent of the solids' content at carrier-to-solids (C/S) mass ratios as low as one, whereas with more solids, the heat transferred increased dramatically. The temperature rise in the gas stream was as little as half of that seen in the solids at these low C/S ratios. The heat transfer coefficient from the wall to a solids-free gas was found to follow traditional convective heat transfer relationships, but to be 1.8 times higher in the cyclone than in a straight tube for the same entering tube diameter and entering gas velocities (6). A reported property of a cyclone is that above an entering Reynold's number of 3000, the cyclone has plug flow (7). The cyclone is an interesting reactor concept for the pyrolysis of biomass, as reported in the literature (7, 8). However, the reactor of interest in this paper is a vortex tube, which has many similarities to a cyclone separator.

Vortex tubes have a tangential entrance into one end of a cylindrical tube and an exit at the other end of the tube. If a second exit is added near the tangential

entrance, but in an axial location, a Ranque-Hilsch tube is created which can be fed warm gas in the tangential entrance and produce cold gas coming out of the near axial exit and hot gas out of the far exit. The vortex tube is commercially used for reliable refrigeration where the cost of the compressed gas is of no concern. Research into the aerodynamics of the vortex tube revealed that in the Ranque-Hilsch tube there was an outer vortex which exited the hot end and an inner vortex which exited the cold end. If the cold end was not open, the vortex tube was reported to have a third concentric vortex, which flowed toward the hot end (9). The pitch of the vortex near the cylindrical wall was reported to be about 1.2 times the diameter of the vortex tube. This results in a coarse helical path of the gases near the wall, as measured by pitot tubes (9, 10). This coarse helical path on the wall also exists for the more conventional cyclone separator (11). The effect of the coarse path is that entrained solids, which are centrifuged to the wall, follow the same coarse path through the reactor. This has two deleterious effects: only a narrow path of the cylindrical wall would be used for heat transfer; and the residence time of the solid particles is only a fraction of what it would be with a tighter helical path.

The vortex tube reactor which we developed is shown in Figure 2 and has some unique features, which were found necessary to achieve the desired reactor performance in the fast pyrolysis of biomass. The carrier gas is pressurized to between 75 and 150 psia, depending upon the desired flow rate, and passes through a supersonic nozzle. Biomass in the form of minus 3-mm sawdust is metered into, and is entrained by, the supersonic carrier gas stream. Cold-flow studies with 4000-frames-per-second movie coverage established that this entrainment method results in rapid acceleration of the sawdust particles to velocities over 125 m/s. The cold-flow studies also verified that the entrained particles were following the reported coarse path of the gas flow near the wall. This coarse helical path appeared to be independent of the entrance angle, the entrance duct shape, and the flow rate of the carrier gas (12). The pitch angle of the solids flow in the conical section of a conventional cyclone was observed to be about one-fifth that in the cylindrical section (11), but the cylindrical vortex tube has more heat-transfer surface area per unit length. To force the entrained particles into a tight helical path, the 316 SS cylindrical vortex tube wall was machined to leave a 3-mm high and 3-mm wide raised helical rib. High-speed movies taken of the cold-flow system verified that the raised rib forced the solids to take the desired tight helical path (13). A tracer gas experiment, following the progress of propane pyrolysis, verified that this reactor design was essentially plug flow, with the inner vortices contributing a very small amount of internal recycling (14).

Initial operation with this vortex tube as a reactor for the fast pyrolysis of biomass was with heating the reactor wall to relatively high temperatures of 800°C or so. At that time, the goal was to crack the primary vapors to gases, rather than the preservation of the primary oils. Under these conditions, the sawdust had ample time to pyrolyze, as well as the char having time to partially gasify to produce char yields of only about 5%. However, as the vortex reactor wall became hotter, the tendency increased to accumulate a layer of secondary tar and char on the wall. By reducing the wall temperature to 625°C, the buildup of an insulating char-tar layer became negligible, but the rate of pyrolysis of the sawdust particles was so low that about 30% of the feed could be recovered in the char cyclone as scorched feed. A tangential exit was then added to the vortex tube reactor to allow the unreacted feed and large char particles to be recycled to the entrance of the reactor. The carrier gas nozzle acts as an ejector to create the pressure differential to drive the recycle loop. The recycle stream blows the sawdust off the feeder screws to positively entrain the feed to the carrier gas ejector.

