

FLASH PYROLYSIS PRODUCTS FROM BEECH WOOD

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ABSTRACT

Flash pyrolysis products from beech wood obtained in an original pyrolysis apparatus were analyzed. The analytical procedure is described, and the composition of pyrolytic oil presented with more than 50 compounds. Comparison of pyrolytic products of cellulose, hemicellulose, and wood indicates the origin of each product.

Keywords: Pyrolysis, wood, beech.

INTRODUCTION

Each year the wood carbonization industry produces about five million tons of charcoal in the world. Pyrolytic oils formed as a by-product of this process are collected but very seldom used. Yet this oil could be a source of valuable chemicals, as was the case in the past; during the last century, dry distillation of wood provided a unique source of useful chemicals for the first chemical industry. This route was then abandoned, when the direct synthesis of acetic acid, acetone, and methanol which were the principal products of wood distillation, became economically attractive.

Recent problems of natural oil supply have renewed interest in pyrolytic oils: with modern technology, the recovery of acetic acid becomes economically attractive. In addition, pyrolytic oils contain other very complex components that cannot be synthesized easily but that could be recovered along with acetic acid.

Several difficulties are involved in the industrial processing of pyrolytic oil: the mixture is highly complex and contains chemicals of different natures that may react together so that the oil is not stable. Part of the mixture has not yet been identified.

The present study attempts to analyze more thoroughly a typical pyrolytic oil. Another study is in progress in our laboratory to develop a performing separation technology based on distillation and liquid-liquid extraction.

Chemical analysis studies of pyrolytic oils have been reviewed by Fagerson (1969): the most complete is the work of Heyns et al. (1966), on glucose pyrolytic products: they identified about 70 components with a predominance of furans. These are not found in the very different oils resulting from food thermal treatment (coffee beans—Gianturco (1967), or cigarette smoke (Spears 1963). Most of the works are concerned with the pyrolysis of cellulose (Glassner and Pierce 1965; Lipska and Wodley 1969; Schwenker and Beck 1963). Hileman et al. (1976) have studied the products of α -cellulose and Douglas fir pyrolysis under neutral and oxidative environments.

Our study is devoted to beech-wood pyrolysis, as a typical European hardwood. Analysis of pyrolytic oils was performed by gas-phase chromatography (GPC), mass-spectrometry, and chemical derivation.

