PACIFIC NORTHWEST NATIONAL LABORATORY

Fast Pyrolysis Conversion Tests of Forest Concepts' Crumbles ™

Final Report

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Purpose

Forest Concepts is a forest product company based in Auburn, WA, that offers various wood products. According to their website, one of these products, Crumbles™ particles, is a highly uniform sized feed that is claimed to have advantages to conventional shredded and hammer milled particles including improved biomass handling and potential end-use in energy production. The purpose of this project was to conduct limited thermochemical conversion process (specifically pyrolysis) experiments in order to confirm the desirability of this new biomass product form and to specifically determine if particle length had an impact on pyrolysis. The method for evaluating this new product was accomplished using PNNL's fast pyrolysis system.

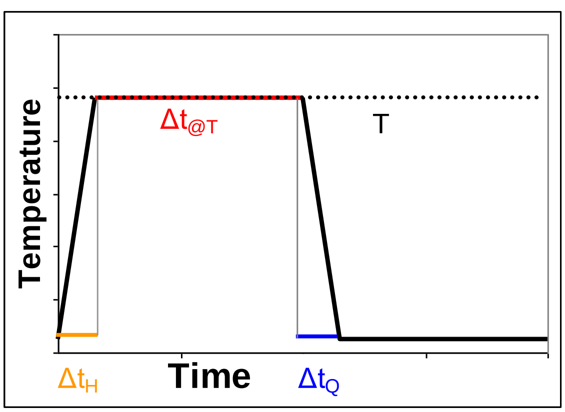
Biomass performance test at PNNL

As one of many thermochemical conversion capabilities at PNNL, the fast pyrolysis system has been demonstrated to produce a liquid product, bio-oil, originating from multiple feed sources such as pine sawdust, maple sawdust, oak wood sawdust, douglas fir sawdust, switchgrass, sorghum, corn stover, coffee, as well as some feeds provided by VTT of Finland in a collaborative effort.

The impact of Crumbles ™ particles in this system was evaluated mainly based on bio-oil yield and quality. In terms of yields, quantity of bio-oil was compared to the baseline particle length (2x2x2mm) as particle length increased (2x2x4, 2x2x8, and so forth). In terms of quality of the bio-oil, the liquid product was measured by ultimate analysis result, or in wt% of carbon, hydrogen, nitrogen, sulfur, oxygen and approximate analysis of ash and moisture. Higher carbon and hydrogen wt% typically indicates higher energy value. Exact heating values are typically measured experimentally using a bomb calorimeter [1], but multiple publications are available in estimating high heating value (HHV) of pyrolysis oil empirically [2], [3] . In this test, trends of increasing/decreasing C,H,O values in the product oil as a function of the feed size were evaluated.

Bio-oil production

Biomass fast pyrolysis is defined as heating of biomass under low oxygen/no oxygen atmosphere at a moderate temperature (approximately 500°C) to produce bio-oil. [4] Controlled high-heating rate of biomass is vital in this process in order to maximize pyrolysis liquid production (Figure 1). If heating rate is too low, the process favors carbonization/charring (belowFigure 1), and if the high temperature is sustained too long (>2s), gas production is favored. To maximize liquid yield, biomass is generally quickly heated at an intermediate temperature 500°C-600°C and under relatively high heating rates with the main product as bio-oil (60-70%), char (10-15%), and gas (15-20%).



- As $\Delta t_{@T}$ ↑: Gas ↑ Oil ↓
- As Δt_H ↑: Char ↑ Oil ↓
- As Δt_Q ↑: Gas ↑ Oil ↓

Figure 1 Optimization of liquid yield in Fast Pyrolysis Process

In terms of particle size or dimensions, only a few studies have been done to compare feed size to pyrolysis yield with specific feed dimension such as length or thickness. Most of the studies on relations between particle dimension and pyrolysis liquid yield were done on a smaller system and couldn't show significant effect on particle size on the yield [5]. Bridgewater et al suggested that attrition of larger feed particles to smaller sizes from an interaction with sand bed particles resulted no significant change in bio-oil yield [6]. This current study examined the correlation between varying feed length and liquid yield and quality.

<u>Equipment</u>

PNNL's fast pyrolysis system is a continuous bench-scale system capable of feeding 1 kg/h of biomass, and capable of rapidly heating biomass to 450-550°C using nitrogen gas (Figure 2 and Figure 3). Controlled gas flow enables control of vapor residence time in the reactor, nominally less than two seconds for optimum liquid yield. The system is also equipped with an integrated hydrocarbon quench to ensure immediate cooling of pyrolysis vapors. A series of separators are then designed to capture the quenched products.

