TASK 34

Pyrolysis of Biomass

Technical Report No. 1

Lignin fast pyrolysis:
Results from an international collaboration

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Lignin fast pyrolysis: Results from an international collaboration

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ABSTRACT
An international study of fast pyrolysis of lignin was undertaken. Fourteen laboratories in eight different countries contributed. Two lignin samples were distributed to the laboratories for analysis and bench-scale process testing in fast pyrolysis. Analyses included proximate and ultimate analysis, thermogravimetric analysis, and analytical pyrolysis. The bench-scale test included bubbling fluidized bed reactors and entrained flow systems. A concentrated lignin behaved like a typical biomass, producing a slightly reduced amount of a fairly typical bio-oil, while a purified lignin material was difficult to process in the fast pyrolysis reactors and produced a much lower amount of a different kind of bio-oil. It was concluded that for highly concentrated lignin feedstocks new reactor designs will be required other than the typical fluidized bed fast pyrolysis systems.

KEYWORDS:
Fast pyrolysis; lignin; bio-oil; fluidized-bed

1 INTRODUCTION

Lignin is the second most abundant biomass component and the only renewable aromatic resource in nature. Lignin pyrolysis has been studied for almost 100 years with the focus on two different aspects: (1) unravelling the structure of the aromatic biopolymer, and (2) production of monomeric phenols. Good overviews on both pathways covering the years 1920-1980 are given by Goldstein [1] and Allan and Mattila [2]. In the past 25 years little attention has been paid to the use lignin as chemical resource. This time period has been recently reviewed by Amen-Chen et al. [3]. Lignin was rather used for studying degradation mechanisms by advanced pyrolysis methods combined with hyphenated separation and detection systems (GC/MS). The current understanding of the influence of pyrolysis conditions on the kinetics of lignin pyrolysis was recently investigated by Britt et al. [4]. Only recently, with the upcoming focus on biorefineries, lignin has gained new interest as chemical resource, as again the supply of fossil feedstocks is becoming more and more insecure and expensive.

On the other hand, in the past 20 years fast pyrolysis techniques have been developed for the conversion of whole plant biomass into a liquid (bio-oil) using mainly fluidized bed reactors from laboratory to demonstration scale [5].

Therefore, the objectives of this international study were to attempt to carry out fast pyrolysis of several lignin samples and analyze the products in order to firstly establish the potential for this method of lignin processing and secondly to compare procedures and results. The

research was carried out in the IEA Bioenergy Agreement Pyrolysis Task 34 - PyNe. This paper summarises results from the tests performed in the participating laboratories.

Fourteen laboratories agreed to participate in the project and each was supplied with samples of two lignins. The participants included:

- Aston University, UK
- Pacific Northwest National Laboratory, USA
- vTI-Institute of Wood Technology and Wood Biology, Germany
- Cirad- Forêt, France
- ECN, The Netherlands
- Forschungszentrum Karlsruhe GmbH, Germany
- IFP-Lyon, France
- National Renewable Energy Laboratory, USA
- STFI-Packforsk AB, Sweden
- University of Napoli, Italy
- University of Nottingham, UK
- University of Twente, The Netherlands
- USDA Eastern Regional Research Center, USA
- VTT Technical Research Centre of Finland, Finland

Of the 9 laboratories with small fast pyrolysis reactor systems who attempted fast pyrolysis of the lignin feedstocks, seven laboratories provided fast pyrolysis processing results. The others reported failure to obtain any meaningful results arising from handling problems at high temperature. Other laboratories provided complementary results of thermogravimetric analysis (TGA and DTA) and other analytical pyrolysis methods.

Two lignin feedstocks were provided to the participating laboratories along with a specification of requested analyses as provided in Table 1 and a requested pyrolysis test data sheet, shown in Table 2. Two types and sources of lignin were evaluated:

1. A sulfur-free lignin obtained from annually harvested non-woody plants (wheat straw and sarkanda grass *Saccharum munja*). The pulping method was the soda pulping process (aqueous NaOH). It was a highly purified lignin recovered by precipitation, followed by washing and drying.
2. A concentrated lignin material which was a residue from ethanol production by weak acid hydrolysis of softwood. This lignin contained a significant fraction of cellulose and hemicellulose degradation products and was not purified.

Table 1. Analytical specification for lignin pyrolysis tests

	Method	**Reporting unit**
Feedstock		
Moisture content of lignin	Dry at 60 C in vacuum oven	wt.% moisture based on as-received lignin
Product Bio-oil		
Water content	Karl Fischer Titration	wt.% water based on wet bio-oil
Viscosity	capillary or rotary viscosimeter, 2 temp. @ 20 and 40°C	cSt @ 20°C and 40 °C

Solids in bio-oil	insolubles in ethanol, filter pore size 3µm or lower	wt% based on wet oil
pH	use pH-meter	pH unit
Elemental analysis	elemental analyzer (complete oxidation)	wt%C, wt%H, wt%N, wt%O, based on wet bio-oil
Pyrolytic lignin	add 60 ml oil to 1 L of ice-cooled water under stirring, filter and dry precipitate below 60 C	wt% based on wet bio-oil
Gas Chromatography	column type DB 1701 dimensions: 60m x 0.25 mm film thickness: 0.25 µm injector: 250 °C, split 1:30 FID detector: 280 °C oven programme: 45 °C, 4 min const., 3 °C/min. to 280 °C, hold 20 min. sample conc.: 6 wt%, solvent acetone	

Table 2. Requested Data from fast pyrolysis tests

	RESULTS	**Method used**	**Difficulties and Suggestions**
SAMPLE NAME:			
DATE of ARRIVAL:			
MOISTURE CONTENT of LIGNIN	wt%		
PYROLYSIS REACTOR description			
FEEDER description			
BED type			
CARRIER GAS			
BIO-OIL COLLECTION system			
TEMPERATURE	°C		
RESIDENCE TIME at temperature	seconds		
BIO-OIL YIELD	wt%		
CHAR YIELD	wt%		
GAS YIELD	wt%		
WATER CONTENT	wt.% (based on bio-oil as produced)		
VISCOSITY of BIO-OIL	cSt @ 20 °C		
	cST @ 40 °C		
SOLIDS based on wet bio-oil	wt.%		
pH			
ELEMENTAL ANALYSIS	wt.% C		
(based on bio-oil as produced)	wt.% H		
	wt.% O		
PYROLYTIC LIGNIN	wt.% (based on bio-oil as produced)		

2 FEEDSTOCKS AND CHARACTERISTICS

Two types and sources of lignin were evaluated:

1. The ALM lignin, manufactured by Asian Lignin Manufacturing India Pvt. Ltd., SCO 26-27, 1st Floor, Sector 8-C, Chandigarh - 160009, INDIA, was a sulfur-free lignin obtained from annually harvested non-woody plants (wheat straw and sarkanda grass *Saccharum munja*). It was a co-product in the manufacture of pulp for printing and writing papers. The pulping method was the soda pulping process using aqueous NaOH. The properties of the ALM lignin, provided by the manufacturer, are presented in Table 3. The ALM lignin was supplied via Granit SA, Lausanne, Switzerland.

