THE COMPOSITION OF OILS OBTAINED BY THE FAST PYROLYSIS OF DIFFERENT WOODS

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Introduction

During the last six years a fluidized bed fast pyrolysis process for biomass has been developed at the University of Waterloo (The Waterloo Fast Pyrolysis Process). This process gives yields of up to 70% of organic liquids from hardwoods or softwoods, which are the highest yet reported for a non-catalytic pyrolytic conversion process. A fluidized sand bed is used as a reactor and optimum liquid yields are normally obtained in the range of 450°-550°C at about 0.5 seconds gas residence time with particles of about 1.5 mm diameter or smaller. Two units are in use, one with a throughput of 20-100 gms/hr, and another with a throughput of 1-4 kg/hr. Details of the process have been published by the authors in several publications [1], [2], [3].

Several studies have been published describing results from the flash pyrolysis of biomass. Most of these studies were carried out at higher temperatures and were intended to promote biomass gas production. However, the work of Roy and Chornet [4] reported high liquid yields from biomass pyrolysis under vacuum conditions. More recently, Roy et al. [5] have described a vacuum pyrolysis system for the production of liquids from biomass, based on a multiple hearth type of reactor. Knight et al. [6] have developed an upward flow entrained pyrolyzer for the production of liquids from the thermal pyrolysis of biomass.

However, few details of the chemical nature of the pyrolytic oils produced from wood or other biomass have been reported. Some recent studies of the composition of pyrolysis oils obtained from poplar wood were carried out by workers of the Pacific Northwest Laboratories of Battelle Institute [7] and the Universite de Sherbrooke [8]. Methods of quantitative determination of functional groups in the pyrolytic oils from wood were tested in our laboratory by Nicolaides [9]. However, more detailed characterisation exists in the literature for the products of the thermal degradation of cellulose [10,11,12,13,14]

Results

In previously reported tests (3), yields have been classified as gases, organic liquids, char and product water. Mass balances generally close to 95% or better. Elemental analyses were also reported for many runs, but identification of individual compounds was done only for non-condensable gases and for some volatile organics such as methanol, acetaldehyde, furan,

etc. However, more detailed analyses of liquid products have recently been carried out, and some of these preliminary results which are of particular significance are reported here.

All experimental results given were obtained at conditions of close to optimal feed rate, particle size and residence time for maximum liquid yield at the stated temperatures, as determined by over 200 bench scale runs and 90 pilot scale runs.

Table 1 shows the experimental yields of products from selected runs for four different woods whose properties are given in Table 2.

High organic liquid yields are characteristic of all four materials when undergoing fast pyrolysis in our process. The total liquid yield, including water of reaction, varies from 70% to 80% of the dry biomass fed, all of which can be directly used as a substitute fuel oil if desired. The liquids are single-phase, homogeneous fluids, which pour readily, and which contain from 15% to 25% water depending on the feed material and its moisture content.

These liquids are quite stable at room temperature. The water content, in a period of twelve months, was found to increase slightly presumably due to the slow processes of condensation-polymerization going on even at room temperature. At higher temperatures, 120°C and above, the oils become increasingly unstable and decompose with evolution of gas, and finally charification of a polymeric residue. All the pyrolysis vapors produce an oil mist following rapid quenching, but their polar character allows the easy utilisation of electrostatic precipitation in the recovery system of a pyrolysis process.

Preliminary small scale combustion tests carried out with the pyrolysis oil as produced (20% water content) showed that it burns readily in a furnace with a conventional pressure atomizing burner, providing the combustion box is preheated. If an air atomizing nozzle is used with a pilot flame, no pre-heating of the combustion chamber is necessary. Larger scale tests for extended periods have not yet been done, but preliminary work shows that the pyrolysis oil has potential as a substitute fuel oil.