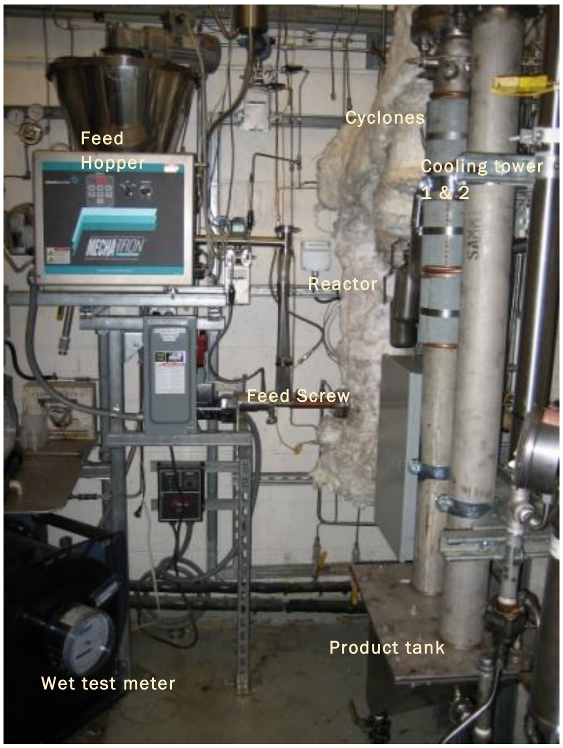


Figure 2 Overview of fast pyrolysis system at PNNL

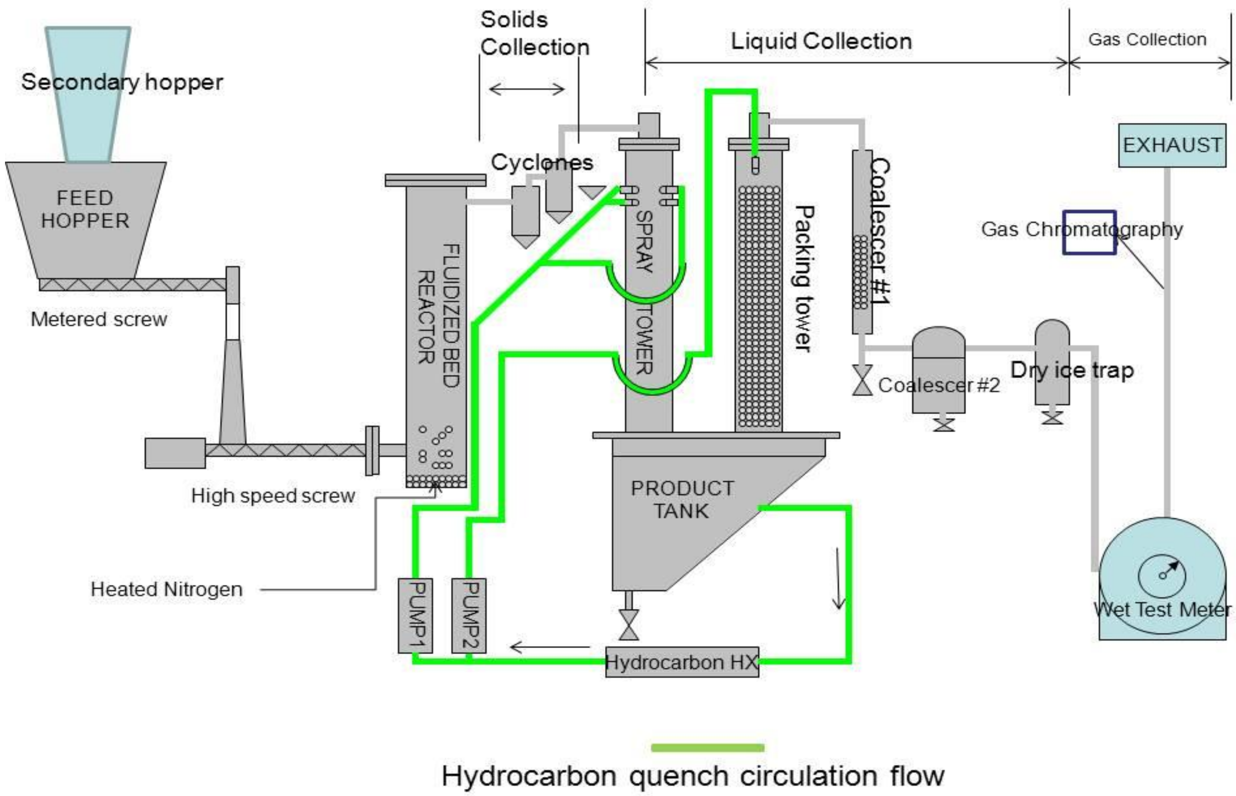


Figure 3 Diagram of fast pyrolysis process at PNNL

Feed Hopper: A sealed, conical mass flow hopper system with a low speed metering screw leading to a water-jacketed high speed screw.
Secondary hopper: An attachment unit to help re-feed biomass continuously into the hopper under pressure.
Reactor: Fluidized bed with glass media. The reactor uses a temperature controller to maintain the bed at the target operating temperature. On the third test with largest particle (2x2x8 mm), we installed a reducing sleeve to cut the vapor residence time from 1.6 to 1.3 seconds.
Cyclones: Two identical cyclones in series. The exit line from cyclone 2 has been fitted with an internal thermocouple to report vapor temperature. The line is heat traced to prevent built-up.
Cooling Tower 1: Empty spray column also functions as a condenser, equipped with perpendicular nozzles using Isopar V hydrocarbon as quench liquid for liquefaction of pyrolysis vapors.
Product Tank: Angled tank, with internal weirs for gross separation of bio-oil from recirculating Isopar.
Cooling Tower 2: Packed with plastic rings and sprayed with countercurrent flow of Isopar.
Coalescer#1: Room temperature coalescer.
Coalescer#2: 5um pleated stainless steel cartridge filter at room temperature. This polishes the remaining oil from the exhaust gas.
Dry ice trap: packed with mixed ceramic and glass wool immersed in rice-type dry-ice.
WTM: Wet test meter for measuring exhaust gas volume.