Table 3. ALM lignin properties[1]

Solids Content	95+%
Composition (dry basis)	>94% Lignin, 4% Protein, <2% Hemicelluloses Sugar, <0.2% Cellulose, <4% ash
pH (10% slurry)	2.5-4
Functional groups	8-10% Carboxyl, 2-3% Aromatic OH, 3-4% Aliphatic OH
Particle size	Approximately 100-110 microns
Molecular weight	M_N 1000 daltons, M_W 2500-3400 daltons
Appearance	Low odour, brown powder
Thermal Behavior	Softening temperature ~ 120-180^{0}C
Bulk density	450 kg/m^3
Solubility	Very low solubility in water, high solubility in aqueous alkali, CMF, 2-methoxyethanol, furfuryl alcohol, 90% acetone/10% H_2O

2. The ETEK lignin from Sweden was a residue from ethanol production by a 2-stage weak acid hydrolysis of softwood. This lignin was not a high-purity product but contained carbohydrate polymer degradation products (up to 50% cellulosic) as well as lignin.

The lignins are shown in Figure 1.

Figure 1. ALM lignin (left) and ETEK lignin (right)

[1] http://www.asianlignin.com/pages/products1.html [6]

3 ULTIMATE AND PROXIMATE ANALYSIS

The elemental and ash content analysis for both types of lignin is presented in Table 4. The Asian lignin had higher carbon and lower oxygen content than the ETEK lignin, which correlates with a higher lignin content. The ALM lignin also had significantly higher ash content than the ETEK lignin as expected due to its origin from straw and grass.

Table 4. Elemental and ash content analysis

wt %	Lab	C	H	N	S	O	Total	Ash
ALM	ALM	61	7	0.9	<0.03	31	99.9	<4%
ALM	1	62.32	5.91	0.66	<0.10	31.01#	100.00	1.31
ALM	8	63.7	6.3	1.3	ND	28.7#	100.0	1.2
ALM	9	63.81	5.82	1.21	0.31	26.81	97.96	1.15
ALM	13	62.35	6.12	2.63	ND	22.90#	94.0	6
ALM	5	62.05	5.95	ND	ND	32.00#	100.00	ND
ETEK	ETEK	54.28	6.11	ND	0.17	39.44#	100.00	0.2
ETEK	1	53.62	5.82	<0.10	<0.10	40.37#	100.00	0.5
ETEK	8	58.0	5.9	0.2	ND	35.9#	100.0	0.2
ETEK	9	57.18	ND	0.12	0.19	ND	ND	0.62
ETEK	13	51.33	5.7	1.55	ND	37.42#	96.0	4
ETEK	5	53.71	6.03	ND	ND	40.26#	100.00	ND

by difference

Some inorganic components including sodium, calcium, magnesium, potassium and silica were determined in ETEK and ALM lignins. Concentrations of these components as provided by Laboratory 9 are given in Table 5.

Table 5. Inorganic components determined in ETEK and ALM lignins

Inorganic component, ppm	ETEK lignin	ALM lignin
Na	25	745
K	220	439
Mg	<20	192
Ca	221	243
Si	<20	165

4 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is a pyrolytic method which has often been applied to biomass and biomass components. However, TGA is performed in a heating environment very different from fast pyrolysis. The slow heating rate used is an attempt to allow the chemistry in the sample to equilibrate as it moves through the temperature range of interest. Fast pyrolysis is inherently a non-equilibrium process.

All the data sets can be compared in tabular form as shown in Table 6. The heating rate affects the outcome with the slowest heating rate (longest residence time) achieving the highest volatility. None of these heating rates even approaches that seen typically in fast

pyrolysis (300-1000°C/second) and should not be considered as a reasonable representation of that chemistry. It is also interesting to compare these TGA curves with those in the literature [6] for other biomass and biomass components. The ALM curve appears very similar to a lignin curve, while the ETEK shows a stronger correlation to a cellulose or a biomass with a large cellulose component. However, cellulose would be expected to leave a 10% residue or less at 500°C, and the higher residue amount from these samples supports the lignin analysis.

Table 6. Comparison of TGA data

	1 (25°C/min)	2 (100?°C/min)	3 (5°C/min)	6 (10°C/min)
ALM (dry basis)				
volatiles to 500°C	56.9	54.8	59.5	48.6
total volatiles (temp)	66.9@900°	66.5@1384°	59.5@500°	59.6@700°C
ETEK (dry basis)				not analyzed
volatiles to 500°C	68.8	52.1	70.5	
total volatiles (temp)	76.6@900°	57.0@1384°	70.5@500°	

5 ANALYTICAL PYROLYSIS

The methods of analytical pyrolysis have also been applied to biomass materials by some of the participants. The resulting product can approach that of a fast pyrolysis reactor with careful attention to the instrumental operating conditions. An understanding the product components can be used to evaluate the structure of the biomass feedstock.

The significant amount of carbohydrate (cellulose and hemicellulose) degradation products (39.46%-60.02%), such as levoglucosan, identified in the ETEK's chromatograms, support the assumption that the ETEK lignin is not a pure lignin, in contrast to the ALM lignin that contains very small amounts. The highest amount of phenols was identified in the ALM lignin's chromatogram. The highest amount of guaiacols was identified in the ALM lignin's chromatogram along with a large fraction of syringols, suggesting herbaceous biomass source. The lack of syringols in the ETEK chromatograms suggests the softwood biomass source.

As can be seen from the results, there are substantial differences in the pyrolysis product composition between the two samples. The ETEK lignin produces products typical of a softwood lignin. The most significant difference between the samples is the presence of high amounts of carbohydrates in the ETEK lignin whereas the ALM lignin appears to be a more pure lignin sample. Some syringyl units from herbaceous lignin are also found in the ALM lignin products, but not in the ETEK lignin products.

The analytical pyrolysis results from the four participating laboratories consistently show:

- ETEK lignin contains a substantial amount of non-lignin carbohydrate
- ALM lignin is either herbaceous- or hardwood-derived based on syringyl components
- ETEK lignin lacks the syringols and therefore is softwood derived.

- Pyrolysis of lignins at 600°C or higher produces a much larger portion of volatile components in contrast to biomass pyrolysis which can be effectively analysed at 500°C

6 FAST PYROLYSIS EXPERIMENTS

Seven laboratories carried out and reported fast pyrolysis experiments in bench-scale reactor systems. Feeding modifications were required in many cases. Two other laboratories were not able to effectively feed the ALM lignin into their reactors and did not try the ETEK lignin.

6.1 Laboratory 1

The 150 g/h test rig, presented in Figure 2, consisted mainly of a pneumatic feeder, a bubbling fluidized bed reactor and a liquid product collection system. Nitrogen was used as the fluidized gas and sand (150 g) with particle size in the range of 355 to 500 μm as the fluidizing and heat transfer medium. The reactor was placed in an electric muffle oven to provide the heat required for the process.

When the lignin was fed into the bed, heat was transferred from the sand to the biomass particles by conduction and convection and the biomass particles decomposed to vapours including aerosols, water and non-condensable gases and generated the residue solid char. The product mixture was carried out of the reactor through the cyclone where the solid was separated and collected in the char pot. The vapours together with some char fines that were not removed by the cyclone passed through a water-cooled condenser where they were partially condensed. The liquid together with the uncondensed vapours flowed into the electrostatic precipitator (ESP) where most of the uncondensed vapors together with aerosols and char fines were captured by the electrostatic charge supplied.