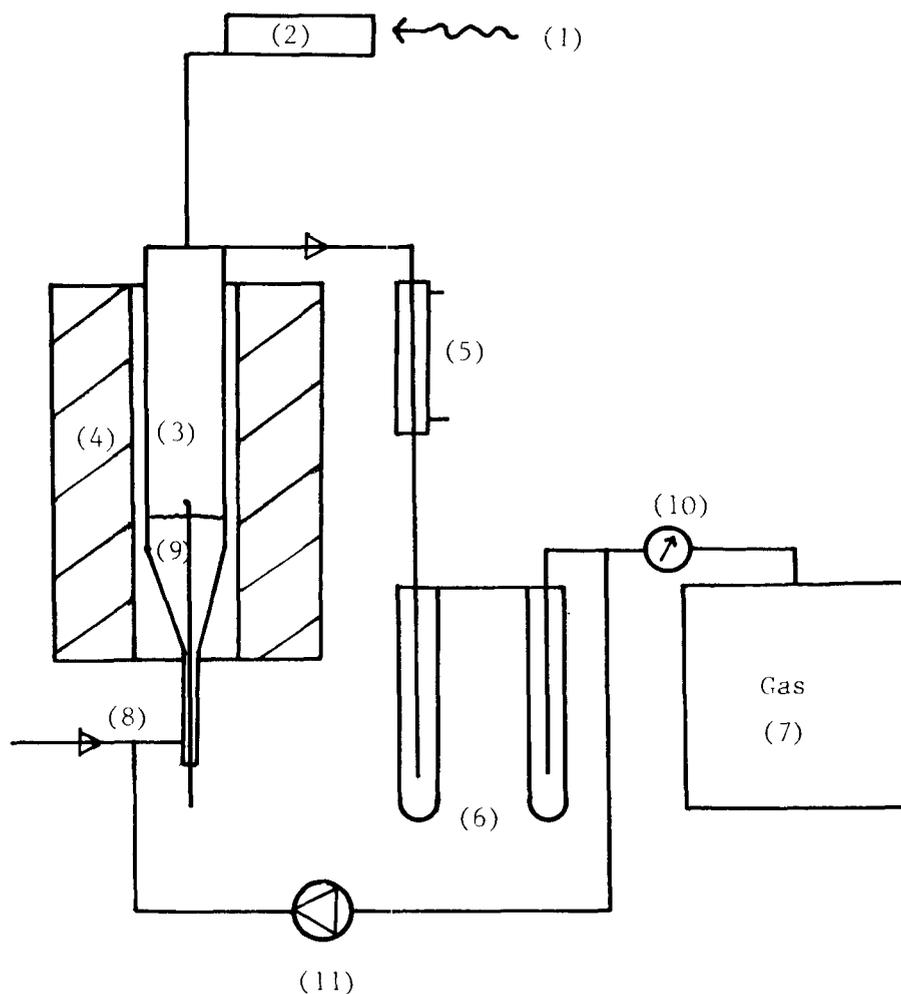


FIG. 1. Experimental Setting for Sawdust Pyrolysis. (1) Vibratory Device, (2) Feedstock (Wood), (3) Pyrolysis Chamber, (4) Electric Furnace, (5) Condenser, (6) Cold Traps, (7) Tight Gas Tank, (8) Sweeping Gas Stream, (9) Packing Material, (10) Gas Volume Measure, (11) Peristaltic Pump.

EXPERIMENTAL PROCEDURE

Pyrolysis unit

The experimental setup allows pyrolysis of wood sieved sawdust in a gaseous sweeping stream of nitrogen (Fig. 1). This gaseous stream rapidly sweeps the pyrolysis products out of the furnace where they are condensed and cooled (residence time under 20 sec). This precaution avoids as much as possible the secondary degradation of the volatile products; an "extractive" pyrolysis is thus carried out (see Beaumont 1983).

A supplementary tubing with peristaltic pumping equipment allows part of the gas to recirculate to obtain high specific flow rate in the furnace without excessive dilution of the pyrolytic products in the sweeping gas. The recirculating gas is

