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# Ablative Fast Pyrolysis of Biomass in the Entrained-Flow Cyclonic Reactor at SERI

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any biomass which is located more than a calculated 15 μm from the pyrolyzing surface is still at the low initial temperature and is unaffected by the ablative pyrolysis taking place. Consequently, this charless, ablative pyrolysis will proceed in a similar manner whether the biomass is a 1-cm chip or a fine, 50-μm powder [4]. Because the pyrolysis front moves so quickly through the biomass, the temperature gradient is very steep with a calculated heating rate of about 500,000°C/s [5].

The ability to use wood chips rather than a fine powder or dust as feedstock, improves the overall process with respect to an estimated 10 to 15% process energy reduction, less equipment to amortize, and enhanced safety by eliminating dust explosion hazards in storage bins, transfer lines, etc. The pyrolysis reactor concepts, which we are developing, involve a very high throughput reactor in which entrained biomass particles at high velocities enter tangentially into a cyclone or vortex tube as shown in Fig. 1. The vortex tube wall is externally heated so that pyrolysis takes place as the biomass slides and bounces along on the inside surface. This intimate contact and relative motion of the hot wall and the biomass particles is analogous to the hot-wire pyrolysis mentioned above. The vortex section of the reactor is followed by a long tubular vapor cracking section to maximize gas formation. Detailed descriptions of the experimental hardware are given in references 6 and 7.

## PROGRESS

### Solids Feeding

The smooth, even feeding of the biomass particles into the pyrolysis reactor system is quite critical to successful operation. This is particularly true with this ablative pyrolysis system because there is virtually no hold-up of solids in the reactor as there is with updraft or downdraft gasifiers which have a large bed of biomass particles at all times. Variations in solids' feeding rate result in pressure and gas flow fluctuations which make precise measurements of variables difficult and subject to error. Because our sophisticated solids

depending upon the reactor conditions selected. The products can be almost entirely gaseous and contain a significant amount of very desirable unsaturated hydrocarbons such as ethylene and propylene. The chemistry of these unsaturated hydrocarbons is very well known and is the basis for a large part of the existing petrochemical industry. In the past they have been used by the petroleum industry to make gasoline and by the petrochemical industry to make alcohols, plastics, etc.

Historically, the energy and chemical industries have used the most economical feedstock available, which was wood or cellulose until the fossil fuel age arrived. With the advent of cheap petroleum and natural gas, the industry became based on low-molecular-weight compounds, such as ethylene, for use as starting materials to make rubber, plastics, alcohols, and liquid fuels. Although the highest yields of ethylene may be made from ethane, the increase in cost and the decrease in availability of ethane has gradually shifted the industry toward using less desirable feedstocks, even though the yields may be lower and the processing more difficult. The use of biomass as a source of ethylene via a rapid thermal reaction would have considerable merit especially in areas without assured access to petroleum sources.

The conversion of biomass to ethylene via fast pyrolysis has been demonstrated by several isolated researchers at scales ranging from a few milligrams in batch experiments to continuous flow, bench-scale experimentation at nominal flow rates of 5 kg/h. In addition to the fundamental pyrolysis studies by Milne and Soltys [1], DOE's Biomass Energy Systems Branch has sponsored a fast pyrolysis program at SERI having three areas of effort: laboratory-scale pyrolysis of a few milligrams of material from monolithic pieces of biomass to determine optimal heat transfer mechanisms; the bringing together of the several isolated fast pyrolysis researchers to compare methods, results, and conclusions as to the fast pyrolysis phenomenon [2]; and the scaling-up of the fast pyrolysis of biomass to an engineering research scale to pave the way for a pilot plant demonstration using practical, non-



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exotic heat transfer techniques and biomass feedstocks larger than fine powders. Efforts since our last meeting have been concerned with the engineering research phase.

## BACKGROUND

As was reported and demonstrated at the 11th Biomass Thermoconversion Contractors' Meeting [3], the laboratory-scale heat transfer experiments have shown that when biomass is moved relatively to a red-hot Nichrome wire, the wire will cut through the biomass. The rate of cutting, or pyrolysis, can be as high as 3 cm/s when it is a very localized surface phenomenon. With this method of heat transfer, pyrolysis appears to proceed by the depolymerization, melting, and vaporization of the biomass without observable char formation; the term "ablative" seems to best describe this fast pyrolysis mechanism.

The rate of heat transfer from the red-hot metal surface to the biomass is extraordinarily high. Based on an assumed energy of pyrolysis of 2000 J/g, the 0.025-cm diameter wire moving across the biomass at 20 cm/s and penetrating at a rate of 3 cm/s was transferring 3500 $W/cm^2$, which is very impressive compared to the mere 15 $W/cm^2$ radiated by a black body reactor wall at 1000°C. Thus, this solid convective approach to heat transfer for pyrolysis transfers energy to the biomass at rates over two orders of magnitude greater than black body radiation at similar wall temperatures. This would imply that a pyrolysis reactor relying on solid convective heat transfer could have over 100 times the throughput of a similarly sized reactor relying only on radiative heat transfer.

The mechanism of this solid convective heat transfer appears to be the conduction of heat across a very thin film (thought to be about 10 μm thick) from a nearly isothermal metal surface at 1000°C, while the biomass depolymerizes at about 300 to 400°C to primary tars which are wiped away and/or vaporized. Since heat conduction is proportional to this large temperature difference divided by the very thin film thickness, very high heat fluxes are predicted. Because the surface regression rate is nearly the same as the thermal penetration rate,

any biomass which is located more than a calculated 15 μm from the pyrolyzing surface is still at the low initial temperature and is unaffected by the ablative pyrolysis taking place. Consequently, this charless, ablative pyrolysis will proceed in a similar manner whether the biomass is a 1-cm chip or a fine, 50-μm powder [4]. Because the pyrolysis front moves so quickly through the biomass, the temperature gradient is very steep with a calculated heating rate of about 500,000°C/s [5].

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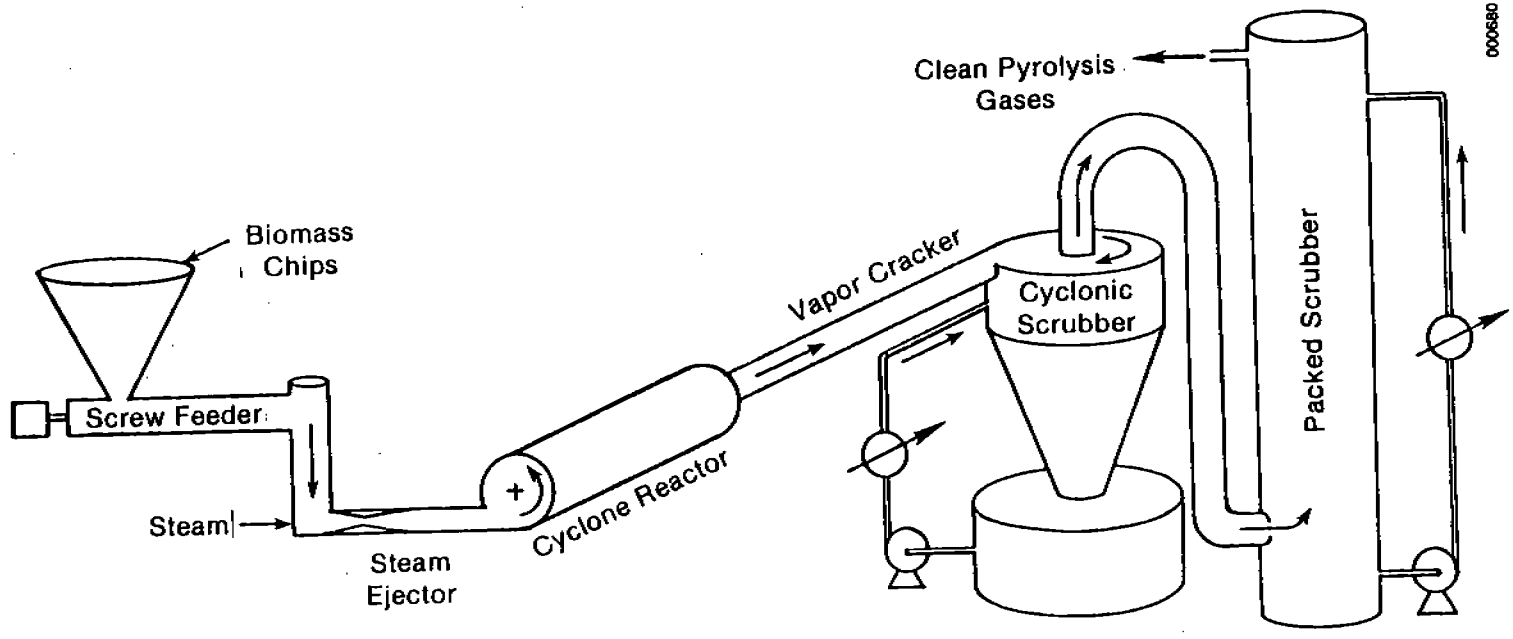



Figure 1. Original Entrained-Flow, Ablative-Pyrolysis Reactor Schematic

feeder was not delivering the desirable constant mass flow rate, a major effort was successfully spent on the feeder subsystem. The feeder can be either operated with constant screw speed (volumetric mode) or with an electronically-controlled screw speed designed to deliver a constant mass flow rate (mass mode).