Some properties of "wet" liquids as produced are given in Table 3. The elemental analyses of the pyrolytic liquids as given in Table 3 are very similar to those of the starting materials - wood. One could probably fairly accurately describe these liquids, therefore, by the term "liquid wood". Two major characteristics of these liquids are high oxygen content and high density (much higher than wood). Another specific property is a limited water solubility. In the case of pyrolytic sirups produced by the Waterloo process, water is dissolved in the organic phase. The addition of more water to the level of about 60% by weight causes a phase separation and this behaviour has been utilized in our work for analytical purposes, in that both

fractions were analyzed separately after dilution of the original oil product.

The details of the HPLC technique developed for analysis of the water soluble fraction are given below:

Column	:	Aminex® HPX-87H, high performance cation exchange resin in hydrogen form 300 x 7.8 mm from Biorad
Eluant	:	H_3PO_4 0.007 N
Flow Rate	:	0.80 ml/min, isocatic
Temperature	:	65°C
Detector	:	Waters R 401 Differential Refractometer
Internal Standard	:	n-propanol

The quantitative data obtained by the HPLC technique are presented in Table 4. A typical HPLC-chromatogram is shown in Figure 1.

To obtain relative response factors and retention times, the pure compounds were fed and then eluted, although some of them, such as cellobiosan and 1,6 anhydro-β-D-glucofuranose, had to be synthesized in-house [13]. Confirmation of compound identification was obtained by GC-MS [Hewlett-Packard 5970 Mass Selective Detector coupled to 5890A Gas Chromatograph]. For GC-MS analysis, sugars and anhydrosugars were first trimethylsilylated to the corresponding ethers. Small amounts of simple phenols and of furanoid compounds were also detected by GC-MS in the water soluble fraction. These components were not quantified by HPLC.

The yields of the water insoluble fraction are given also in Table 4. This fraction separated as a dark brown viscous liquid which solidified during drying into a hard, black, easily powdered material.

The carbon-13 NMR spectrum of this pyrolytic product is shown in Figure 2 together with similar spectra published by Marchessault et al. [15] for milled wood lignin (MW) and steam exploded lignin (EXW). The similarity of the spectra of the steam exploded lignin and our pyrolytic lignin is quite striking. It appears that the oils produced by the Waterloo Fast Pyrolysis process contain a significant fraction which is apparently derived from the natural wood lignin. This "pyrolytic lignin" represents nearly 80% of the original content of wood lignin. Evidence for this conclusion was first reported from the work of H. Menard [16] using thermogravimetric and infrared analysis.

The Waterloo NMR spectrum was recorded using a 9% solution in DMSO-d_6 at 62.9 MHz and 50°C with broad-band proton decoupling. Delay time between pulses was 10 seconds.

Conclusions

Four different woods under conditions of fast pyrolysis yielded very similar liquid products. Analyses show that this product is a complex mixture of chemicals.

The pyrolytic "wet" tar-sirup can be readily separated into two principal fractions by water extraction. The water-insoluble fraction is derived from lignin while the water-soluble fraction is carbohydrate in origin. Analytical results indicate large amounts of low molecular weight (<100) lactones and aldehydes, and a significant fraction of these are multifunctional in nature. Four major classes of chemicals can be differentiated,

1. sugars and anhydrosugars
2. carbonyl and hydroxycarbonyl compounds
3. acids - formic, acetic
4. "pyrolytic" lignin.

Results in Table 4 show that 81-92% of the content of the pyrolysis oils produced in this work from wood has been quantitatively identified.

Detailed analysis of pyrolytic oils is needed in order to allow possible mechanistic or kinetic models to be formulated which can explain the various observed aspects of fast biomass thermal degradation. A knowledge of chemical composition of these oils may also assist in the eventual future utilization, up-grading or separation of these compounds as higher value products.