The liquid mixture was collected in a round bottom flask (oil pot 1) located under the ESP in full. The water and light volatile compounds such as formaldehyde, acetaldehyde and some ketones with low boiling points contained in the pyrolysis vapours were condensed by using a series of two dry ice/acetone condensers (T=-30^{o}C). Some light volatiles still escaped from the dry ice/acetone condensers due to their low partial pressure because of the dilution effect of the nitrogen carrier gas. These were captured in the cotton wool filter. After the cotton wool filter the nitrogen fluidizing gas together with the non-condensable pyrolysis gases passed through a gas meter where the volume of the exit gas was recorded. Then part of the mixture was pumped into an on-line chromatograph for gas composition analysis and the rest was vented.

In the case of lignin, pneumatic feeding in the fluidized bed reactor proved impossible. As soon as the lignin reached the air-cooled feeding tube inside the fluidized-bed reactor, it melted and then partially decomposed to char resulting in a blockage. As a result, alternative batch feeding solutions were sought-after and tested, while the rest of the test rig remained unaltered. Firstly, a lock hopper configuration was tried consisting of two on/off ball valves and a nitrogen supply in between (see Figures 3). The tube connected to the reactor had a water-cooled jacket to avoid any melting of the lignin before entering the reactor. During a

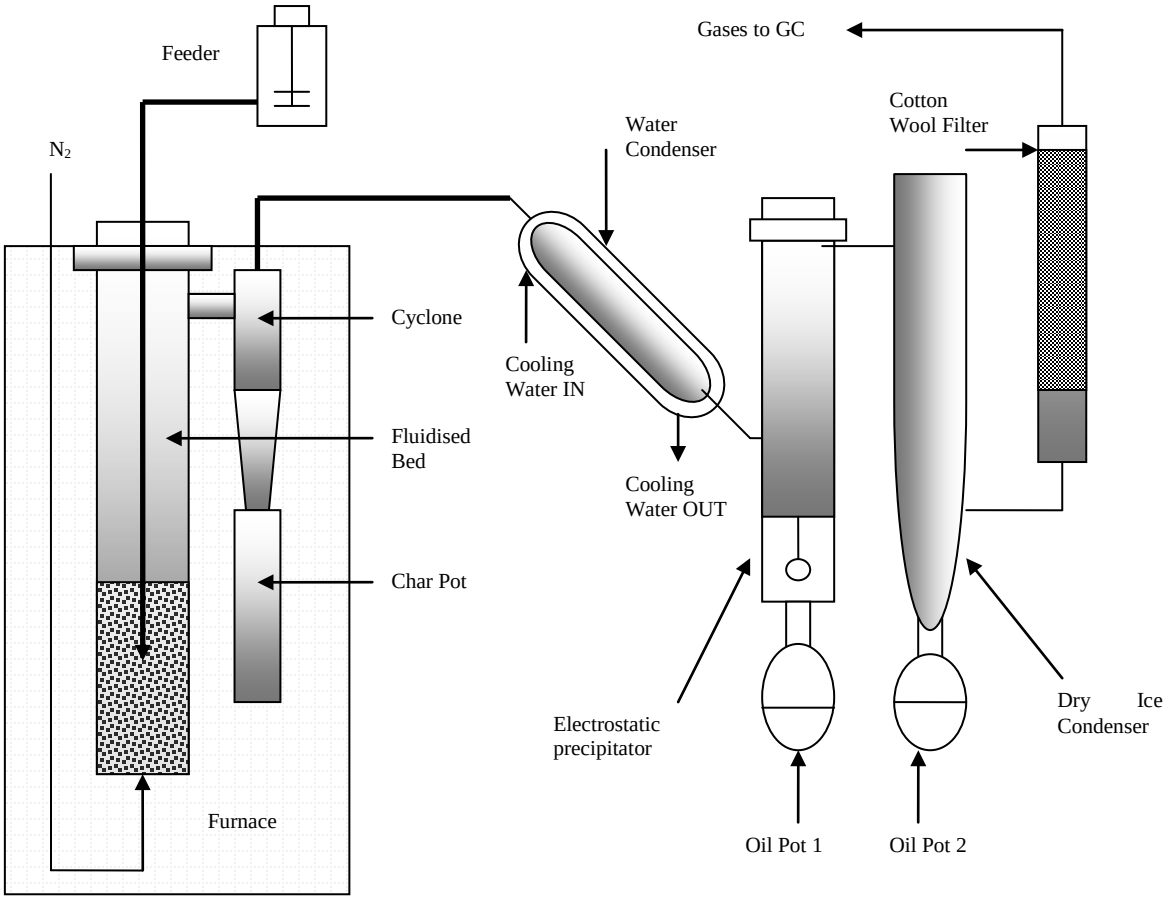

Figure 2. 150g/h fluid bed test rig

Figure 3. Lock hopper

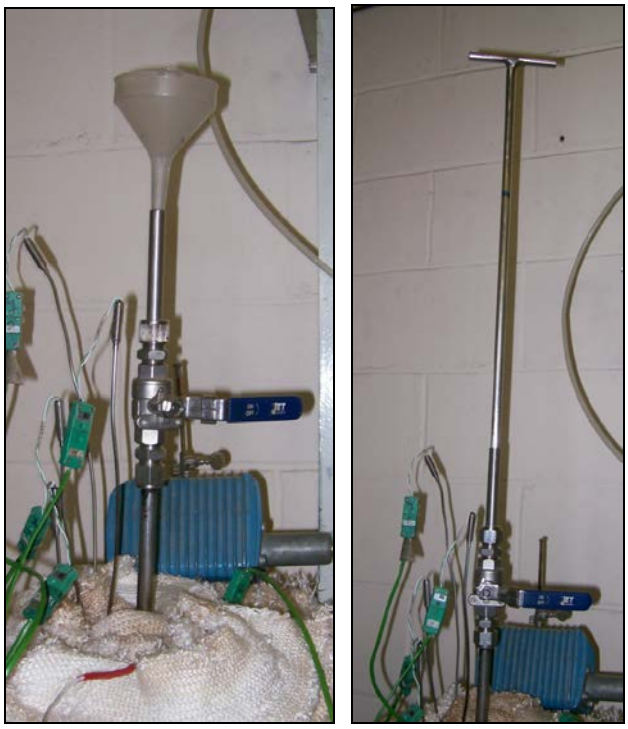

Figure 4. Single valve with push rod

test run at 530°C, 25g of Asian lignin were fed in batches of 2 to 3 g. At the end of the run some heavy tar was collected in the condenser and some partially decomposed lignin in the ESP. No char had been collected by the cyclone and no bio-oil was collected in oil pot 1. After dismantling the reactor it was observed that significant amounts of char were in the bed and they had caused bed agglomeration.