Inside the feed hopper are two bladders whose purpose is to periodically compress the feed to collapse any bridging or rat-holing of the feed. These bladders were supposed to have been made of a material capable of operation at 250°F (121°C) or higher. However, the bladder material had become embrittled and failed during operation. The factory (K-Tron) was contacted and two more bladders were sent on warranty which were to be capable of the high temperature operation. The new bladders are made of a silicone impregnated fiber-glass cloth and should be able to withstand the elevated temperatures (~125°C) for extended time periods without degradation.

While we were waiting for the delivery of the new bladder materials, a pneumatically-driven vibrator was added to the feed hopper to determine if this would allow interim operation of the system. Extensive testing with the new bladders revealed that even when used with the air-driven vibrator, the -80 mesh pine flour was not free flowing and was still able to bridge and/or "rat-hole" in the hopper.

To increase the displacement of the feed in the hopper and collapse the bridged feed, hinged plywood sheets were installed on top of the bladders. It was found that by alternating the inflation of the bladders during vibration that the bridging tendencies could be minimized. Unfortunately, the movement of the feed by the bladder system caused the electronic system to generate false weight data, which in turn confused the electronics controlling the mass flow rate. It was therefore necessary during the bladder actuation to electrically switch the feeder controller to the volumetric mode (constant screw speed) to avoid the false weight data being used to erroneously adjust the screw speed in the mass mode. The controller was automatically switched back to the mass mode by the same timer that turned the bladder solenoids on and off.

Even with these improvements, the feeder controller in the mass mode did not provide a significantly smoother mass flow than just a constant screw speed, as exemplified by a series of one minute grab samples. In addition, during pyrolysis system operation, it was observed that when the bladders were inflated, the gas flow in the system drastically increased to result in a system upset. This was originally thought to be due to leaky bladders. However, after the bladders were replaced, it became apparent that when the bladders were inflated in the closed hopper, an equal volume of the steam/nitrogen atmosphere in the hopper would be displaced into the pyrolysis system. Much of this gas was observed to blow through the screw augers in spite of a pressure equalizing tube. A similar volume of gas would then be sucked back into the hopper during the deflation of the bladders. This unexpected flow of gases tended to blow the fine flour along with it. This flow or flooding of the screws would tend to dump a significant amount of extra feed into the pyrolysis system. With the electronics in mass mode, this flooding weight loss would cause the screws to slow down to try to maintain the mass-flow set point. However, after the slug of feed had pyrolyzed, the system pressure would increase and cause a back flow into the hopper which would keep the feed cleaned off of the screws. This gas flow back and forth through the screws is apparently responsible for the large variations in product gas flow rate through the system in spite of a 1.9-cm-diam. by-pass hose originally installed to prevent such a gas flow. This action of the bladders was clearly unacceptable to the goal of smooth continuous operation of the system.

During the course of feeder calibrations, it was recognized that the vibrator alone would not eliminate bridging and that the feeder controller was responding very sluggishly to changes in the feed bulk density. This sluggishness resulted in the feeder delivering a feed rate with an error band of about ± 7% in the absence of bridging. This feed rate error band is sufficient to result in system upsets during operation and is therefore undesirable. Since the feeder specifications call for an error band of less than ±1%, different adjust-

ments to the electronics in the controller were evaluated. When the adjustments failed to reduce the error band to less than ±1%, the factory was contacted. After several additional tests, it was concluded that the controller was defective.

The manufacturer of the solids feeder was supportive of our efforts to fine tune the feeder. On the possibility that our controller was faulty, they shipped us an identical controller on loan. However, the new controller did not perform any better than our original controller and, in fact, appeared to control the mass flow rate less precisely. A factory trained technician was in the Denver area on another job and was able to spend several hours going over our system. He concluded that the electronics were alive and well, but that our feed was not filling the screws uniformly. He managed to take a series of catch samples which showed that ±2 standard deviations was within the specified ±1/2% of the "range". Unfortunately, this method of specification allows deviations from the mean which can allow operational upsets and which make data gathering less precise than desired. This indicated that work was needed to determine how to smooth the delivered solids flow rate, especially during total system operation.

The problem of uniformly feeding sawdust and wood flour was identified as having two different mechanisms, both of which resulted in gas flow instability in the system. Due to the low pressure drop across the gas clean-up systems, there was virtually no effective damping action in spite of the relatively large volume. The damping ability of the gas clean-up system was greatly improved by restricting the gas flow with an orifice plate at the outlet of the new char cyclone (to be discussed later) and with valves at the outlets of the cyclone scrubber and the packed scrubber. This increased the pressure drop, but allowed the three gas clean-up subsystems to act as gas accumulators to smooth out variations in gas flow from the pyrolysis reactors due to variations in solids feeding rate. The other source of problems was the temporary, incomplete filling of the screw augers, which would result in a drop in mass flow through the system and a

drop in the system gas pressure. As the system pressure dropped, the gaseous atmosphere in the feed hopper would be sucked through the screws which would blow an excess of feed off the screws. This would cause a momentary rise in system pressure and a consequent reverse gas flow past the screws preventing the feed from entering the screws.

The reproducible feeding of solid materials, is an art in which the designer attempts to fill some sort of an augering device with solids having a uniform bulk density. With a constant auger speed, this results in the very difficult-to-attain constant mass flow rate. To achieve a uniform bulk density, the state-of-the-art practice is to mechanically agitate or fluidize the solids immediately above the augering screw. These fluidized solids have some properties similar to compressible real fluids, e.g., the apparent density is a function of fluid depth. To achieve a uniform bulk density, the height of fluidized material above the augers should be kept constant and the sudden addition of large chunks of non-fluidized (high density) feed should be avoided. (These large, high density chunks are thought to immediately sink to the augers without proper fluidization and result in a momentary high mass-flow rate.)

Unfortunately, the mechanical fluidization of the solids requires a considerable amount of energy, so that only a small portion of the entire contents is normally agitated. As the level of solids drops in the hopper during normal operation, the fluidized bulk density above the augers has a tendency to decrease which results in a decrease in the solids mass-flow rate. Small variations in the bulk density of the fluidized solids can be compensated by placing the entire hopper and contents on a scale which produces an electronic signal which can be processed to increase or decrease the auger speed. (Non-exclusive examples of feeding systems with fluidized solids above the auger and with the automatic screw speed control are those made by the K-Tron Corporation, P. O. Box 548, Glassboro, NJ 08028 and by Acrison, Inc., 20 Empire Blvd, Moonachie, NJ 07074.)

Our experience with the electronically controlled feeder made by K-Tron has been that relatively even mass flow was attained if the

solids were fairly free-flowing with a low angle of repose. However, with fibrous solids having a very high angle of repose, such as wood flour or sawdust, the mass of solids in the hopper tended to form a stable arch or bridge above the agitator while the fluidized solids in the agitator section were fed to depletion. A variant of the bridged feed is the "collapsing bridge" which can form a vertical "rat-hole" in the feed. The existence of these bridges or rat-holes prevents the flow of feed into the agitator and results in a decrease in bulk density and delivered mass flow. With wood flour having an angle of repose of nearly 90°, a 20-cm diam. rat-hole would typically form above the agitator and break through to the top surface of the feed in the hopper. With sawdust, the rat-hole tended to have a larger diameter at the top than at the bottom (an inverted, truncated conical shape).

To collapse the bridges and the rat-holes, K-tron had designed and installed inflatable bladders inside the hopper. When these bladders inflated, they were supposed to compress the feed. However, these bladders did not reliably collapse the feed and in addition they severely upset the system when operated. When feeding the solids directly into a reactor with the hopper lid battened down, the inflation of the bladders caused a displacement of part of the gaseous atmosphere in the hopper through the auger. This caused a surge of gas and solids to enter the reactor which resulted in system pressure and mass flow upsets as previously discussed.

The vibrator by itself did not seem to upset the electronics, but this device was marginally effective, consumes quite a bit of compressed gas and the long term effects of vibration on the electronics was unknown (the electronics employ a taut, harmonically vibrating wire for weight determination). It was reasoned that a device which would affect only the solids in the hopper rather than the whole hopper and its contents would use considerably less power and be less apt to confuse the electronic controls. An additional mechanical agitator or paddle to fluidize the rest of the hopper contents could have been used, but this would require substantial

power to operate, might have upset the sensitive electronic weighing device, and the bulk density would change considerably during the feeding operation as well.

We have developed a device which encourages the rat-hole to form initially above the feed agitator, but thereafter it maintains a constant level of feed, just above the agitator. The device senses when the feed level drops and then causes a small amount of feed to fall off of the walls of the rat-hole. When the feed above the agitator accumulates to the desired level, the sensor in the device causes it to stop sloughing off the walls of the rat hole. This results in a very uniform bulk density above the augers and consequently a uniform mass flow rate at a constant auger speed.