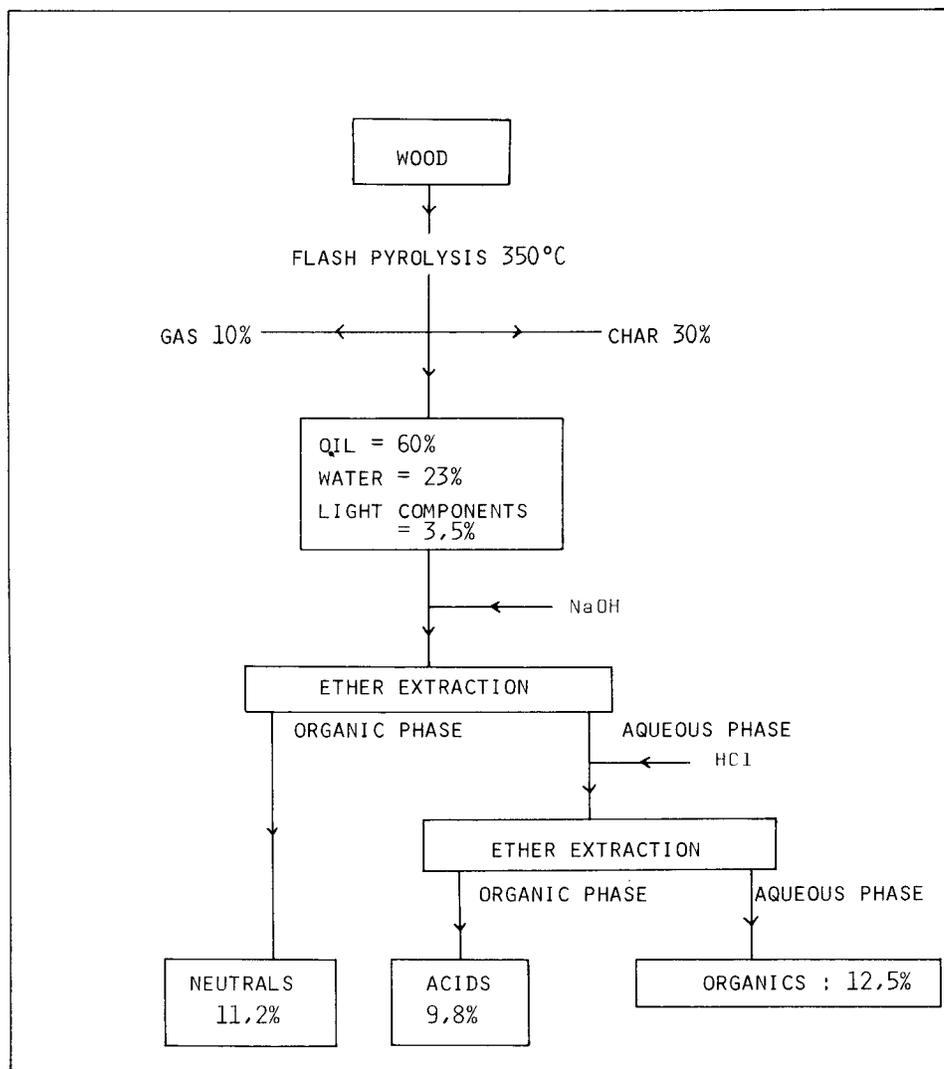


FIG. 2. Pretreatment of Pyrolytic Oil before GPC analysis.

taken after recovery of pyrolysis products. (The second cold trap is maintained at -60 C.)

The temperature of the furnace is controlled by a programmed regulator monitored by a $\frac{1}{8}$ -in. Chromel-Alumel thermocouple placed near the heating coils of the furnace. Another thermocouple of the same type placed just over the packing material filling the pyrolysis chamber bottom measures the effective temperature. The temperature gradient in the furnace was found to be homogeneous radially, and the vertical dispersion was less than 4 C.

The furnace is preheated at a temperature of 350 C and the sweeping gas stream is established. The wood powder is then introduced by a vibratory divide in the furnace. The rate of introduction is adjusted so that the furnace temperature is

not disturbed: 10 g of wood are introduced during each experiment at the rate of 0.5 g per min. Afterwards temperature is maintained for completion of the processing. It was found that the char residue underwent no additional transformation after 30 min. The furnace is then rapidly cooled, and the condensed pyrolytic oil is collected in the trap for analysis.

Pretreatment of the pyrolytic oil

A pretreatment of the crude oil is necessary to facilitate its analysis by GPC and mass-spectrometry.

The first possibility is distillation. However, this method was abandoned after a few attempts because the separation by volatility resulting from this technique does not facilitate further analysis by GPC. It is preferable to separate the products first, according to their chemical functions, and then to analyze by GPC each fraction, composed of the same chemical function. Even vacuum distillation of pyrolytic oil leads to a tarry residue of about 15%.

The difference in solubility properties allows a good separation by a sequence of liquid-liquid extractions (see Fig. 2). After neutralization with highly concentrated sodium hydroxide, the oil is extracted with diethyl-ether in a continuous apparatus during one night. The organic fraction is dried and evaporated; a neutral fraction is obtained (11% of the crude oil).

The aqueous phase is acidified to pH 1 and reextracted with diethyl-ether in the same way. The acid fraction is obtained after drying and evaporation of the solvent (9.8%). A portion of the oil is totally insoluble in ether (12.5%).

Chemical derivation

Girard's reactivities allow the extraction of ketones from a complex mixture with good specificity and their concentration into a very small volume (Girard and Sandulesco 1936). This method has led to partial results because most of the oil components are soluble both in water and in ether so that the extractions needed in this method are not easily carried out. Four ketones, however, were isolated and identified by this method (see Table 2). Lactones are not extracted by Girard's reactivities.

The carboxylic acids were isolated as benzyl-esters and analyzed apart by GPC according to the method of Bethge and Lindstrom.

Numerous works (for example Shafizadeh 1976) have shown that pyrolytic degradation of cellulose leads to an anhydro-sugar derivative, called levoglucosan (1,6-anhydro- β -D-glucopyranose). By vacuum pyrolysis of cellulose, this chemical can be prepared with high yield (30 to 50%). We have looked for this product in the pyrolytic products of wood under atmospheric pressure with the same analytical procedure: the tarry fraction is evaporated (oven, 105 C) and silylated following the procedure of Brobst and Lott (1966). The analysis of silylated carbohydrates is then carried out by GPC (see Bishop 1964). Identification of levoglucosan was made by comparison of retention volumes with the authentic product prepared by the method of Wolff et al. (1968) and confirmed by the quantitative hydrolysis of the product to D-glucose.

Separation of cellulose and hemicellulose of wood

The separation of cellulose and xylan was performed by the procedure of Jones et al. (1961).

TABLE 1. Conditions and columns used for gas chromatographic analysis of pyrolytic oils.