Since the first batch feeding configuration did not resolve all the problems, for example some partially decomposed lignin was found in the ESP, an alternative solution was tried. Due to the absence of any signs of melted lignin on the tube connected to the reactor, it was concluded that there was no need for a water jacket. Therefore, the configuration was simplified to one on/off ball valve and a push rod which was used to introduce the lignin inside the bed. The rod fitted exactly the diameter of the tube to avoid escape of gases and vapours (see Figure 4). A test run was conducted with the simplified batch feeding system at 530°C with Asian lignin. Only about 9g of lignin were fed due to the solidification of the fluidized bed from agglomeration of the sand and char.

The influence of the small particle size of lignin (<100 microns) in the process was two-fold. Firstly, the dusty powder created a sticky layer inside the tube increasing the resistance of the push rod and hindering feeding. Secondly, the finer particles elutriated out of the reactor before decomposition, ending up in the ESP. In order to suppress these effects, a pretreatment process, adopted from the Laboratory 3 pretreatment procedure, yielding bigger particles was employed (see Figure 5).

Another run was conducted at 530°C with the valve and push rod feeding system and the pretreated ALM lignin particles. About 100 g of lignin were fed in batches of 3g every 2 minutes. The run was stopped after 70 minutes due to the collapse of the fluidized bed caused by char and sand agglomeration. However, heavy tar was collected in the condenser and a mixture of bio-oil and partially decomposed lignin was collected in the ESP. It was noted that the lignin particles were easier to feed and the amount of partially decomposed lignin ending up in the ESP was reduced but not eliminated. Therefore the pretreatment had managed to resolve some of the problems caused by the small particle size. Still there was no char collected by the cyclone. The mass balance of this run is shown in Table 7.

Table 7. Mass balance for pretreated ALM lignin

Mass balance (dry feed basis)	g	%
Total feed less solid deposits (dry basis)	83.78	
Total pyrolysis liquids (estimated)	26.18	31.2
Organics (estimated)	16.61	19.8
Reaction water	9.56	11.4
Char	40.88	48.8
Gas	4.74	5.7
Closure		85.7

Figure 5. ALM lignin before pre-treatment (<100 microns) (left) and after pre-treatment (355 to 1000 microns) (right)

The normalized product gas composition for the run conducted with the ALM lignin particles was 43% carbon dioxide, 32% methane and 18% carbon monoxide with no hydrogen and only traces of C_2 and C_3 aliphatic and olefinic hydrocarbons.

Another run was conducted with the valve and push rod feeding system and the ETEK lignin at about 500^{o}C. About 44 g of lignin were fed. In contrast to the runs conducted with the ALM lignin, bio-oil was collected in oil pot 1 (see Figure 6) and no partially decomposed lignin was found in the ESP. However, like the runs with the ALM lignin no char was collected by the cyclone and the bed experienced sand and char agglomeration (see Figure 6), although not as extensive as that with the ALM lignin. The mass balance is shown in Table 8.

Table 8. Mass balance for ETEK lignin

Mass balance (dry feed basis)	g	%
Total feed less solid deposits (dry basis)	44.06	
Total pyrolysis liquids	25.42	57.7
Organics	19.96	45.3
Reaction water	5.46	12.4
Char	11.98	27.2
Gas	4.54	10.3
Closure		95.2

The normalized product gas composition from the run with ETEK lignin was 37% carbon dioxide, 19% methane and 39% carbon monoxide with no hydrogen and only traces of C_2 and C_3 olefinic hydrocarbons.

Char removed from the bed

Bio-oil collected in oil pot 1 from the run with ETEK lignin

Figure 6. Products from ETEK lignin

With the valve and push rod feeding system the lignin was introduced in the freeboard of the reactor. Then the coarser fraction fell on the hot sand bed, bubbled and solidified causing bed agglomeration, while the finer fraction elutriated out of the reactor before decomposition and ended up in the ESP. Consequently, an appropriate feeding system needs to be developed to avoid the elutriation of lignin out of the reactor before total decomposition. A screw feeder may resolve this problem. Moreover ways of controlling and minimizing bed agglomeration caused by the "bubbling" effect of lignin need to be investigated.

6.2 Laboratory 3

Both lignins were pyrolyzed in a bubbling fluidized-bed test facility (typical biomass feed rate 1 kg/hr, see Figure 7). This fluidized-bed test rig was not been specifically developed for

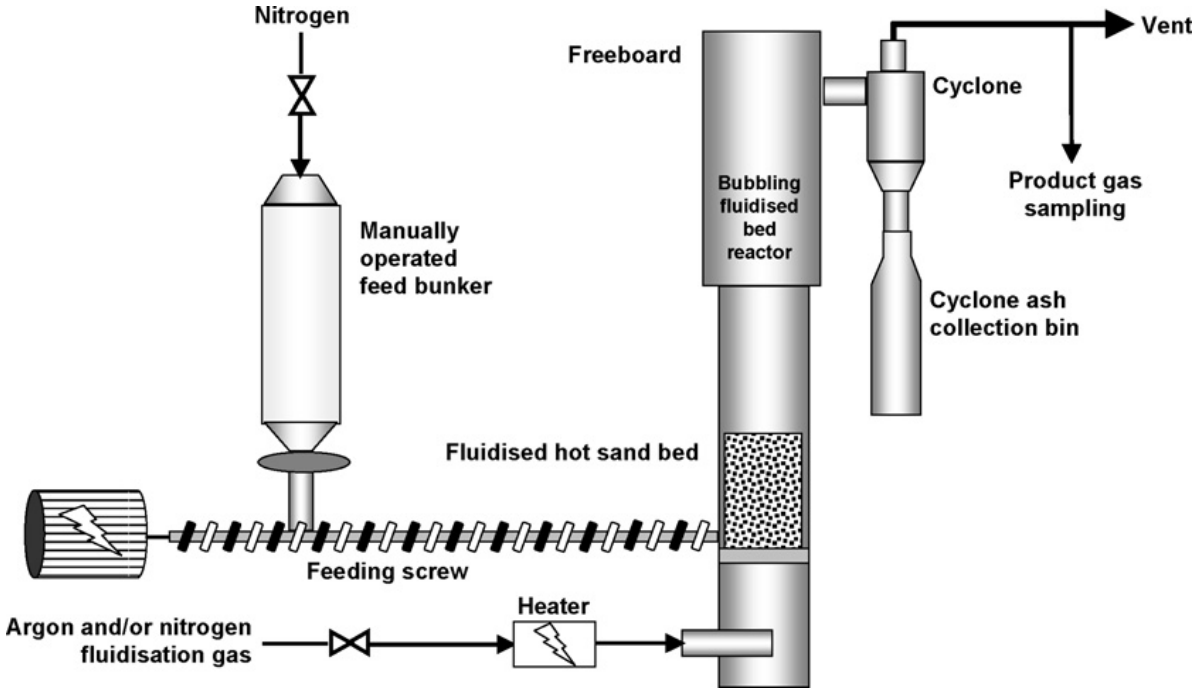

Figure 7. Schematic of the bubbling fluidized-bed test facility

fast pyrolysis. The sampling setup consisted of a high-temperature particle filter (soxhlet), teflon adiabatic cooling tube, and a series of impinger bottles in which the pyrolysis gases and aerosols were effectively trapped in a solvent (iso-propanol) as described by tarweb [8]. In addition, a bio-oil collection pot was used consisting of an approximately 0.5 liter, water-cooled, double-walled steel vessel equipped with an internal particle/aerosol trap.