In grab sample tests, the delivered mass flow rate of -80 mesh pine flour with the new device at a constant auger speed was much smoother with a coefficient of variation of only 1% (twenty-three consecutive one-minute samples). This compares to 2% with the same feed with thirty-one one-minute samples with the bladders alternating and vibration during bladder actuation (the electronics were automatically switched to the constant auger speed mode during the 25 seconds of upsetting bladder action and the remaining one minute of the cycle was in the electronically-controlled variable auger speed mode). Thus, with the new device, the feeder delivers such a constant mass flow at a constant auger speed, that the expensive electronics to vary the auger speed may prove to be superfluous. In addition, the device has a relatively low energy requirement and a mild impact on the hopper system itself so that the electronics are not upset by the its action. In operation with the pyrolysis reactor attached to the feeder with the device installed, very smooth system operation in both the constant and the controlled variable screw speed modes was attained, as evidenced by the relatively constant pressures throughout the system and product gas flow rate. A patent disclosure has been prepared and sent to SERI's legal council. It has been assigned the title "SERI Invention No IR #82-7; Low Power, Solid Particle Fluidizer

and Level Controller" and has been forwarded to the DOE Office of Patent Council in Chicago.

Reactor Modification

As was reported at our last contractor's meeting, extensive cold-flow testing in a Plexiglas reactor model showed that the desired tight helical path of the solids could be attained with a helical guide vane on the ID of the cyclone reactor. No other feasible physical changes to the existing reactor had any substantial effect on the solid's path on the reactor wall [7].

The pyrolysis reactor has been modified with the addition of an internal, handmade helical spiral of 1/4-in.-diam. 316SS tubing. The helix has a 12.5-cm-diam. and a 3-cm pitch. This helical spiral was chosen for evaluation rather than a more ideal machine-turned spiral made of square rod due to the relative nonavailabilty of the square rod in a high temperature alloy. The use of the handmade spiral was to verify the effectiveness of the concept to guide the particles at elevated temperatures in a tight spiral rather than the natural path consisting of a coarse spiral with a pitch greater than the ID of the cyclone reactor. From cold-flow studies made with the Plexiglas model, it is known that where the handmade helix doesn't quite touch the reactor ID, the feed particles will take an undesirable shortcut and pass between the helix and the wall.

During pyrolysis runs made with the helical coil in place, the inside cyclone reactor surface appeared to have a uniform color (temperature) gradation from relatively dark red near the entrance to a brighter red near the exit. This uniformity suggested that the entraining steam and the entrained biomass particles were spread out uniformly on the reactor surface, whereas, without the helical coil the particles had a preferred narrow pathway which utilized only a small fraction of the total heat transfer surface.

Drawings were sent to fabricators for bids for a new cylindrical section for the cyclone reactor which would have a raised helical rib intregally cast on the inside of the tube. A high temperature cast-

able alloy such as HK-40 would have been used for this casting. However, fabricators' response to the request for bids have been nonexistent or very expensive, primarily because of the raised internal rib. Due to the relative success of the helical tube in the cyclone reactor, the procurement of a new reactor with an integral, internal, helical rib has been postponed.

Miscellaneous System Modifications and Improvements

The seals in the scrubbing pumps have been replaced with acetone-compatible materials so that the originally-intended, closed-system solvent wash can be accomplished without damage to the pumps. The use of acetone through the pumps and piping for cleanup between runs has been progressing and appears to be a feasible approach to reducing the labor required for system turnaround. The pyrolysis tars seem to be quite readily soluble in acetone, although residual scrubbing water in the system (when mixed with the acetone) drastically reduces this solubility. When excess water is added to the tar-acetone solution, a colloidal tar precipitate results. Acetone recovery by distillation could be practiced with the tars probably being left in suspension in the water phase. Currently, it is considered cheaper not to recover the dirty acetone from this small R&D scale system.

The electric heaters have had problems with the electrical junctions overheating. This problem was identified as being due to an increased junction resistance after the stainless-steel-heating-elements' lead wires became severely oxidized. As the resistance increases, so would the temperature and the extent of oxidation, which in turn further increases the resistance until electric arcing occurs which tends to melt through the lead wires. Preliminary evaluation indicates that the use of silver solder to cover the junction will satisfactorily resolve this problem and lead to a decrease in heater problems.

Although ablative pyrolysis can result in the virtually complete vaporization of the feedstock, process variable studies often require the operation of the system at conditions which do produce some char

and/or partially pyrolyzed feedstock. In the past, much of the char and/or partially pyrolyzed feed was entrained into the vapor cracker and eventually recovered in the primary scrubber. This resulted in the need for filters to prevent the plugging of the scrubber spray nozzles. A surplus four-inch diameter cyclone from the air gasification project was located and installed between the vapor cracker and the primary scrubber as shown in Fig. 2. This char cyclone would be expected to collect all particles greater than about 10 μm and nearly eliminate the need to filter the primary scrubber water. The separation of the hot char from the tar vapors in this new char cyclone replaces the time consuming post-run, acetone-extraction of the tars from the char and greatly decreases the system turnaround time between runs.

The four-inch diameter cyclone has been doing a good job of dropping out entrained char before entering the first scrubber. By keeping this cyclone over 125°C, the collected char was found to be a dry powdery material (with wood flour feed) which can be weighed without the time consuming steps of drying, acetone tar extraction, and subsequent drying operations to determine char yields. Based on the brown caramel appearance of the tars collected from the less severe cracking experiments, it appears that very little fine char or carbon black is entrained through the char cyclone. Perhaps the very fine char (<10 μm), which could escape the char cyclone, is being preferentially oxidized due to its high surface-to-volume ratio by the hot steam environment in the vapor cracker section.

To alert the operators of impending system failure, pressure switches have been installed which will activate panel lights if: the cooling water, the nitrogen purge, or the secondary scrubber water pressures drop below the desired values; or if the primary scrubber water, the primary-scrubber-water disposal, or the secondary-scrubber-water-disposal pressures are too high (plugged nozzles).

Problems were encountered with the plugging of the feeder adapter, especially when the aerodynamic spoiler rod was used to prevent the steam ejector from evacuating the feeder system. The aerodynamic

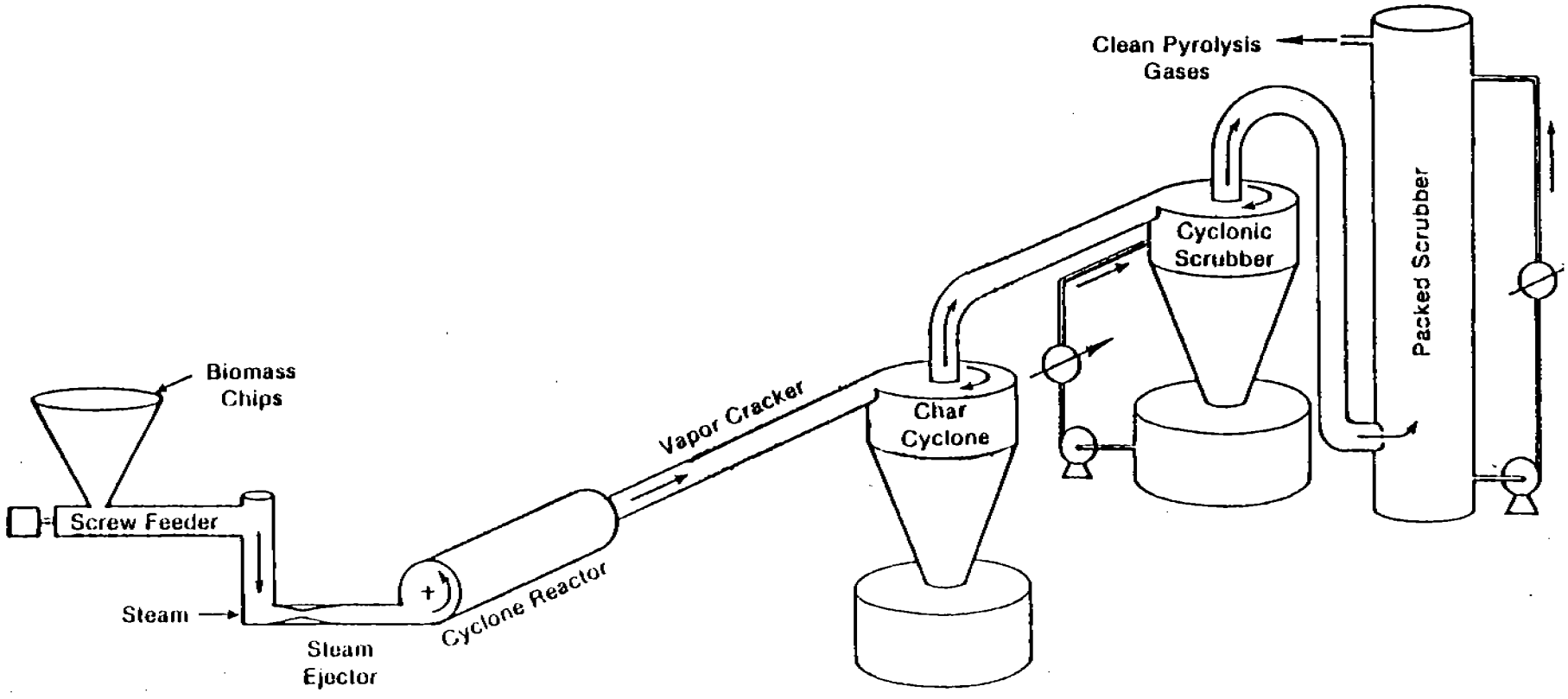



Figure 2. Ablative Macroparticle Pyrolysis Flow Schematic

spoiler rod was found to be causing a swirling motion in the feed as it fell from the feeder to the steam jet. This swirl caused the feed to be centrifuged to the conical wall of the feeder adapter where it had a tendency to accumulate and bridge over. The aerodynamic spoiler rod has now been removed and a steam ejector bypass loop has been added which adds steam to the feeder adapter to prevent evacuation of the feeder system. The bypass loop has a pressure gauge, thermocouple, and a sonic orifice which allow the bypass steam flow rate to be calculated. Steady, even feeding of sawdust now appears to be in hand.