The temperature at the exit of the insulated, but unheated, recycle loop is typically 400° to 450°C. The carrier gas is preheated to between 600° and 700°C prior to expansion through the ejector nozzle. With these conditions, the temperature of the pyrolysis stream is 480° to 520°C, as it exits the vortex reactor system. About 10% of the feed is converted to char, which is recycled with the scorched feed until it is attrited to less than 50 micrometers in size. The vortex reactor system acts as a particle size classifier, and the char fines are entrained out of the vortex system to be removed by a cyclone separator having a higher collection efficiency. The fine char has a volatile content of 15% to 20% and burns readily, especially when hot. The bulk density of the fine char is between 0.18 and 0.24 g/mL, depending upon whether it was freshly poured or has been allowed to settle (the bulk density of the sawdust feedstock was 0.24 g/mL). The empirical formula for this volatile char is $\text{CH}_{0.53}\text{O}_{0.12}$, and it has a heating value (HHV) of 33 kJ/g (14,000 Btu/lb). A microscopic examination of the char fines shows that the particles have the appearance of broken thin-walled tubes; i.e., charred and broken cell walls.

As noted above, the primary vapors are cracking significantly even at 500°C and a residence time of half a second. If the recycle loop of the vortex reactor is removed, the yield of permanent gases is about 3%, based on the reacted feed. The initial gases, which are formed under these conditions, are extraordinarily rich in carbon dioxide and are associated with the formation of char. With the recycle loop open, some of the primary pyrolysis vapors are recycled along with the carrier gas, unreacted solids, and large char. The additional time, which the recycled primary vapors spend in the vortex reactor leads to a small loss in the yield of primary vapors and a higher yield of noncondensable gases of about 7%. The composition of the gases shifts considerably from the initial gases formed to that associated with a small loss of primary vapors. An even greater shift in the gas composition occurs with more extensive cracking of the primary vapors to produce an asymptotic gas composition as the primary vapors near extinction, which is low in carbon dioxide, as shown in Table 1.

The experimental determination of the feed consumed, the char yield, and the noncondensable gas yields are relatively straightforward. However, the primary vapor and water yields have proven difficult to measure directly due to the formation of aerosols. These aerosols escape high-pressure sprays, cyclonic separators, and impingement or inertial collection techniques. The use of condensable steam as the carrier gas makes the water yield very sensitive to small measurement errors in the steam carrier gas flow. The use of noncondensable gases as the carrier tends to strip the volatile organics and the water of pyrolysis from the condensate. These considerations have led to the use of a noncondensable carrier gas, nitrogen, and to the determination of the water formed during pyrolysis and the primary oil yield by difference. By analyzing the recovered condensate for water, the yield of water may be determined. These techniques led to the conclusion that yields of about 70% primary vapors were achieved, based on taking the difference between the sawdust fed and the measured gas flow and char collected, correcting for the water content of the condensates. After elemental compositions were obtained for the feed and the collected products, an elemental balance was computed which verified the high primary vapor yields of 69 to 77 wt %, as shown in Table 2, based on the yield of recovered char (2).

The primary pyrolysis oils, which have been recovered from the vortex reactor, are highly oxygenated and have nearly the same elemental composition as the biomass feedstock. The oils have a dark brown color and are acidic with a pH between two and three. The heating value (HHV) of the dry oils is 20 to 22 kJ/g (8700 to 9500 Btu/lb). The oils can absorb up to about 25% water before forming two

phases. The viscosity of the oils was 1300 cp at 30°C, and the density was 1.3 g/mL (15). Although the primary vapors have a low molecular weight as determined by the FJMBMS (16), they rapidly polymerize upon physical condensation to form high-molecular-weight compounds in the oils (17). Attempts to slowly distill the oils led to the rapid polymerization of the oils boiling above 100°C (15). The oils have significant chemical activity, which suggests their potential use in low-cost adhesives, coatings, and plastics.

The concept of supplying heat through the wall of a vortex reactor to drive endothermic processes is in its early development. The scale-up potential of this concept depends upon the angular momentum of the swirling carrier gases to keep the entrained feed particles moving on the wall. The heat flux delivered to tubular pyrolysis reactors typically ranges between 5 and 15 W/cm² (20,000 to 50,000 Btu/hr-ft²). Reported data for vortex tubes indicates that with diameters larger than 2.5 cm most of the angular momentum is retained even after traveling a tube length equivalent to 20 tube diameters. The major momentum losses are due to the frictional contact of the solids and the gases with the vortex-tube wall. With larger vortex tubes needed for scale-up, the angular momentum of the process stream will increase more than the frictional losses. The heat transferred to the reactor will scale by the product of the diameter AND the length. These considerations have led to calculations which suggest that a vortex reactor with a 250 TPD capacity would have a diameter of only about 0.5 m and a length of 9 to 12 m. The fabrication technique would most likely be by the welding up of a spirally wrapped tube to form the raised, helical rib.