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Table 1

Pyrolysis Yields from Different Woods

	Brockville Poplar			White Spruce			Red Maple			IEA Poplar		
Run #	51	58	50	42	43	45	14	63	81	27	59	A-2*
Temperature, °C	497	504	555	485	500	520	532	508	515	500	504	497
Moisture content, wt%	*	5.2	*	*	7.0	*	3.8	5.9	9.5	6.2	4.6	3.3
Particle Top Size, μm	*	1000	*	*	1000	*	590	590	1000	590	1000	590
Apparent Residence Time, sec	0.64	0.47	0.57	0.70	0.65	0.62	0.69	0.47	0.44	0.55	0.48	0.46
Feed Rate, kg/hr	2.24	2.10	4.12	2.07	1.91	1.58	2.16	1.98	1.32	2.24	1.85	0.05
Yields, wt% of m.f. wood												
Organic liquid	62.9	62.9	59.0	63.1	66.5	66.1	67.3	67.9	65.0	65.8	66.2	65.7
Water	10.3	9.7	10.2	10.7	11.6	11.1	7.4	9.8	10.0	9.3	10.7	12.2
Char	14.4	16.5	10.6	16.3	12.2	12.3	9.0	13.7	12.1	12.1	11.8	7.7
Gas:												
H_2	0.02	0.02	0.07	0.04	0.02	0.01	0.04	0.01	0.02	0.02	0.01	--
CO	4.95	4.71	8.40	4.16	3.82	4.01	6.96	4.12	4.83	5.32	4.44	5.34
CO_2	6.14	5.89	7.06	3.38	3.37	2.69	4.02	4.89	5.36	6.30	5.75	4.78
CH_4	0.45	0.44	0.97	0.34	0.38	0.43	0.75	0.36	0.57	0.48	0.37	0.41
C_2H_4	0.22	0.19	0.40	0.16	0.17	0.16	0.24	0.16	0.21	0.20	0.13	0.19
C_2H_6	0.06	0.05	0.11	0.02	0.03	0.05	}	0.04	0.07	0.04	0.05	--
C_3	0.06	0.07	0.10	}			}	0.07	0.10	}	0.08	0.09
C_4	0.13	0.16	0.28	} 0.03	0.04	0.06	} 0.04	0.14	0.41	} 0.09	0.19	3.10
Total Gas	12.0	11.5	17.4	8.1	7.8	7.4	12.1	9.8	11.6	12.4	11.0	10.8
Overall recovery wt%, m.f.	99.7	100.5	97.2	97.8	97.7	96.7	95.7	101.2	98.7	99.7	99.8	96.4

* Bench Scale Unit

Table 2

Properties of Feed Materials

	Whole Tree Poplar	White Spruce	Red Maple	IEA Poplar Wood
Source	Brockville Plantation, Whole Tree Except Leaves and Roots Ontario MNR Clone C-147	Eastern Canada Clean Wood Sawmill Sawdust and Mill Scrap		Clean Wood only Ontario MNR Clone D-38
Moisture, wt%	5.2	7.0	3.8 - 25.2	4.6
Ash, % mf	1.19	0.50	0.40	0.46
Elemental Analysis, %				
C	49.06	49.63	48.5	49.45
H	6.23	6.36	6.1	6.05
O	43.6	43.1	--	44.4
N	1.08	0.2	--	0.07

Table 3

Properties of Pyrolitic Liquids

	Brockville Poplar			White Spruce			Red Maple	IEA Poplar
Run #	51	58	50	42	43	45	63	59
Yields, wt% of wood as fed	74.1	73.3	70.5	75.2	79.2	78.5	77.9	77.6
Water content, wt%	19.8	18.7	21.7	21.9	22.4	21.8	18.0	18.6
pH	2.6	2.4	2.8	2.1	2.1	2.3	2.4	2.4
Density, g/cc	1.19	1.20	1.18	1.22	1.22	1.22	1.19	1.23
Elemental analysis, wt%, m.f.								
Carbon	54.1	54.7	55.6	53.5	54.0	56.6	54.7	53.6
Hydrogen	7.1	6.9	6.9	6.6	6.8	6.9	6.4	7.0