Additional electrical heater tapes have been added to the feeder system to eliminate apparent cold spots where steam had a tendency to condense and result in wet feed and a weight gain which introduced errors to apparent feed flow rates.

The cross-sectional area of the entraining tube at the cyclone reactor entrance has an inverse effect on the velocities of the entering carrier gas and the entrained feed particles. This effect of increased entering velocity with a smaller entraining tube was observed throughout the reactor length as evidenced by the higher particle velocities at the wall of the cold-flow Plexiglas model. An entrainment tube of 1.09 cm ID was inserted into the 2.5 cm ID entrainment tube and successfully used in several runs. This smaller entrainment tube serves to increase the entering particle and gas velocities by a factor of five. The equilibrium particle velocity in the cyclone reactor is also apparently increased by a factor of five, due to the slow decay of the gas velocity down the cyclone length.

## PYROLYSIS EXPERIMENTATION

### Preliminary Softwood Sawdust Feedstock Evaluation

Additional pyrolysis runs were made with -3/16 inch softwood sawdust in the pyrolysis system shown in Fig. 1 to evaluate the function of the solids-feed system with the feed-hopper bladders properly inflating. Run G was made with a feed rate of 9 kg/hr with a steam-to-biomass ratio of 2. The reactor heaters were set at 950°C and the vapor cracker heaters at 850°C. The thermocouples in the cyclone

reactor indicated temperatures of between 810° and 950° C, whereas the vapor cracker thermocouples indicated temperatures very close to the set point as shown in Fig. 3. However, due to radiation and conduction effects, these indicated temperatures are partway between the wall temperatures and the true gas temperatures. The apparent gas temperature 15 inches downstream of the last vapor cracker heater was 720°C, which is probably the best value for the final pyrolysis product temperature. With high temperatures and an associated long residence time due to the low volumetric throughput, the pyrolysis gases were severely overcracked with a molar ratio of ethylene-to-propylene of nearly 50. The water in the first scrubber had a naphthalene (moth ball) odor, but was relatively clean. A significant amount of the char-tar mixture in the first scrubber was soluble in acetone and it is thought to contain polycyclic aromatic compounds formed by the cracking reactions of propylene, butenes, and ethylene. The char material collected in the recycle cyclone contained no acetone-solubles, implying that the solubles in the char-tar material were possibly aromatic tars formed by vapor phase reactions and probably not partially cracked biomass which had failed to vaporize.

Run H was similar to Run G except that the temperatures of the vapor cracker were set about 40°C lower at 810°C. This lowered the cracking severity so that more of the propylene survived with a molar ratio of ethylene to propylene of 15. Sampling at the entrance, middle, and exit of the vapor cracker indicated that the residence time of the gases in the cyclone reactor was so long that only fairly small gas compositional changes occurred in the vapor cracker. Due to cold spots in the feed hopper, steam condensation occurred which interfered with the feeding of the sawdust (more heater tapes were later installed). The recovered char and char-tar amounted to only about 5% of the sawdust fed into the reactor, implying that a very high percent of biomass vaporization was being attained and that ablative pyrolysis of particles as large as sawdust is feasible.

The helical coil was then installed and several pyrolysis runs were next made at feedrates between 9 and 25 kg/hr and steam-to-

biomass ratios between 1.6 and 3.7. It appears that with these relatively low reactor throughputs, the resultant long residence times can easily result in the secondary cracking of the propylene and butenes to form the corresponding dienes which readily react to form polycyclic aromatics (tars) with the aromatic vapors. To reduce the cracking severity to preserve the desired hydrocarbons at these long residence times, the vapor cracker temperatures have been lowered to the 700-750°C range, which results in very low energy input requirements for the vapor cracker heaters.

Figure 3 shows how a lowered cracking severity (lower temperature and residence time) affects the product slate at a steam-to-biomass weight ratio of 2. The lower severity runs have lost less propylene and aromatic vapors to secondary cracking reactions which produce unwanted polyaromatic tars. It is interesting to note the relative stability of the molar methane-to-ethylene ratio at 2.2 to 2.5, whereas the highly sensitive molar methane-to-propylene ratio varies between 10 and 116. This reflects the highly reactive nature of propylene at these temperatures and the importance of cracking severity on the product slate.

Two runs were made to determine the upper limit for feeding rates with -3/16 inch sawdust. Repeated attempts to operate at 33 kg/hr resulted in plugging the feeder adapter. With a steam-to-biomass weight ratio of 1.4, a biomass feed rate of 25 kg/hr was successfully evaluated in Run P. This resulted in an apparent 74% gasification, 14% char, 1.5% acetone soluble tars, and about 10% unaccounted (presumed to be water-soluble organics). All temperature controllers were set at 800 to 850°C, however, only the last vapor cracker section was able to maintain the set point as shown in Fig. 4. The final gas temperature (as measured downstream of the last heated section) was 756°C. Considering the relatively low gasification obtained with this high a throughput, it appears that the useful upper limit for throughput is currently about 15 kg/hr or less.

A comparison of Run P to Run L is shown in Fig. 4. Run L had a much lower temperature profile, especially in the cyclone reactor.

**Figure 3. Preliminary Pyrolysis Results**

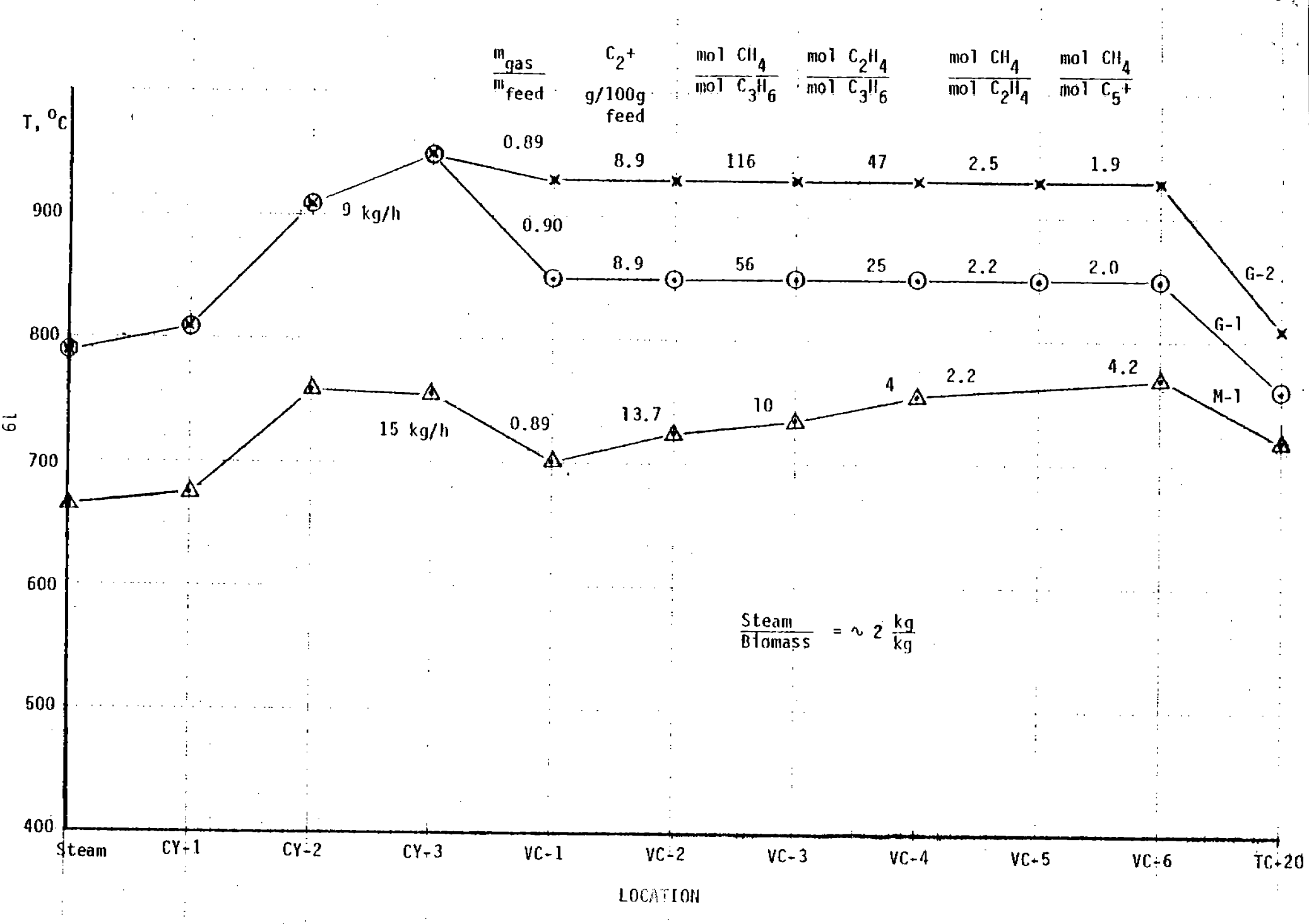
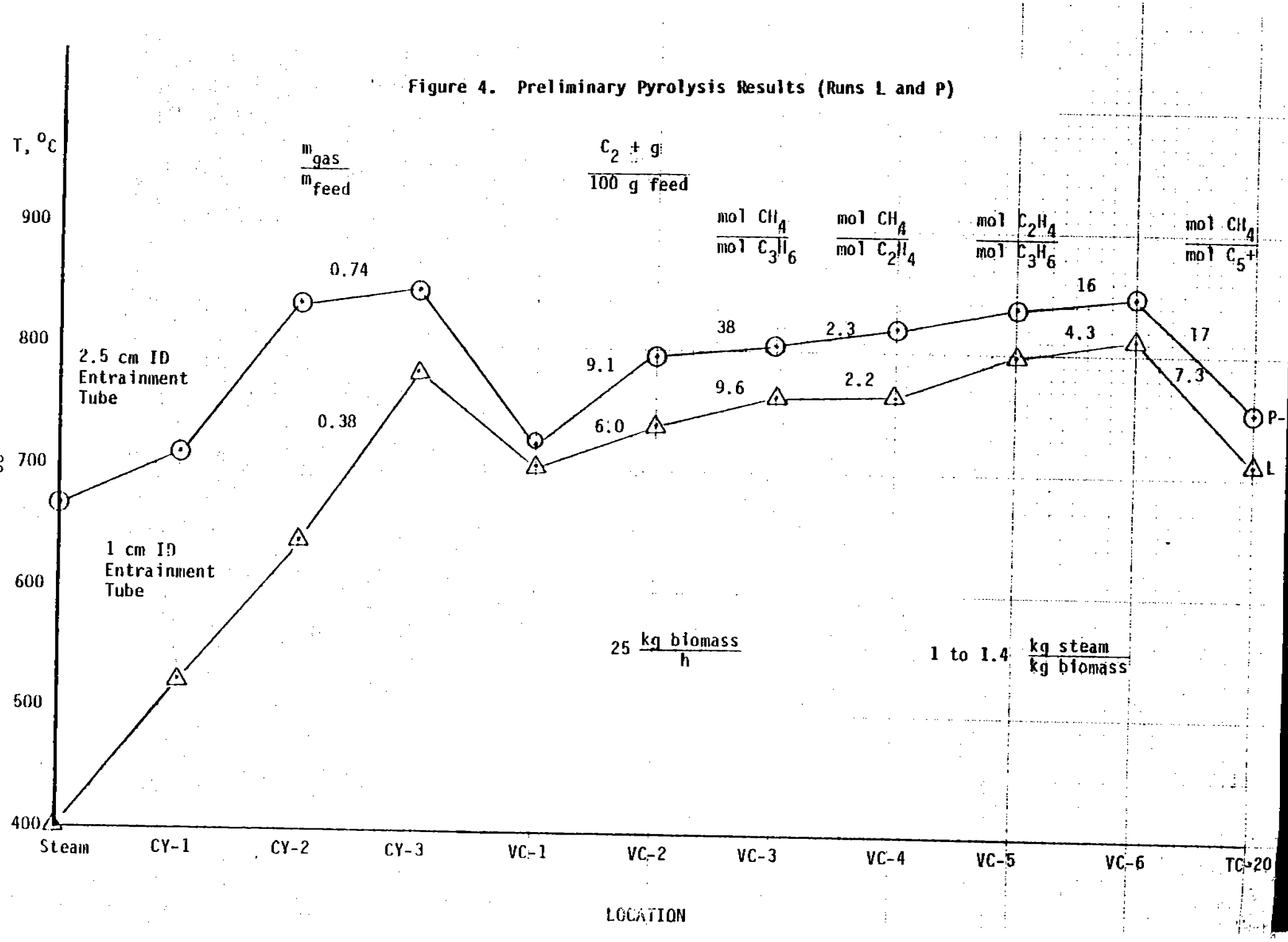