Gas Chromatography: Flame Ionization and Thermal conductivity detector-equipped gas chromatography.

Flow description

Feed was loaded into the hopper prior to the beginning of the experiment. As the system was heated to operating temperature, heated nitrogen was continuously fed through another port at the bottom of the reactor. After the system reached the target temperature, biomass was fed continuously through a metered screw at a pre-calibrated feed rate, nominally at 1 kg/h. A second screw system continuously injected the feed to the bottom of the fluidized bed reactor. As the biomass entered the system, it rapidly heated to 480°C undergoing thermal decomposition to vapor, non-condensable gases and solids (Figure 2 and Figure 3). The offgas is subjected to multiple separation stages. First, the majority of char is captured at the cyclones. Next, the offgas is quenched in the cooling towers through an Isopar V hydrocarbon spray. This condenses the vapors into bio-oil and scavenges some of the aerosols formed. Last, cooled offgas is subjected to aerosol polishing and a dry ice trap to collect any lighter fractions of the bio-oil. The non-condensable gases are then measured by a wet test meter prior to exiting to the stack.

Methods

Feed handling

Crumbles™ products received by PNNL to be tested were de-barked Douglas fir wood chips that originated from wood . There were 5 batches that consisted of 2x2x2mm, 2x2x4mm, 2x2x8mm, 2x2x12mm, and 2x2x16mm particle sizes shown in Figure 4. Feed was kept in dry and cool storage prior to testing,