To allow use of the existing feed system, the ALM lignin had been brought in a feedable form by crushing and sieving an evaporated lignin/ethanol slurry as described in Figure 8. Dried lumps of the ETEK lignin were used as received.

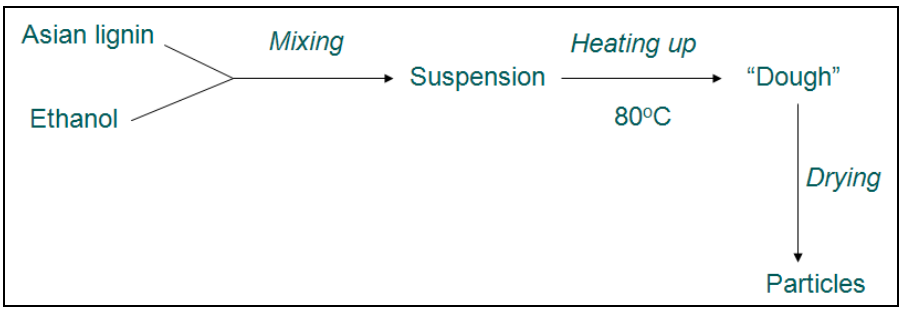

Figure 8. Flow diagram of ALM lignin pretreatment

Using a standardised methodology for measuring biomass derived tars (European certified standard) the GC/FID – GC/MS characteristics of the lignin pyrolysis-oil were assessed. The distribution of chemical products from fast pyrolysis experiments for ETEK and ALM lignin are compared in Figure 9.

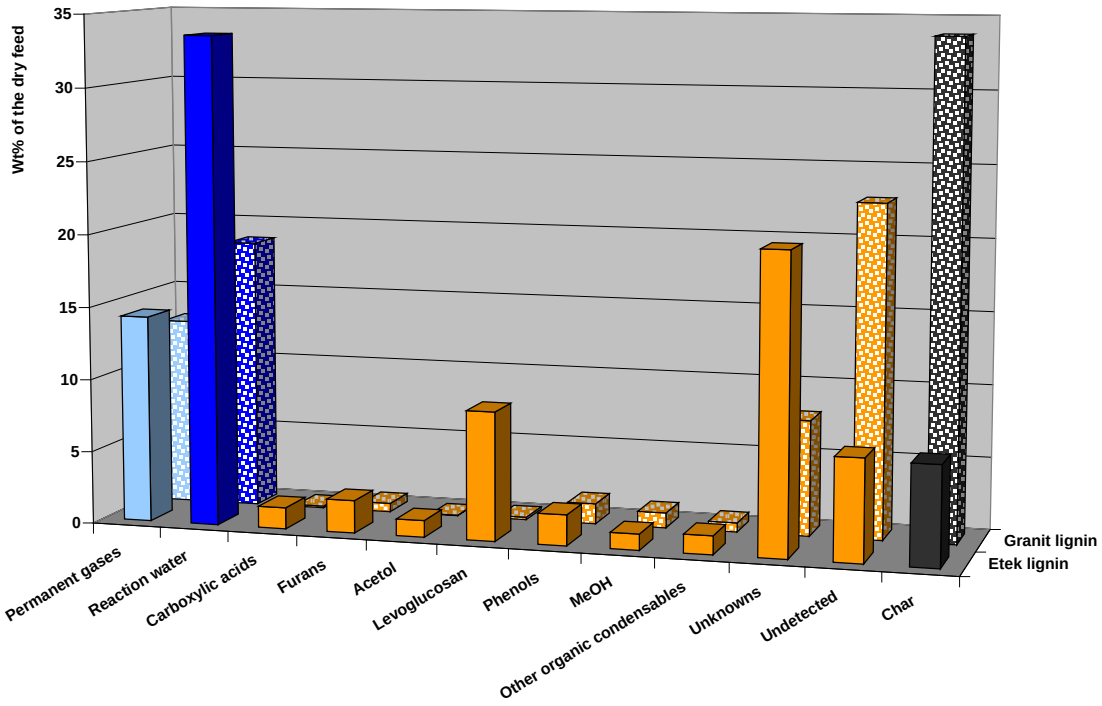

Figure 9. Comparison of fast pyrolysis products for ETEK and ALM (Granit) lignins

Pyrolysis of the ETEK lignin was successful, yielding approx. 38 wt% organic condensables of which only 1.4 wt% were identified as monomeric phenols. The mass balance closure was estimated as 93%. Pyrolysis of the ALM lignin was much more difficult due to its melting behaviour causing bed agglomeration and subsequent defluidization. In the second trial, a batch of 50 g ALM lignin was fed in a semi-continuous way with 10 g at a time. The time lapse in between two feedings was approximately 1-2 min. This feeding procedure appeared to be satisfactory, although some agglomeration could not be prevented, only slowed. The agglomerate grows until, inevitably, defluidization of the hot sand bed occurs. Large temperature gradients developed and the final situation was a poorly packed bed with a pumice-like black material sticking to the gas distribution plate and the reactor walls.

To investigate the effect of a lower reactor temperature the temperature of the sand bed was adjusted to 400°C instead of the prescribed 500°C. Table compares the yields of the GC-detectable species of the runs at 400°C and 500°C. Total organic yields are equal (11 wt% based on the dry feedstock weight) with the experiment at 400°C with approximately 4 times more identified monomeric phenols than the experiment at 500°C. This is partly due to the "more sensitive" GC/MS analysis method. Consequently, the amount of unknowns is two times smaller when compared to the results obtained with the GC/FID analysis method. The quantitation is based on peak area and is not corrected for specific response; as such, it is only approximate. For both trials, mass balances could not be calculated for various reasons (like the formation of molten-lignin-sand clumps in the bed) but were estimated to be 70-80%, at best. It was speculated that assuming that the amount of unknowns could be ascribed to (monomeric) phenolic substances, the overall amount of phenolic substances was roughly equal for both the pyrolysis experiments at 400 °C and 500 °C (approx. 8 wt%).

6.3 Laboratory 4

Initial tests in Laboratory 4 were made with the ALM lignin. Fast pyrolysis experiments at about 500^{o}C were performed in a fluidized bed reactor with an auger screw feeder. Bio-oil was collected by a collection system of four condensers followed by an electrostatic precipitator (ESP). Feeding the powder feedstock was difficult due to melting of the lignin in the non-cooled auger feeder. Pelletizing the lignin provided little improvement as the pellets broke down to a similar powder in the feeder and melted in the auger, as shown in Figure 10.