Figure 4. Preliminary Pyrolysis Results (Runs L and P)



This lower temperature profile, as well as the shorter residence time due to the higher velocities of the smaller entrainment tube, produced a much lower gasification yield of 38% for Run L although the total vaporization yields of 83% of the feed appeared to be fairly good (based on the mass of biomass fed minus the char recovered). The preservation of the propylene in the gas products is reflected in the low molar ratios of methane-to-propylene and ethylene-to-propylene. The relative ratios of these products to each other are fairly constant over the range of 38 to 89% conversion to gases when exposed to temperature profiles of similar severity. An increase in the $C_2^+$ yield will be sought through more complete gasification and the reduction of secondary reactions which produce aromatic tars and methane by the use of shorter residence times at the elevated temperatures.

Preliminary Softwood Flour Feedstock Evaluation

Two runs were made with -80 mesh pine flour. In the first run, a layer of char built up on the inside of the cyclone reactor. The deposited char was quite frangible and had a very porous, sintered appearance. It is hypothesized that the fine flour particles were centrifuged to the wall and were pyrolyzed to a sticky tar, but were not immediately vaporized due to the wall temperatures being too low at about 700 to 800°C. The tar particles were apparently then pyrolyzed to a sintered char. The flour particles are thought to be fine enough to be entirely within the gas boundary layer, and could sit on the wall in the absence of larger particles to stir them up into the high velocity gas stream. (The deposition of fine particles on the wall was also observed with quartz flour during the early preliminary operation of the cyclone.) Only 3% of the pine flour was converted to char and 85% of that char was found in the cyclone reactor. In the second run with pine flour, higher temperatures of 850 to 890°C were maintained in the cyclone reactor, and the amount of deposited char on the wall appeared to be negligible. An apparent gasification of 94% was calculated based on gas flow measurements with only 1% char recovered. A total of 15% weight per cent of $C_2+$ hydrocarbons was achieved, with about 30% of them being in the $C_5+$ backflush presumed

to be low molecular weight aromatics such as benzene, toluene, and xylene (BTX).

The wood flour had a strong tendency to plug the pressure lines in the feeder adapter to make the pressure readings very erroneous. This was remedied by the use of a partially inflated rubber bladder in the feeder adapter which isolates the pressure gauge lines from the wood flour and steam atmosphere. Good pressure readings are now available during the run without the added complication of steam condensation or plugging with feed.

Process Variable Studies

During this reporting period two series of pyrolysis experiments were successfully performed with minus 5-mm softwood sawdust to investigate two different temperature profiles at steam-to-biomass ratios between 1.4 and 4.1 with inlet steam temperatures between 720 and 760°C. In addition, injecting quench water into the vapor cracker section was demonstrated for the first time and shown to thermodynamically "shorten" the vapor cracker as expected.

Series X experiments utilized a temperature profile in which the recorded temperatures steadily rose from the above-mentioned inlet steam temperatures to about 880°C in the third cyclone section. The vapor-cracker section temperatures were held at about 800°C which resulted in a final gas temperature of 695 to 730°C (see discussion of temperature measurements later).

Series Y experiments had similar temperatures in the cyclone reactor, but the temperatures in the vapor cracker were 80 to 90°C lower at about 710°C, resulting in cooler final gas temperatures of 645 to 660°C. In experiment Y-5, quench water was sprayed into the number five vapor cracker section to effectively reduce the thermodynamic length of the vapor cracker by about one-third. The water spray dropped the indicated vapor-cracker temperatures to about 500°C, with a final gas temperature of 430°C.

Run series Z steam temperatures were also in the range of 740 to 760° C with biomass flow rates of 8.4 kg/h and steam-to-biomass ratios

of 2.2 to 3.7. The indicated reactor temperatures were relatively low and gasification levels were in the 50 to 60% range due to this.

The steam-to-biomass ratio was varied from 1.4 to 4.0 in series X by holding the biomass flow constant at 8.5 kg/h and varying the steam flow from 11.8 to 33.5 kg/h. In series Y, the biomass flow was varied between two levels (8.2 and 11 kg/h) at steam flows between 21 and 34 kg/h. This was to try to differentiate between the effects of residence time and steam-to-biomass ratio. In series Z, the effect of quenching the product gases at the exit of the cyclone reactor was investigated.

Run series 1 was plagued with faulty heaters. This caused some thermocouples to be located a considerable distance from active heaters which tended to decrease the radiative and convective errors in the thermocouple measurements. This vividly illustrated that there were temperature measurement errors of between 40 and 100°C. To minimize these errors, the heater elements were moved downstream one-half element length. This placed the controlling thermocouple just downstream of the heating element where radiation and conduction from the hot vapor-cracker wall would be less severe. The primary purpose of run series 2 was to demonstrate proper temperature control with the newly placed controlling thermocouples. As expected, gas or steam flow is needed during heater operation for proper control.

## DISCUSSION OF PROCESS VARIABLE RUNS WITH SAWDUST

The run series X and Y had gasification yields of between 68 and 83 per cent by weight. However, the char yield was only 1 to 4 per cent. By difference, this leaves 13 to 31 per cent by weight of the products as tars and as condensible materials which passed through the char cyclone in the vapor state, but which condensed in the water scrubbbing systems. These condensible materials are thought to be of two general classifications: (a) primary pyrolysis products (oxygenated fragments of biomass components); and (b) tertiary pyrolysis products (polycyclic aromatic compounds formed by the pyrolysis of the secondary pryolysis products, i.e., gaseous olefins). The optimization of ablative pyrolysis to olefins must first deal with the pyroly-

sis of the biomass to the primary tar-vapor products. These primary tar products are oxygenated compounds formed by the depolymerization of the biomass, tend to be water soluble, and typically have molecular weights between 50 and 400. These compounds are optimally vaporized to reduce their tendency to polymerize to higher molecular-weight tars, which can be quite stable at the reaction temperatures and have a char-like appearance. The global reaction of the primary biomass tar vapors to the olefin containing gases is apparently strongly influenced by temperature and is thought to consist of unimolecular decompositions, i.e., first-order reactions.