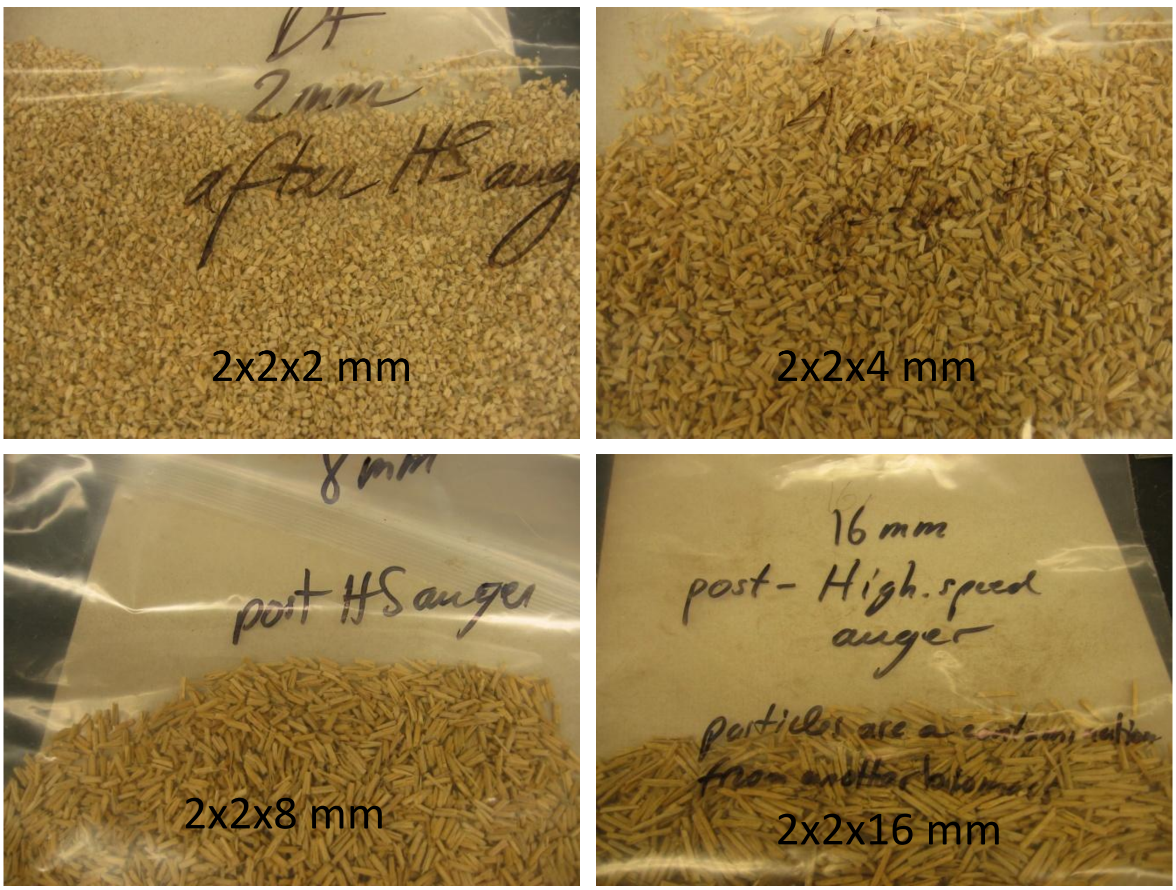
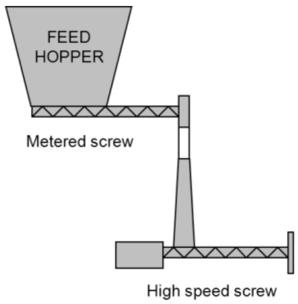


Figure 4. Crumbles™ Particles tested

Feed screening test

Prior to the main pyrolysis test, an initial screening test of the feed was done to ensure particle compatibility with the current feeding system for PNNL's pyrolysis system and to also confirm that the feed system would not substantially reduce the particle size. This was necessary to reasonably confirm that the original particle size was actually being fed into the pyrolysis reactor. The Accurate Schenk hopper and feeding system was designed to handle relatively uniform saw dust feed below 2mm. The test was done by feeding a small batch of feed (300-g or less) in to the dual stage screw system in the hopper.

Table 1. Summary of initial feed testing on the Fast pyrolysis system.



Feed Type	Metering screw	Metering and High Speed Screws
2x2x2mm	Pass	Pass
2x2x4mm	Pass	Pass
2x2x8mm	Pass	Torque caused screw slip
2x2x12mm	Not tested	Not tested
2x2x16mm	Pass	Torque caused screw slip

These initial screening tests confirmed that the feed system could reasonably feed the particles into the reactor and did not substantially reduce the feed particle size. In this test, it appeared that the narrow clearances on both the metered auger and the high speed auger resulted in additional friction and caused some compression of the feed. This was most pronounced at the high-speed auger which was designed to be high speed but low torque. However, there was no evidence of fines during the initial screening tests of the feed low feed rates. However, as the feed rate was increased to 1 kg/h fines from attrition were visible, but at an insignificant amount, suggesting that the feed was holding its integrity prior to entering the reactor.