Figure 10. Auger feeder with ALM lignin plug formed between flights

Table 9. Yields of GC-detectable organics from the fast pyrolysis of ALM lignin at 400°C and 500°C

	500°C	400°C
Analysis method	GC/FID	GC/MS
	Wt% dry basis	Wt% dry basis
Methanol	0.96	2.18
Acetaldehyde	0.05	
Methylformate	0.08	
Formic acid	0.03	0.12
Acetic acid	0.08	
Propanal+furan	0.09	
Acetone+Isobutyraldehyde	0.06	0.17
Me-acetate+Et-formate	0.06	
2-Butenal	0.06	
Acetol	0.03	
1-Hydroxy-2-butanon	0.02	
Angelicalactone	0.03	
Furfural	0.29	0.20
Methylfurfural	0.03	
Furfurylalcohol	0.02	
2(5H)-Furanon	0.02	
5-hydroxymethyl-2-furaldehyde	0.06	
Levoglucosan	0.16	
3,4,5 Trimethoxytoluene	0.03	
1,2,4 Trimethoxybenzene	0.15	
Guaiacol	0.26	1.31
4-Methyl-guaiacol	0.20	0.69
4-Ethylguaiacol		0.60
Eugenol	0.02	
Iso-Eugenol	0.17	
Syringol	0.21	0.68
4-Methylsyringol		0.33
Acetosyringone		0.29
Phenol	0.40	0.41
3-Ethylphenol	0.02	
4-Ethylphenol		0.30
Pyrocatechol		0.24
Hydroquinone	0.03	
Unknowns	7.4	3.4
Total yield monomeric phenols	1.3	4.8
Total yield organic condensables	11	11

A very limited amount of bio-oil was collected in the ESP and the data is given in Table 10.

Table 10. Compounds identified in ALM lignin ESP bio-oil

RT		Grouping	Wt %
N/A	Water (Karl Fischer)		2.52
21.4	2-methyl-2-cyclopenten-1-one	Ketone	0.15
26.5	3-methyl-2-cyclopenten-1-one*	Ketone	0.32
31.8	Guaiacol	Phenol	0.53
36.6	2-methoxy-4-methyl phenol	Phenol	0.10
48.4	isoeugenol	Phenol	0.33
45.2	2,6-dimethoxyphenol	Phenol	0.51
31.0	Phenol	Phenol	4.77
33.4	o-cresol	Phenol	1.11
34.0	2,5-dimethylphenol	Phenol	0.10
35.0	p-cresol	Phenol	1.67
35.1	m-cresol	Phenol	0.99
37.2	2,4-dimethyl phenol	Phenol	0.53
38.9	3,5-dimethylphenol	Phenol	0.21
39.1	4-ethyl phenol	Phenol	1.28
39.2	3-ethylphenol	Phenol	0.20
36.9	2-ethylphenol	Phenol	0.16

A more successful fast pyrolysis experiment of ETEK lignin was also reported. Prior to pyrolysis the lignin sample was dried at 60^{o}C in air flow for 24 hours and then ground using a Wiley Mill with a 2 mm screen. Fast pyrolysis experiments at between 484 and 519^{o}C were performed in the fluidized-bed reactor with the auger screw feeder cooled with dry ice. Bio-oil was collected by the same system of condensers followed by an ESP. The product gas composition (determined by Agilent Micro GC 3000, in line) was 66% CO, 17% CH_4, 12% H_2, 5% CO_2 on a nitrogen-free basis.

Different fractions of bio-oil (collected in condensers 1-4 and ESP) were characterised using liquid GC and HPLC methods. An Agilent 6890N GC with DB-1701 column (60m by 0.25 mm with 0.25 μm film thickness) with the injector heated to 250°C was used with a 1:30 split. Analysis was made using an Agilent 5973 MSD detector. The GC oven was set for 45 °C for 40 min initially, then heated at 3°C/min to 280°C and held for 20 min. Samples were diluted in acetone. Fluoranthene was used as an internal standard. The quantitation is based on peak area and is not corrected for specific response; as such, it is only approximate. The HPLC was equipped with an Aminex HPX-87 column (300 x 7.8 mm @ 30°C) with a mobile phase of 0.007 N H_3PO_4. 1-propanol was used as an internal standard. The liquid components characterised by GC-MS and HPLC are given in Table 11.

6.4 Laboratory 5

The pyrolysis of the lignins in the normal fluidized-bed system failed in several attempts due to problems during feeding. Feeding time of only a few minutes led to either blockage of the screw feeder or loss of fluidization resulting from the formation of lignin-derived charred foam.

Table 11. Components of bio-oil obtained from ETEK lignin

Method	Compound	Grouping	Cond 1	Cond 2	Cond 3&4	ESP	TOTAL
	% of Total Bio-oil		12.35	8.55	6.18	72.92	100.00
KF	water	Water	2.3	2.04	4.09	3.63	3.36
HPLC	acetic Acid	Acid		0.73	0.61	0.18	0.23
GC	propionic Acid	Acid		X	X		X
GC	hydroquinone	Alcohol	X	X		X	X
GC	toluene	Aromatic				X	X
GC	indene	Aromatic		X		X	X
GC	naphthalene	Aromatic	X	X	X	X	X
GC	methyl naphthalene	Aromatic	X	X	X	X	X
GC	1-ethyl-4-methoxybenzene	Ether	X	X	X	X	X
GC	butyrolactone	THFuran	X	X	X	X	X
GC	furfural	Furan	0.17	0.2	0.26	0.31	0.28
GC	furfuryl Alcohol	Furan		0.1	0.18	0.02	0.03
GC	1-(2-furanyl)-ethanone	Furan	X	X	X	X	X
GC	4-methyl-5H-furan-2-one	Furan	X	X	X	X	X
GC	2-methyl-2-cyclopenten-1-one	Ketone		0.11		0.02	0.02
GC	3-methyl-2-cyclopenten-1-one	Ketone		0.12		0.04	0.04
GC	corylone	Ketone	X	X	X	X	X
GC	3-ethyl-2-cyclopenten-1-one	Ketone		X	X	X	X
GC	2,3-dihydroxy-1H-inden-1-one	Ketone	X	X		X	X
GC	hydroxyacetaldehyde	Oxygenates	X	X	X	X	X
HPLC	acetol	Oxygenates	0.58	2.29	4.79	2.74	2.56
GC	4-hydroxy-4-methyl-2-pentanone	Oxygenates	0.09	0.1		0.08	0.08
GC	guaiacol	Phenol	0.36	0.43	0.36	0.38	0.38
GC	2-methoxy-4-methyl phenol	Phenol	0.32	0.37	0.25	0.31	0.31
GC	eugenol	Phenol	X	X	X	X	X
GC	isoeugenol	Phenol	0.24	0.27	X	X	X
GC	2,6-dimethoxyphenol	Phenol	X	X	X		X
GC	phenol	Phenol	0.68	0.86	0.9	0.62	0.67
GC	o-cresol	Phenol	0.30	0.36	0.33	0.28	0.29
GC	2-hydroxy-5-methyl benzaldehyde	Phenol	X	X	X	X	X
GC	p-cresol	Phenol	0.33	0.42	0.31	0.27	0.29
GC	m-cresol	Phenol	0.30	0.37	0.28	0.27	0.28
GC	2,4-dimethyl phenol	Phenol	0.27	0.28	0.21	0.25	0.25
GC	2,4,6-trimethyl phenol	Phenol	X	X	X	X	X
GC	3,5-dimethyl phenol	Phenol	0.13	0.05	0.02	0.09	0.09
GC	4-ethyl phenol	Phenol	0.12	0.16	0.09	0.12	0.12
GC	3-ethyl phenol	Phenol	0.06	0.07	0.04	0.05	0.05
GC	2-ethyl phenol	Phenol	0.05	0.06	0.04	0.04	0.04
GC	4-ethyl-3-methyl phenol	Phenol	X	X	X	X	X
GC	vanillin	Phenol	X	X	X	X	X
GC	2,3-anhydro-d-mannosan	Sugar				X	X
GC	1,4:3,6-dianhydro-α-d-glucopyranose	Sugar		X	X	X	X
HPLC	levoglucosan	Sugar	2.05	12.87	3.62	11.64	10.07

X = detected but not quantified

An entrained-flow reactor system was devised which allowed fast pyrolysis results for both lignin feedstocks with operation at 700°C with a 1.5 s residence time. At these conditions the bio-oil yield was much lower than typical for fast pyrolysis of biomass, only 11.7% for ETEK lignin while the highest bio-oil yield, 36.6%, was recovered for ALM lignin.