The kinetics of first-order reactions are relatively well understood, i.e., the rate of change of the concentration of the reactant ($C_V$) is equal to the concentration of the reactant times the reaction rate constant ($k_T$) for the given absolute temperature (T):

$$\frac{dC_V}{dt} = k_T C_V = \left(A_V e^{\frac{-E_V}{RT}}\right) C_V \ ;$$

where $E_V$ and $A_V$ are Arrhenius rate constants and t is time. By rearrangement and integration the following is obtained:

$$\ln\left(\frac{C_{V2}}{C_{V1}}\right) = A_V \int_{t1}^{t2} e^{\frac{-E_V}{RT}}\, dt$$

This expression is difficult to evaluate from experimental results because it requires that the temperature history be known precisely. However, at a constant reaction temperature, the equation reduces to:

$$\ln\left(\frac{C_{V2}}{C_{V1}}\right) = k_T \Delta t = 2.303 \log\left(\frac{C_{V2}}{C_{V1}}\right)$$

When this relationship is plotted on semi-log graph paper, a straight line is generated with a slope of $(k_T/2.303)$ for a specific temperature. With this brief background in kinetic theory, an examination of the experimental conditions and results is in order.

The measurement of the true gas-stream temperature in high temperature reactors is technically difficult because the thermocouples are being simultaneously heated by radiation and conduction from the externally heated reactor walls and cooled by convection by the cooler endothermically reacting gases. Thus, the thermocouples will always indicate temperatures part way between the true gas temperature and the reactor wall temperatures. With higher velocity gases, the convective heat transfer will be enhanced and the error of temperature measurement will be somewhat reduced. Heat transfer theory can be used to calculate a corrected temperature, which for our conditions can be shown to be in the range of 50 to 100°C. However, a more direct method which we have used is to compare the indicated temperature of the last thermocouple in the vapor cracking section (TC-18) to a thermocouple in the gas stream 38 cm downstream of the last heater (TC-20). Since the process tube walls at this location are heated only by the gas stream and are well insulated, the temperature of this thermocouple should be very close to the true gas temperature. The temperature error by these measurements (TC-18 minus TC-20) has been between 40 and 90°C and does qualitatively decrease with an increase in gas flow as predicted by convective heat transfer concepts. This approach assumes that the gas temperature is not affected by any chemical reactions taking place in the dilute product gas.

As a first approximation of the gas-temperature history in the cyclone reactor and vapor cracker, the twelve temperatures involved were all corrected by the difference between that indicated by TC-18 and TC-20. Each corrected thermocouple value was equally weighted along with the uncorrected inlet steam temperature and the uncorrected TC-20 temperature to calculate a "corrected average" temperature. (The inlet steam temperature was not corrected because it is also outside of the furnaces.) This ignores the expansion of the gas volume due to temperature increases or to gasification, but these effects

lose their importance if the temperatures are fairly constant and if the overall gas composition in the reactor is primarily steam (e.g., at a steam-to-biomass ratio of 2.7, the final volume fraction of the product gases is only ~20%).

The volumetric gas flow was calculated, based on adding the molar steam-flow rate to the molar flow rate of the final product-gas. The total molar flow rate was then used with the "corrected average" temperature and the cyclone-reactor pressure to calculate the volumetric gas flow rate using the ideal gas equation. The residence time of the gases in the reactor was found by dividing the physical internal volume of the cyclone reactor and the vapor cracker by the volumetric gas flow rate. The inverse of this residence time is often referred to as the "space velocity" in reactor design. This assumes that the product gases are formed instantaneously at the reactor entrance, which admittedly introduces a bit of error.

Since the reactor volume used in these calculations was the full physical volume of the reactor, this residence time will be referred to as the "full-volume" residence time. In reality, the gas flow in a cyclone or vortex tube is quite complex and experimentation by others has shown that only an outer annulus of the vortex tube (comprising two-thirds of the cross-sectional area) is actively used by the swirling gases to move toward the exit. In addition, the axial velocity was found to be a function of radial location and to be proportional to the tangential entering velocity [8,9]. The true average residence times of the gases in the pyrolysis reactor may easily be 1/3 to 1/2 that predicted by the "full-volume" simplification. A refinement in the residence time will be sought, but the "full-volume" residence time will be used for discussion in this report.

The effect of residence time on the weight fraction yield of condensible products for series X and Y are plotted in Fig. 5. The condensible products were defined as the feed minus the gases and char produced. The "corrected average" temperatures are indicated at each point. Although the data are preliminary and further experimentation

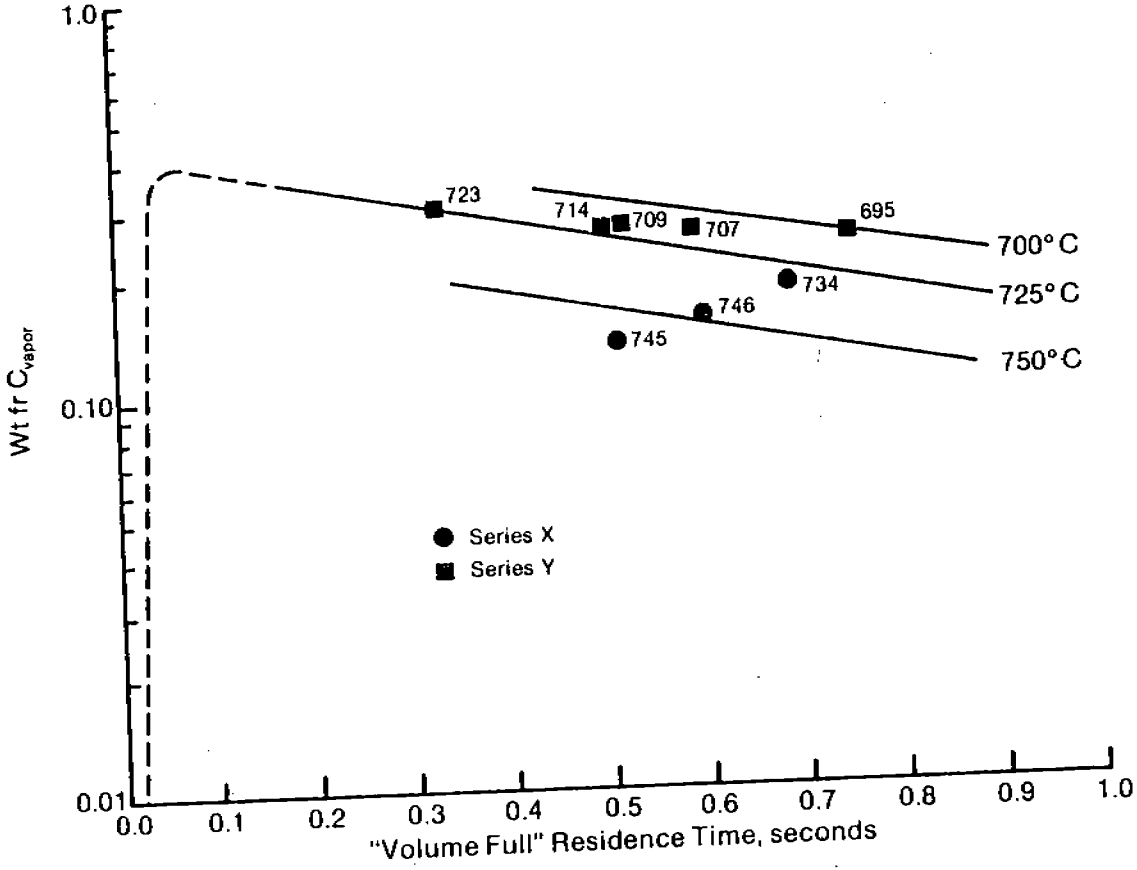



**Figure 5. Uncracked Biomass Vapors vs. Residence Time**

is needed, temperature parameter lines have been added by visual interpolation. These parameter lines will be refined as additional data are generated. Note that if the biomass vapor had all been formed at time equals zero, the straight parameter line should have had a common starting point at zero time of 1.0 weight fraction of vapors. However, the sawdust particles require a finite time to vaporize. Thus, one would expect the biomass vapor concentration to start at zero and rapidly rise until the vapor-cracking reactions proceed faster than the biomass vaporization, as indicated by the dashed line in Fig. 5.

The importance of temperature is shown dramatically in Fig. 5 by the significant change in the amount of biomass vapor cracked caused by a 25°C change. Note that linear isotherms seem to fit the data as was predicted by the kinetic theory. Considering the uncertainty of the residence times and temperature corrections, there seems to be a very good correlation based upon the application of first-order kinetic theory concepts to the cracking of the biomass vapors to gases. Significant improvement in the accuracy of the temperature measurements have since been made by moving the vapor cracker furnaces downstream 38 cm (1/2 furnace length). This places the thermocouples in the 5-cm gap between the furnace elements where the vapor cracker wall more closely approaches the gas temperature and errors due to radiation and conduction from the hotter walls will be reduced.