Subsequent testing with the hopper full of each feed resulted in jamming the hopper stirrer with the x4 and x8 feeds, but not with the x2 feed. This is not a finding from this report, as the hopper was designed for handling powders. This resulted in erratic feed delivery, which is detrimental to maintaining consistent temperature in the pyrolysis reactor. The jamming was occurring at a low clearance pass between the stirrer and a structure bar. Thus, the larger feeds were processed with the main hopper partially filled, and a secondary hopper was used to periodically refill the main hopper as shown in Figure 3. This method allowed for consistent feeding of the x4 and x8 feeds..

However, the x12 and x16 feeds caused complete failure of the internal stirring system and were unable to be processed in this system. Thus, only actual pyrolysis tests with select feed sizes (2x2x2, 2x2x4 and 2x2x8 mm) were conducted. Again, this is not a finding from the experiment, only that different equipment would be needed to handle the feed at the bench scale.

Analysis

Bio-oil from the product tank, cooling towers, and coalescing filters were combined for sampling and analysis. Analysis of carbon, hydrogen, nitrogen was performed by ASTM D5373/D5291 and sulfur by D4239/D1552, The oxygen content was calculated by difference. Bio-oil moisture analysis was conducted using the Karl-Fischer titrimetric method (ASTM D 1744) and ash content was determined using a vacuum oven. Biomass and char solids were also analyzed for their elemental composition using the above methods. Moisture analysis on solids was done by drying at 105°C overnight. Gases were analyzed via gas chromatography.

For the x4 and x8 feeds an abnormal amount of solids were observed in the bio-oil from the product tank making full collection problematic. As a result, both liquid and solids from the main tank were collected through multiple solvent rinsing steps. In order to complete the mass balance, solids analysis in bio-oil was determined by ASTM D7579-09 to determine wt% of char contaminating the product oil. This char/oil split was then used to estimate the mass of char lost to the product tank. These steps were more exhaustive than the standard oil recovery procedure which relies on gravimetric oil collection which can lead to slightly lower recovery due to tank and line heel.

Results

Pyrolysis tests were performed with the parameters shown in Table 2 which also includes a comparative test using <2mm Douglas Fir saw dust prepared from commercially available pellets in a separate effort reported as FP030. All feeds were tested under similar operating conditions with exception of the x8 feed which was processed at reduced vapor residence time and reduced feed rate due to difficulty of feeding the larger particles. Feeds were processed in order of size from smallest to largest. As feed size increased, the difficulty of the experiment also increased, resulting in shorter tests

Table 2. Run parameters for the biomass evaluation.

Run ID:	FP030	FP033	FP034	FP038
Feed rate (Kg/h)-actual	1.0	1.0	1.2	0.7
Feedstock Size	<2mm saw dust	2x2x2 mm	2x2x4mm	2x2x8mm
Feed weight (g)	5023.6	4454.0	4857.1	2036.8
Residence time (s)	1.6	1.6	1.6	1.3
Run on feed (h)	4.8	4.4	4.0	2.9
Temperature (°C)	480	480	480	480

Results for the fast pyrolysis test are given in Figure 5

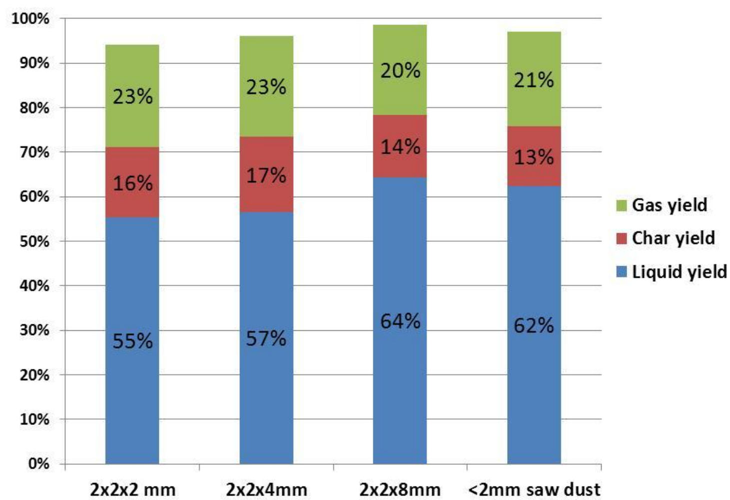


Figure 5. Comparison of mass yields from fast pyrolysis

Below, in Table 3, both as-reported and normalized mass yields are shown.   Table 3 demonstrates the composite bio-oil quality.