Feeding with the entrained flow system (see Fig. 11) was accomplished with a double jacket lance cooled with running polyethylene glycol at – 20°C. Nitrogen was used as entraining gas. Feeding was much better than with the fluidized bed, but the feeding rate was rather slow (40 g/h). The reactor was a quartz tube followed by a glass flask for char collection, a coil cooler and an electrostatic precipitator with subsequent wash bottle. Residence time was calculated as 0.7 s. A qualitative comparison with the Py-GC/MS results revealed, that much more aromatic and phenolic structures were formed at the mitigation of typical lignin degradation products such as guaiacyl- and syringyl-compounds.

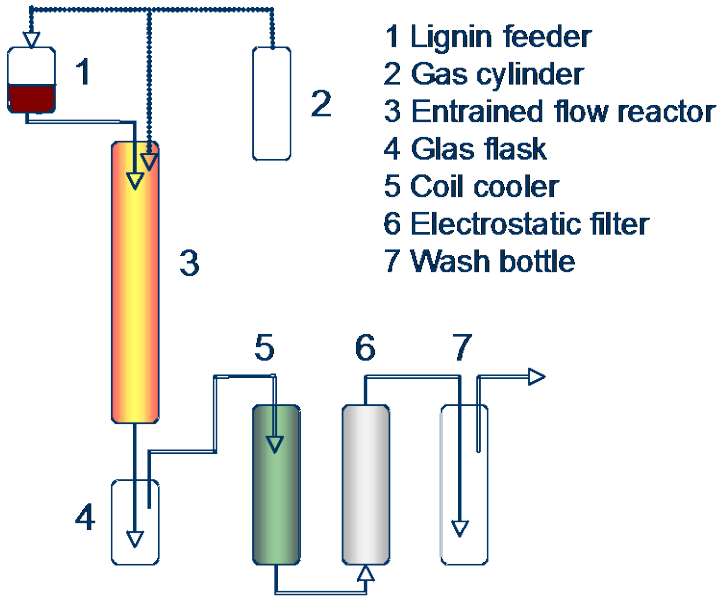

Figure 11. Laboratory 5 Experimental setup

6.5 Laboratory 6

The ALM lignin was pyrolyzed in a fluidized-bed reactor system. The lignin was first pelletized and crushed to a particle size between 1 and 2 mm. The fluidized quartz sand bed was fed 100 g lignin at a rate of 240 g/h with a residence time in the bed of 1-2 s. Condensate products were captured in two electrofilters operated at 8-10 kv and 4 kv. The condensate in the cooling traps was 93.1% water; there was a small amount of separate organic phase, ~10%, which was solid at room temperature.

6.6 Laboratory 12

A nominal 1 kg/h fluidized bed rector was used to fast pyrolyze each of the lignin feedstocks. The bed was fluidized with nitrogen gas and operated in an overflow mode such that char and sand were continuously removed from the top of the bed and new sand was added with the lignin powder by a water-cooled screw [9]. The gas/vapor stream leaving the reactor contained sand fines and some char; a knock-out pot captured the sand and most of the char

particles. Residual char in the vapor/gas stream was separated in cyclones and the bio-oil was collected by two condensing spray towers and a final condenser.

Operations with the ALM lignin were unsuccessful. Using a feed rate of only 500 g/h the test extended for 2 h. Early on there were problems with fluidization. Upon opening the reactor after the test the lignin and sand were found in large clumps (up to 5 cm in diameter) of very hard material. The feeding screw was also surrounded by solid lumps and at the feed entrance to the bed there was a 3 cm lump of lignin/sand on the screw.

Tests in a batch reactor were also attempted with the ALM lignin but did not produce enough bio-oil for analysis. Lumps of lignin were formed inside the reactor bed at an early stage of heating, as they were found after heating to 480°C and were not formed in cool-down. The pyrolysis of the small particles of lignin began very quickly (due to a short heat up time or by heating to less than the reactor temperature) yet continued reacting longer than a minute, which is longer than typical biomass.

There were no operational problems with the ETEK lignin; however, the lignin flow rate was reduced to only 100 g/h. The duration of the test was 3 h and the mass balance closure was 95%. The normally-used nitrogen overpressure on the feed screw was not used as the nitrogen blew the lignin dust through the screw and made feed control impossible. Also, a higher sand to feed ratio (8 versus 2 for typical biomass) was used. No lumps of lignin/sand were found in the reactor nor in the char collection components. The oil quality was poor, as it separated into two phases. There was a larger amount of gases and water produced than with typical biomass.

6.7 Laboratory 13

The Laboratory 13 fast pyrolysis rig (Figure 12) includes a pre-heating chamber that heats the nitrogen before its entry in the reaction chamber and the main chamber where the biomass is pyrolyzed batch-wise in a fluidized bed of alumina. The lignin sample was pushed into the reactor using nitrogen. A tar trap was used to condense the condensable vapours into bio-oil and tar. The time for the thermo-chemical conversion was found to occur over 10 and 60 seconds although the residence time was estimated at 3-15 seconds. As such, these are not actually fast pyrolysis results. The temperature considered during the experiment (480°C) was measured by the thermocouple in connection with the alumina bed. The sample injection has been done four times for total 11.2 g of sample injected for each experiment. The experiments were repeated multiple times with each feedstock. In the case of the ALM lignin it was found that a portion of the feed melted in the injector and never made it into the reactor. The products after the experiments were bio-oil, char and gas.

The weight difference of the collection bottles was measured to determine the bio-oil yield; the weigh difference between the alumina + char minus the initial alumina weigh determined the char yield (including the ash content). The gas yield was not measured. The bio-oils were collected in a container using 50/50 solution of dichloromethane and methanol.