Table 4

Analysis of Liquid Products

	Brockville Poplar	White Spruce	Red Maple	IEA Poplar
Run #			63	A-2
Temperature	504	500	508	504
Yields, wt% of feed, m.f.				
organic liquid	62.9	61.5	67.9	69.8
1. oligosaccharides				0.70
2. cellobiosan	1.11	2.49	1.62	1.30
3. glucose	0.55	0.99	0.64	0.41
4. fructose	1.34	2.27	1.51	1.32
5. glyoxal	1.42	2.47	1.75	2.18
6. methylglyoxal	}	}		0.65
7. levoglucosan	2.52	3.96	2.84	3.04
8. 1,6 anhydroglucofuranose	--	--	--	2.43
9. hydroxyacetaldehyde	6.47	7.67	7.55	10.03
10. formic acid	5.40	7.15	6.35	3.09
11. formaldehyde	--	--	--	1.16
12. acetic acid	6.30	3.86	5.81	5.43
13. ethylene glycol	0.87	0.89	0.63	1.05
14. acetol	1.70	1.24	1.15	1.40
15. acetaldehyde	--	--	--	0.02
16. methanol				
Water-solubles-total above	27.7	33.0	29.9	34.2
Pyrolytic lignin	24.8	20.6	20.9	16.2
Amount not accounted for (losses, water soluble phenols, furans etc.)	10.5	7.9	17.1	18.3

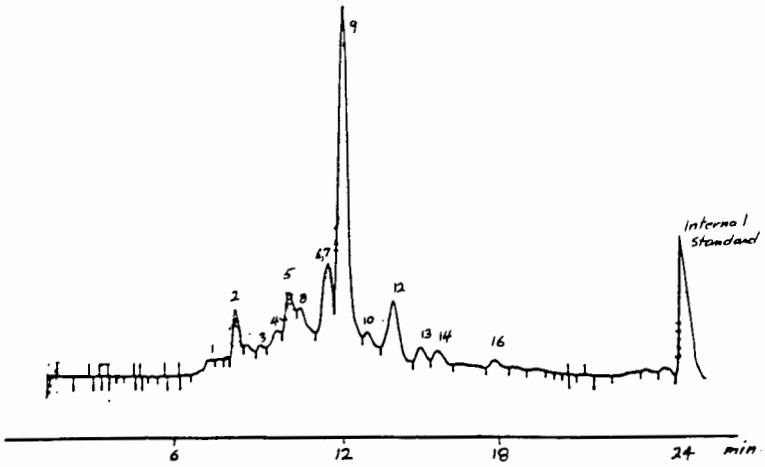

Figure 1 Chromatogram of Wood tar from run # A-2

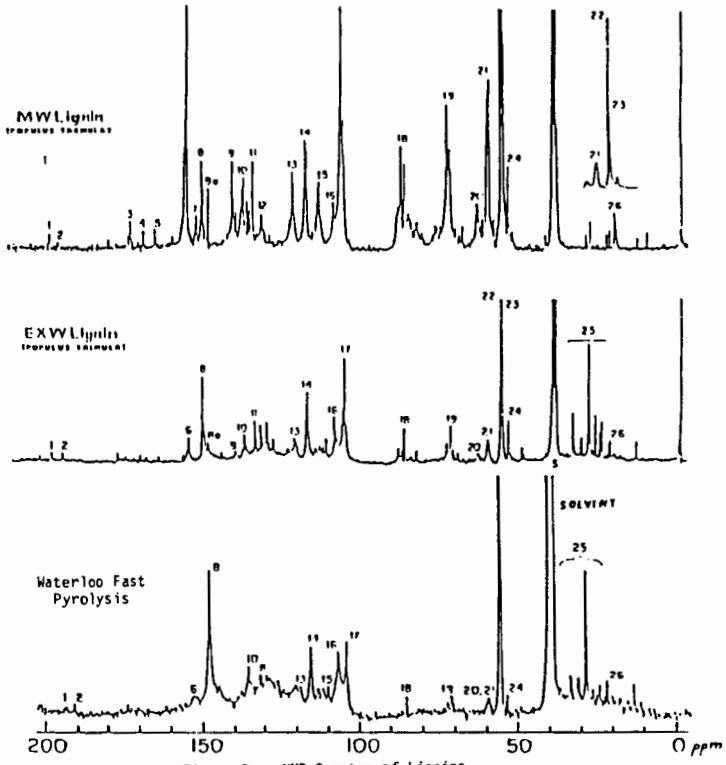

Figure 2 NMR Spectra of Lignins