CONCLUSIONS

For the fast pyrolysis of biomass, a vortex reactor has significant advantages for the production of primary pyrolysis vapors, including: high heat transfer coefficients which allow the use of moderately low temperatures of the vortex reactor walls to supply the endothermic heat of pyrolysis; separation of the partially pyrolyzed feed particles from the char; the ability to recycle the partially pyrolyzed feed; the ability to accept a wide spectrum of particle sizes in the feed; short gaseous residence times; nearly plug flow; and preferential heating of the solid feed over the vapor stream, to preserve the primary vapors. Primary pyrolysis vapor yields in the 70% range have been calculated by mass balances and verified by elemental balances, although physical collection of these vapors has proven to be elusive due to the formation of persistent aerosols and due to the volatility of the vapors in the carrier gas (methods to recover these vapors more completely with practical means are under development).

ACKNOWLEDGEMENTS

The financial support for the development of the vortex reactor and the catalytic conversion of the primary vapors to high-octane gasoline has been provided by the Biofuels and Municipal Waste Technology Division of DOE (FTP 646) with Mr. Simon Friedrich as the DOE program manager and Dr. Don J. Stevens of PNL as the technical monitor. The physical recovery of the primary oils for use as chemicals and adhesives is being developed through the financial support of the Office of Industrial Programs of DOE with Mr. Al Schroeder as the DOE program manager (FTP 587).

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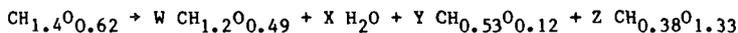
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Table 1. Pyrolysis Gas Composition at Various Cracking Severities (mol %)

	Vortex Exit Gases w/o Recycle (Run 34)	Vortex Exit Gases w/Recycle (Run 58)	Severely Cracked Vapor Gases (Run 58)
H ₂	3.4	8.3	17.8
CO	46.2	49.2	52.2
CO ₂	43.1	27.6	7.5
CH ₄	4.6	8.9	12.0
C ₂ H ₂	--	0.1	1.1
C ₂ H ₄	1.3	2.4	5.9
C ₂ H ₆	0.3	0.7	0.6
C ₃ H ₈	0.1	0.1	--
C ₃ H ₆	0.4	0.8	0.8
C ₄ H ₈	0.3	0.3	0.6
C ₅ +	0.5	1.4	1.4
wt % yield of gases	~4	~6	65%

Table 2. Elemental Balance for Fast Pyrolysis to Primary Vapors

Feed → Primary Vapors + Water + Char + Gas



Exp. Char Yield	Calculated Product Values, Wt %		
	Primary Vapors	Water	Prompt Gas
7.5	76.8	11.7	4.0
10.5	73.1	12.8	4.1
12.7	69.0	14.0	4.3

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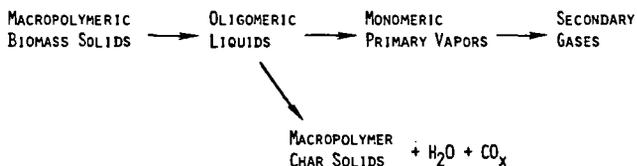


FIGURE 1. GLOBAL REACTIONS IN FAST PYROLYSIS

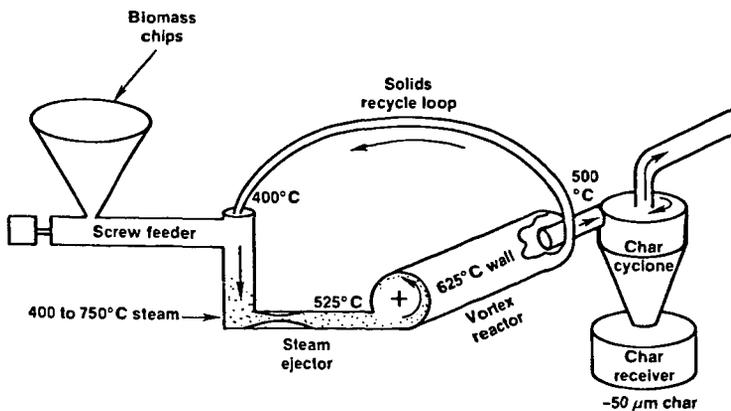


FIGURE 2. VORTEX REACTOR SCHEMATIC