Byproduct Char

Although char is not considered to be a desirable product in our program, some knowledge of the properties of the char produced is of interest. From series X, 3.7 per cent by weight of the feed was recovered as char in the char cyclone for an apparent overall vaporization of 96.3% of the feed. This char was selected arbitrarily for tests. To the naked eye, this char had a particle size and shape resembling the sawdust feed. Examination of the char at a magnification of 30, revealed that it had glossy black surfaces which had apparently been only semi-molten in that the original fibrous nature was still evident. To determine the thermochemical nature of this char, it was submitted for heat of combustion, proximate, and ultimate

analyses. A summary of this testing is shown in Table 1. For comparison, the tests were also run on a sawdust sample and are also shown in the table. The majority of the ash in the feed is recovered in the char, but apparently some ash goes on to the scrubbers. The char is a completely devolatilized material containing 92.5% carbon, 5.5% oxygen, and 2% hydrogen by weight (moisture and ash free basis) with an empirical formula of $C_6H_{1.5}O_{0.3}$. The higher heating value was reported to be 31.4 kJ/g (13,530 Btu/lb), which reflects the low ash and low oxygen content of the char. The lower heating value was 31.1 kJ/g (13,362 Btu/lb) which is within 0.2% of that calculated from the elemental analysis using the Dulong formula developed for use with coal.

In fast pyrolysis processes, the char yield is quite small so that its utilization is currently visualized as one of the sources of process energy, rather than as a marketable byproduct. However, the low volatility of the material caused some doubt as to its combustibility in air. A quick qualitative test was performed in which the char was dropped into the flame of a propane torch. The char was entrained by the flame and ignited. As would be expected from the absence of reported volatiles, the char burned in a glowing combustion rather than flaming combustion mode. The glowing char particles burned very persistently and had sufficient "lift" to remain in suspension as "fireflies" in the room air. When the char was dropped into the air inlet holes of the premixer section of the propane torch, a very luminous flame resulted which would be expected to have an enhanced radiant heat transfer over the non-luminous hydrocarbon gas flame. Consequently, it is thought that in a commercial system, the char could be easily entrained into a byproduct gas-fired furnace for recovery of its energy content and to enhance the heat transfer rates in the radiant section of the furnace. For comparison, a test was made with the dry sawdust used to make the char. This showed that the char was qualitatively much easier to ignite and burn than sawdust. Since sawdust is routinely burned in suspension-fired furnaces, it seems very reasonable to expect equal or better success with this char.

Table 1. Analysis of Sawdust Feed and Char

| | -3/16 Sawdust Feed Wt Per Cent | | Run X Char Wt Per Cent | |
|---|---|---|---|---|
| | As Received | Dry | As Received | Dry |
| Proximate | | | | |
| moisture | 6.62 | 0.00 | 2.02 | 0.00 |
| ash | 0.44 | 0.47 | 5.67 | 5.79 |
| volatile | 76.00 | 81.39 | <0.01 | <0.01 |
| fixed C | 16.94 | 18.14 | 92.31 | 94.21 |
| Ultimate | | | | |
| moisture | 6.62 | 0.00 | 2.02 | 0.00 |
| carbon | 47.60 | 50.97 | 85.35 | 87.11 |
| hydrogen | 5.61 | 6.01 | 1.77 | 1.81 |
| nitrogen | 0.07 | 0.07 | 0.11 | 0.11 |
| sulfur | 0.01 | 0.01 | 0.01 | 0.01 |
| ash | 0.44 | 0.47 | 5.67 | 5.79 |
| oxygen* | 39.45 | 42.47 | 5.07 | 5.17 |
| High Heating Value, kJ/g (Btu/lb) | 18.6 (8024) | 20.0 (8593) | 30.8 (13,256) | 31.4 (13,530) |

*by difference

Many mathematical models of pyrolysis assume that the process involves a skeletonizing of the biomass particle to result in a porous honeycomb material, which would be expected to have a very low bulk density. However, volume and weight measurements of this char showed that it had a bulk density of 0.15 g/cc (9.4 $lb/ft^3$) compared to the original sawdust bulk density of 0.18 g/cc (11.2 $lb/ft^3$). That the char bulk-density was 83% of the original feed bulk-density, but less than 4% of the original weight is difficult to explain with the traditional pyrolysis model. However, if these few surviving particles were to have passed through a plastic stage and shrunk during pyrolysis, in a manner analagous to that exhibited by heat shrinkable polyethylene tubing when heated, then the particle density would not necessarily decrease with pyrolysis. Although particle breakup of the frangible char to form a different particle size distribution could to some extent improve the packing density and significantly increase the bulk density, microscopic examination of the char revealed particles having a glossy surface without obvious skeletonizing. The char was very frangible and formed very small particles quite readily.

Aromatic Vapor Products

A significant amount of the pyrolysis products thought to be hydrocarbons useful for liquid fuels are eluted in the backflush cycle of the gas chromatograph and have previously been referred to as $C_5^+$ products. Benzene and toluene are eluted in a similar manner and it is though that much of the "backflush" material is composed of these vapors.

A sample of product gas was subjected to mass spectrometry by Dr. Gunther Holzer of the Colorado School of Mines to determine the high molecular weight chemical species present as vapors in the product gas. As suspected, acetic acid, propionic acid, and aromatic species such as toluene, indene, naphthalene, and methyl naphthalenes were identified. Quite surprisingly, however, oxygenated sulfur compounds were also reported, e.g., diethyl sulfone or $(C_2H_5)_2\ SO_2$. These sulfones can be made by reacting olefins, e.g., ethylene, with hydrogen sulfide and then oxidizing the resultant sulfide, e.g.

diethyl sulfide, to the corresponding sulfone. Although with low temperature "wet" chemistry, hydrogen peroxide can be used as the oxidant, perhaps steam is an effective sulfide oxidant at the elevated temperatures used in ablative biomass pyrolysis. In any case, the detected presence of the sulfones helps to explain what happens to the trace amount of sulfur in the biomass. The sulfones are water soluble and will tend to be removed from the product gases in the water scrubbers.

The source of BTX in the products could be from the decomposition of lignin which contains the aromatic ring in its structure. However, this is an unlikely source of BTX based on the reported lack of strong peaks for benzene or toluene in Milne's and Soltys' close-coupled mass-spectrometric studies with lignin [1]. Conversely, it is well documented that the pyrolysis of ethylene and propylene forms aromatic compounds, including BTX. Unfortunately, the aromatization reactions are not self-limiting at our pyrolysis conditions, and a large percentage of the BTX formed reacts with additional ethylene, propylene, or butene pyrolysis products to form polycyclic aromatic compounds qualitatively recognized as tars [10,11]. The production of BTX so far appears to be maximized at the milder conditions which also maximize propylene and butenes. However, with a further reduction in cracking severity, there is expected to be a trade-off between propylene and butenes versus BTX production.

The presence of small amounts of oxygen in the pyrolysis reactor act to catalyze both the aromatization of the olefins and the formation of phenols [12]. The presence of oxygen will need to be carefully controlled. The aromatization reaction to BTX rather than to tars is favored at higher hydrogen partial pressures and could be a viable method to produce high octane gasoline at pressures of 200 to 1400 kPa (30 to 200 psi) downstream of the atmospheric pressure pyrolysis reactor [13]. The formation of aromatic liquids at 600 to 800°C probably could be accomplished without the gas purification and higher partial pressures needed for lower temperature thermal polymerization to naphthalenes and polyolefins due to the increased rate of reaction at the higher temperature used for aromatization.

Data Reduction Computer Program

In order to cope with the large amounts of data generated with each pyrolysis run, a computer program has been written for our Hewlett-Packard 9845 desk top computer. This program utilizes raw data such as weights, pressures, temperatures, and gas chromatograph peak integrals and performs a long series of calculations. It prints out on a run summary sheet such items as final product-gas partial pressure in the reactor, weight ratio of steam-to-biomass, steam flow rate, volume of steam per weight of feed, volume of product gas per weight of feed, gas composition in volume fraction, molecular weight of the dry product gas, volumetric heating value of the gases, cracking severity parameters, yields of products, and mass, energy, and elemental balances. A sample of the output is shown as Fig. 6. Between five and ten minutes are required to input the raw data into the computer, compared to several hours to complete the calculations by "hand" with a calculator.