Table 3 As-reported and normalized wt% yields of bio-oil

	T(°c)	Res. Time (s)	As-reported Yield			Normalized Yield		
			oil	**char**	**gas**	**oil**	**char**	**gas**
Douglas Fir (2x2x2mm)	480	1.6	55%	16%	23%	61%	16%	23%
Douglas Fir (2x2x4mm)	480	1.6	57%	17%	23%	61%	17%	23%
Douglas Fir (2x2x8mm)	480	1.3	64%	14%	20%	66%	14%	20%

Normalization was performed on the data by assuming that the missing mass was due to the difficulties in collecting the product oils from the main tank. This was performed on the basis that the very rigorous cleanout method used to handle the x8 feed bio-oil where the system was solvent rinsed demonstrated the highest mass balance. That and the char and gas data are statistically similar among all three tests, with only the liquid recovery as an outlier for the smaller feeds.

Thus, the gas and char yields are essentially similar for all three feed types tested on the as-reported basis. On a fully normalized basis, this results in the oil yield being remarkably similar as well. Any differences in the yields reported may essentially be due to the vapor residence time changes and operational and experimental variation. Thus the slightly higher oil yield in the x8 feed is most likely due to the shorter residence time, consistent with research that pyrolysis reaction time is best kept short to minimize secondary reactions to gas [6].

Thus, we believe that there is no strong evidence that varying the Crumbles™ particle length up to 8mm is detrimental in the overall liquid yield, which is within normal ranges seen for other woody feedstock that have been tested.

Table 4 Composite Oil Elemental Analysis of Bio-Oil Product

Feed	Dry Basis Composite Oil			Moisture
	C	H	O	
2x2x2	59	6	35	19
2x2x4	59	7	34	15
2x2x8	60	6	34	23

Product oil elemental analysis is reported in Table 4. The carbon, hydrogen, and oxygen contents of the oils collected are similar, as expected from the same feedstock. There are differences in the final bio-oil moisture content of the composite oils, however this is frequently due to a combination of variations in the liquid collection systems, It can be concluded from these results that the elemental analysis of the bio-oil produced does not change with feed particle length for this testing.

Table 5. As-reported elemental analysis of gas and char, and elemental balance.

	T(°c)	Res. Time (s)	Char			Gas			Elemental balance		
			C	H	O	C	H	O	C	H	O
Douglas Fir (2x2x2mm)	480	1.6	69%	3%	13%	40%	4%	56%	91%	68%	70%
Douglas Fir (2x2x4mm)	480	1.6	79%	3%	8%	44%	5%	50%	99%	79%	64%
Douglas Fir (2x2x8mm)	480	1.3	80%	4%	12%	41%	4%	54%	95%	72%	66%

As reported elemental analysis of the gas and char and the elemental balance are shown in Table 5 for each experiment. For the char measurements, the elemental balance for each char appears to be low. This is possibly a function of in-homogeneity in the analysis or sampling. In addition, the overall elemental balance for the feed and products also appears low. Thus, the char data was normalized to 100% and shown in Table 6.

Table 6. Normalized yield of gas and char as well as elemental balance.

	T(°c)	Res. Time (s)	Char			Gas			Elemental balance		
			C	H	O	C	H	O	C	H	O
Douglas Fir (2x2x2mm)	480	1.6	81%	4%	15%	40%	4%	56%	95%	69%	71%
Douglas Fir (2x2x4mm)	480	1.6	88%	3%	9%	44%	5%	50%	102%	80%	64%
Douglas Fir (2x2x8mm)	480	1.3	84%	4%	12%	41%	4%	54%	96%	73%	67%

Normalization of the char demonstrates a tighter elemental balance for carbon, but there is not closure in the hydrogen and oxygen numbers. This is not surprising as it is difficult to collect or retain all of the water vapor during operation of the system with the high inert gas sweep required for fluid bed operation.

The gas analyses show low variance in relative carbon, hydrogen and oxygen contents among feeds, and the minor variances do not appear to trend with feed size. This data, while it has some variability and assumptions built in, does not suggest that there are measureable trends observed that correlate with the differences in the feeds.

Conclusion

The key finding from this effort is that there appear to be no significant trends in oil yield and composition that correlate with the feed size for the materials tested between the 2x2x2 and the 2x2x8 particles.

This is after demonstrating confidence that the intact particles were delivered to the fluid bed reactor whole based on preliminary testing with the particles, ensuring that the reaction was observed on the particles in their stated configuration. However, feed particle sizes in the 12mm and 16mm were not tested due to limitations of the feed handling system. Therefore it is not known if differences in pyrolysis performance would be seen for these longer particle lengths.

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