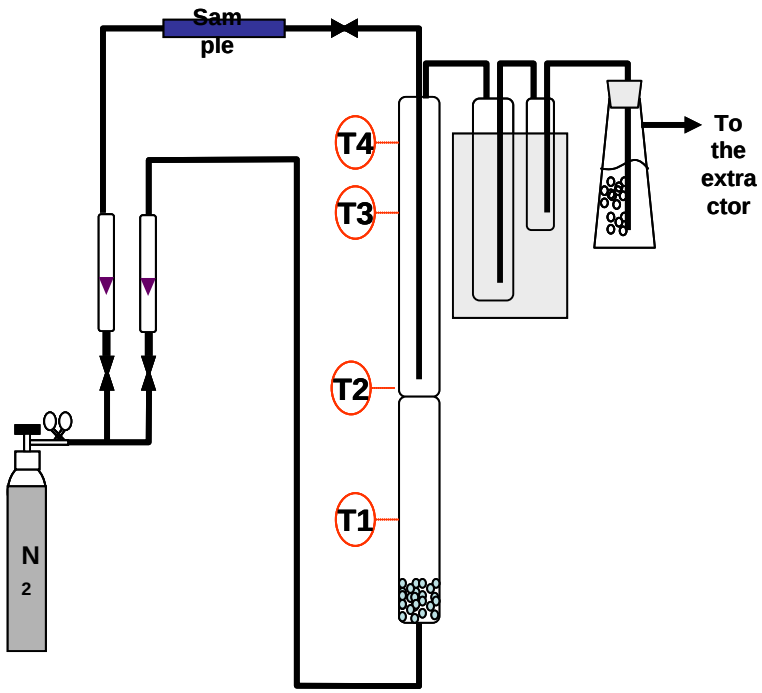

Figure 22. Laboratory 13 experimental set-up

6.8 Comparison of fast pyrolysis experiments

The results of the various bench-scale pyrolysis tests are compared in Table 18. The yield of bio-oil is much lower for both lignin and remarkably lower for the more pure ALM lignin. Processing in conventional fluidized-bed fast pyrolysis systems is difficult with either lignin but nearly impossible with the ALM lignin. "Melting" of the lignin. Probably resulting from lower temperature decomposition caused the feeding systems to plug. Further decomposition and polymerization led to formation of adhered clumps of bed material and lignin coke in the fluidized beds and eventually led to loss of fluidization. Pyrolysis at higher temperature in entrained flow systems seem to provide an operating option.

The bio-oil products from these tests were analyzed by some of the participants. The results are provided in Table 19. Note that Laboratories 1 and 5 did not undertake any of these product analyses. The products were highly variable probably reflecting that some of the laboratories actually produced product oils with more than one phase. The high solids contents in the products from Laboratory 13 reflect the batch reactor mode without a cyclone cleanup step. The bio-oil from the ALM lignin appears to have a higher carbon content.

Table 18. Comparative data from different pyrolysis tests

ETEK	Lab 1	Lab 3	Lab 4	Lab 6	Lab 12	Lab 5	Lab 13
feeder	valve and push rod	N_2 cooled screw	dry ice cooled screw	no result	water cooled screw	entrained in nitrogen	entrained in nitrogen
reactor	fluidized bed	fluidized bed	fluidized bed	no result	fluidized bed	entrained flow	batch
temperature	500	450-510	484-519	no result	500	700	480
time		0.3-0.5	0.1	no result	1.7	1.5	3-15
bio-oil yield	57.7	72	40.1 (79.6)#	no result	47*	11.7	40
char yield	27.2	7	13.9	no result	25	48.8	30
gas yield	10.3	14	6.5	no result	23	39.5#	30#
ALM	Lab 1	Lab 3	Lab 4	Lab 6	Lab 12	Lab 5	Lab 13
feeder type	valve and push rod	N_2 cooled screw	no result		no result	entrained in nitrogen	entrained in nitrogen
reactor type	fluidized bed	fluidized bed	no result	fluidized bed	no result	entrained flow	batch
temperature, °C	530	410-560	no result	475-525	no result	700	480
time, s		0.3-0.5	no result	1-2	no result	1.5	3-15
bio-oil yield, %	31.3	31	no result	49.7*	no result	36.6	22
char yield, %	48.8	34	no result	42.3	no result	35.5	48.3
gas yield, %	5.7	12	no result	8.0	no result	27.9#	29.7#

* two phase condensate product; # by difference

Table 19. Comparative data of different pyrolysis product bio-oils

ETEK	Lab 3	Lab 4	Lab 6	Lab 12	Lab 13
water content	34	3.4	no result	48	<11
viscosity	ND	ND	no result	21 cps	ND
pH	ND	ND	no result	3.51	ND
filterable solids	ND	1.0	no result	1.4	13.6
carbon	47	ND	no result	28	53.7
hydrogen	6.8	ND	no result	9	6.8
nitrogen	0.8	ND	no result	ND	ND
pyrolytic lignin	ND	22.5	no result	18.37*	ND
ALM	Lab 3	Lab 4	Lab 6	Lab 12	Lab 13
water content	19	no result	ND	no result	<15
viscosity	ND	no result	ND	no result	ND
pH	ND	no result	~4.5	no result	ND
filterable solids	ND	no result	ND	no result	15
carbon	54	no result	ND	no result	60.8
hydrogen	6	no result	ND	no result	7.4
nitrogen	0.6	no result	ND	no result	ND
pyrolytic lignin	ND	no result	ND	no result	ND

* water insoluble “pyrolytic lignin” may contain extractives

7 CONCLUSIONS

The work leads to the following conclusions:

7.1 Thermogravimetric analysis

- Decomposition of the ALM lignin starts at 120^{o}C and extends over a wider temperature range than the decomposition of the ETEK lignin.
- The ETEK lignin appears to behave more like whole biomass than lignin.

7.2 Analytical pyrolysis

- ETEK lignin is not a pure lignin as indicated from the high amount of identified carbohydrate derivatives (39.46%-60.02%) in contrast to the ALM lignin.
- The ETEK lignin products suggest a softwood source while the ALM lignin appears to have either a hardwood or herbaceous source.

7.3 Laboratory scale reactor systems

- Both lignins were prone to plugging in pneumatic or screw feeders which were not cooled due to their low melting point.
- ALM lignin bubbled as soon as it was fed in the reactor and formed highly porous char that eventually caused bed agglomeration.
- With ETEK lignin, bed agglomeration also occurred, but was less severe compared to that with ALM lignin.
- Because of the very small particle size (<100 microns) part of the lignin fed seemed to escape from the reactor without decomposition, carry through the cyclones, and end up in the product oil collectors.
- ALM lignin produced a heavy tarry bio-oil in a lower quantity than a whole biomass; conversely the char yields were higher.
- The bio-oil from the lignins was similar to typical bio-oil confirming the source of bio-oil components often speculated in the literature, i.e., the ETEK lignin produced a collection of oxygenates along with phenolics while the ALM lignin produced primarily phenolic components.
- ETEK lignin contained a large portion of cellulose and behaved more like high-lignin wood.
- A modified processing system will be required for fast pyrolysis of actual lignin.

8 RECOMMENDATIONS

Lignin can not be effectively fast pyrolyzed in reactor systems designed for whole biomass materials. However, less purified lignin products, as derived in some hydrolysis-based systems, may be suitable feedstock in conventional fast pyrolysis with minor adjustments for temperature control in feeding and product collection methods. For effective liquefaction of high-purity lignin by pyrolysis, new reactor designs, such as entrained-flow, operated at different conditions, such as higher temperature and longer residence time, will be required. Lignin-derived bio-oil is produced in lower yield and the char byproduct is a larger fraction; however, the bio-oil appears to contain less oxygen and as a result is expected to have a higher energy density.

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