The program first calculates the dry product-gas composition and molecular weight from the raw gas chromatograph data. Using the temperature and absolute pressure at the orifice meter, corrections are made to the dry gas composition assuming that the product gas is saturated with water vapor after it passes through the packed scrubber. A molecular weight is then calculated for the saturated product gases which then is used to determine the mass flow rate of wet gases through the orifice meter. The mass flow rate of dry product gases is then calculated and used with the dry gas composition to determine the product yields in grams per 1000 grams of dry feed. The product yields are used to calculate the heat of combustion for each product species, as well as the elemental amounts of carbon, hydrogen, oxygen, sulfur, and nitrogen. The individual heats of combustion and elemental amounts of the products are totaled and compared to that of the feed material to effect mass, energy, and elemental balances. The dry product gas compositions and the individual heats of combustion are used to calculate the gaseous heating values on on a volumetric basis, e.g., BTU/SCF. The dry product gas composition is also used to calculate several cracking-severity parameters such as molar ratios of

PYROLYSIS SUMMARY SHEET (MOD 4)
(without $H_2O$ balance; R-6-405116 GC calibration)

Run R-1-1543 Date 12/22/81

-80 mesh Pine Flour used for feed

| Temp. Profile Degrees C | Steam | CY-1 | CY-2 | CY-3 | VC-1 | VC-2 | VC-3 | VC-4 | VC-5 | VC-6 |
|---|---|---|---|---|---|---|---|---|---|---|
| | 780 | 785 | 855 | 867 | 779 | 755 | 761 | 770 | 770 | 760 |

Final Pyrolysis Gas Tmeperature: 686 C (1267 F)
Reactor Pressure 90.32 KPa (13.10 psia)
Partial Pressure of Product Gases at Reactor Exit 11.07 KPa (1.61 psia)
4.48 kg wet feed/hr .00 moisture fraction of feed
Steam Flow Rate: 22.3 kg/hr Steam/Dry Biomass = 5.0 kg/kg
6.54 M3 steam/kg wet feed at 15.60, 1 atm (104.70 scf/lb)
.92 M3 net dry gas/kg dry feed at 15.6 C, 1 atm (14.69 scf/lb)
15.00 minutes run time

Pyrolysis Products Per kg Dry Feed

| | Gas Phase Vol Fr | Yield G/Kg | Heat of Combustion K Joules HHV | LHV | Elemental Yield C | H | O | G/Kg Dry Feed S | N |
|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | 0.182 | 14 | 2017 | 1706 | 0 | 14 | 0 | 0 | 0 |
| $C_3H_8$ | 0.000 | 1 | 34 | 32 | 1 | 0 | 0 | 0 | 0 |
| $C_3H_6$ | 0.010 | 17 | 809 | 757 | 14 | 2 | 0 | 0 | 0 |
| 1-Butene | 0.001 | 2 | 80 | 75 | 1 | 0 | 0 | 0 | 0 |
| t-Butene* | 0.005 | 11 | 531 | 497 | 9 | 2 | 0 | 0 | 0 |
| c-Butene | 0.000 | 0 | 19 | 18 | 0 | 0 | 0 | 0 | 0 |
| n-Pentane | 0.001 | 2 | 87 | 81 | 1 | 0 | 0 | 0 | 0 |
| $CO_2$ | 0.081 | 139 | 0 | 0 | 38 | 0 | 101 | 0 | 0 |
| $C_2H_4$ | 0.056 | 61 | 3060 | 2869 | 52 | 9 | 0 | 0 | 0 |
| $C_2H_6$ | 0.006 | 7 | 357 | 327 | 6 | 1 | 0 | 0 | 0 |
| $C_2H_2$ | 0.007 | 7 | 328 | 317 | 6 | 1 | 0 | 0 | 0 |
| $N_2$ | 0.016 | 17 | 0 | 0 | 0 | 0 | 0 | 0 | 17 |
| $CH_4$ | 0.120 | 75 | 4156 | 3745 | 56 | 19 | 0 | 0 | 0 |
| CO | 0.502 | 545 | 5507 | 5507 | 234 | 0 | 311 | 0 | 0 |
| Arom Vap | 0.013 | 47 | 2017 | 1927 | 43 | 4 | 0 | 0 | 0 |
| Char | | 11 | 177 | 177 | 4 | 0 | 0 | 0 | 0 |
| Mass Out | | 954 | 19179 | 18035 | 466 | 53 | 412 | 0 | 17 |
| Mass In | | 1000 | 20462 | 19041 | 505 | 65 | 426 | 0 | 1 |
| In-Out | | 46 | 1283 | 1006 | 39 | 12 | 14 | 0 | -16 |

*1,3 Butadiene is not separated from t-butene

Mol wt of dry gases = 24.33 11.88 mol $CH_4$/Mol $C_3H_6$ 5.52 Mol $C_2H_4$/Mol $C_3H_6$
Yield per kg of dry feed: 74 G $C_2$'s, and 30 G $C_3$ + $C_4$'s, or a total of 153 G $C_2^+$.

HHV of Gases = 556 Btu/ft$^3$ LHV of Gases = 523 Btu/ft$^3$
Mole fraction of water vapor in final product gases was .015

**Figure 6. Pyrolysis Summary Sheet**

methane-to-propylene and ethylene-to-propylene. A subroutine has been separated out which calculates only gas composition and prints it both in volume and weight fractions along with the volumetric heating values. This subroutine is useful for those occasions in which the gas analyses are part of a study which does not involve complete mass balances. "Volume full" residence time and corrected average temperature calculations have recently been added to the program.

## Future Reactor Modifications

The experimentation thus far indicates that the energy for pyrolysis is supplied almost entirely in the cyclone reactor. This places a severe load on the cyclone reactor heaters and is the limiting factor with respect to throughput. Unfortunately, the radiant cyclone-reactor heaters now installed have about the highest heat flux commercially available. The task of providing a higher heat flux to the cyclone reactor will be more involved than an easy changeout of heaters. As the heat flux increases, so does the chance for the development of localized hot spots on the reactor wall due to uneven heat transfer to the pyrolysis stream. These hot spots can lead to reactor damage due to the already marginal mechanical strength at the high operating temperature.

Using heat-pipe concepts, isothermal conditions can be approached and the chance of hot spots eliminated. An examination of the properties of molten sodium reveal that it has a low viscosity, reasonable vapor pressure in the 700 to 900°C range of interest and very impressive heat transfer properties such as high thermal conductivity, low viscosity, high latent heat of vaporization, and a low freezing point. What we propose to do is to close-couple a sodium boiler and the cyclonic pyrolysis reactor. Electrical immersion heaters in the molten sodium will vaporize the sodium. The exterior of the reactor can condense the sodium vapors with heat fluxes of 400 $w/cm^2$ (1,300,000 Btu/h $ft^2$) predicted at a temperature difference of only 6°C. These high heat fluxes will not be reached in our system, so the temperature difference will be even lower between the sodium vapor and the external reactor wall temperature. Design heat flux to the

reactor wall is 20 w/cm$^2$ (65,000 Btu/h ft$^2$) which is a bit higher than the upper limit for large gas fired furnaces. The low viscosity condensed sodium would be gravity returned to the boiler to avoid the complication of the development of suitable wicking. This arrangement is often referred to as a thermosyphon rather than a heat-pipe.

The use of liquid sodium as a heat transfer medium has been studied extensively for the cooling of fast-breeder nuclear reactors at about 650°C. Safety procedures for the handling and transfer of sodium have been established by the nuclear industry. Fortunately, we won't have to concern ourselves with the buildup of radioactive sodium isotopes like the nuclear industry.

Sodium has also been used as a heat-pipe working fluid in the 700 to 900°C temperature range primarily in aerospace applications, but also in central solar receiver designs [14] now being demonstrated. Corrosion problems are fairly minimal with stainless and inconel type steels, although it appears very desirable to keep sodium oxide levels down to only several parts per million [15]. The sodium oxide will be precipitated out with a "cold trap" technique and removed from the sodium at the end of each run by transferring the sodium (while hot) back to a storage container. The sodium oxide is quite insoluble at low temperatures and precipitates out of solution to sink to the bottom of the storage container. The next time the sodium is used, the potentially corrosive sodium oxide would be left behind in the storage container where it is innocuous in the solid phase at low temperatures. The addition of aluminum powder as an effective oxygen getter has been reported and may also be employed [16].

## CONCLUSIONS

The process variable study is still in its early stages. The amount of gas and olefins produced appears to be limited primarily by the extent of cracking of the biomass vapors. This reaction appears to be a first-order reaction, the extent of which is time and temperature dependent. The effects of increasing the amount of superheated steam in the reactor appear to include a lowering of the partial pressure of the product gases, but more importantly it reduces the gaseous

residence time, and increases the temperature of the tar vapors by the mixing of the hot steam with the cooler tar vapors. Using first-order kinetic reaction theory, the extent of vapors cracking to olefin containing gases is qualitatively predictable even though assumptions were involved in the values used for the average temperatures and residence times. The current results indicate that a 15 weight per cent (35 to 40% by energy) conversion of softwood to $C_2^+$ hydrocarbons is feasible and will include significant amounts of aromatic liquids. This yield is lower than reported for processed municipal solid waste (ECO II Fuel) and may reflect compositional differences or the potential for feedstock preparation studies. The sawdust pyrolyzes as well as the fine wood flour indicating that the larger particles are probably ablatively pyrolyzing as expected. Additional studies need to be completed before firm conclusions may be drawn.

## FUTURE PLANS

The system will continue to be operated to generate process-variable pyrolysis data at the 8 to 15 kg/h feeding rate. A mathematical expression for the average gaseous residence time in the cyclone reactor will be generated based on the reported flow patterns for vortex tubes. This will be incorporated into the mass and energy computer program for ease of calculation. This refined residence time will be evaluated with the experimental data for applicability. A final design will be made and costed to increase the heat flux to the cyclone reactor several fold through the use of sodium vapor condensation. This would allow a much higher throughput in the reactor. Such a reactor will be fabricated if it is within our budgetary means. A petrochemical consulting firm will be contracted to offer suggestions and to perform a preliminary technical and economic evaluation. A more sophisticated solids feeder controller has been received from the manufacturer which looks very promising and will be evaluated during pyrolysis operation.

A larger steam boiler and a wood chip drying oven have been ordered with SERI capital equipment funds. These items will be installed to upgrade the capability of the system. The new oven will be

useful to determine if certain feedstock preheating cycles has a beneficial effect on product distribution and yields.

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