	Column number				
	1	2	3	4	5
Fraction analyzed	Light fraction	Acid fraction Neutral fraction Total pyrolytic oils Ketones from Girard's extraction	Tar fraction (T.M.S. derivatives)	Neutral fraction	Benzyl esters of carboxylic acids
Internal standard	Ethyl acetate	2,4-dimethoxyacéto- phénone	D-mannose T.M.S.		Benzyl-butyrate
Stationery phase	Porapak Q	20% Carbowax	5% SE 52	SE 52	10% butane diol succinate
Support	50-80 mesh	20 M-TPA Chromosorb WAW 80-100 mesh	Chromosorb WAW 80-100 mesh		Chromosorb WAW 80-100 mesh
Length	2 m	3 m	3 m	40 m	3 m
Tubing	1/8 in. inox	1/8 in. inox	1/8 in. inox	Capillar column	1/8 in. inox
Detector	Thermal conductivity— 150 mA	FID 250 V	FID 250 V	RIBERT quadrupolar spectrometer	FID 250 V
Carrier gas	Helium 40 ml/min	Nitrogen 20 ml/min	Nitrogen 30 ml/min	Helium	Nitrogen 30 ml/min
Injector temperature	150 C	120 C	120 C		150 C
Reactor temperature	250 C	250 C	250 C		200 C
Temperature programming	110-230 C	100-230 C	120-200 C	80-250 C	130-170 C
Programming speed	5°/min	5°/min	4°/min	5°/min	2°/min

TABLE 2. Chemical composition of pyrolytic oils from flash-pyrolysis of beech at 450 C. (1) The spectrum has been interpreted by comparison with literature data. (2) The spectrum has been interpreted without comparison with literature data. (3) Less than 0.1% but could not be measured precisely.

Number	Compound	Yield vs. dry wood	Number of the analytical column used	Mass spectra		Gillard's derivatives	Found in xylan pyrolytic oils	Found in cellulose pyrolytic oils
				"R" (1)	"S" (2)			
1	Water	39.2	1				x	x
2	Methanol	2.5	1,2				x	x
3	Ethanol	trace	1					
4	2-propanol	trace	1,2					
5	Benzene	trace	2					
6	Toluene	trace	2					
7	Ethyl-benzene	trace	2					
8	Ethanal	0.3	1					x
9	Glycolaldehyde	0.2	1	x				
10	Propanone	0.27	1,2					
11	2-butanone	0.17	1,2					
12	2,3-butanedione	0.3	1,2					
13	2,3-pentanedione	0.3	1,2					
14	Methyl acetate	0.13	1					
15	1-hydroxy-2-propanone acetate	0.52	2					
16	1-hydroxy-2-butanone acetate	0.41	2					
17	1-hydroxy-2-propanone	4.26	1,2	x		x	x	x
18	1-hydroxy-2-butanone	2.11	1,2	x		x	x	x
19	Furfural	1.27	1,2,4	x			x	x
20	Furfurylic alcohol	1.02	1,2,4	x				x
21	5-methyl-furfural	0.2	2,4	x				
22	Methyl-furyl-cetone	0.1	2,4	x		x		
23	Cyclopentenone	0.1	2					
24	2-methyl-cyclopentenone	0.1	2					
25	2-hydroxy-3-methyl-2-cyclopentene-1-one	1.0	2,4	x		x		x
26	3-hydroxy-2-methyl-4-pyrone	0.05	2,4	x				
27	Butyrolactone	0.4	2	x				
28	Valerolactone	0.2	2					
29	Crotonolactone	0.1	2	x				
30	α -angelilactone	1.1	2	x				x
31	Guaiacol	0.5	2,4	x				
32	4-methyl-guaiacol	0.4	2,4	x				
33	3-methyl-guaiacol	(3)	4		x			
34	4-ethyl-guaiacol	(3)	4	x				
35	3-ethyl-guaiacol	(3)	4		x			
36	4-vinyl-guaiacol	(3)	4	x				
37	4-propyle-guaiacol	(3)	4		x			
38	4-propene-guaiacol	(3)	4		x			
39	2,6-dimethoxyphenol	1.2	2,4	x				
40	4-methyl-2,6-dimethoxyphenol	1.1	2,4	x				
41	4-ethyl-2,6-dimethoxyphenol	(3)	4	x				
42	α -vinyl-2,6-dimethoxyphenol	(3)	4	x				
43	4-propyle-2,6-dimethoxyphenol	(3)	4		x			
44	4-propene-2,6-dimethoxyphenol	(3)	4		x			
45	4-butyl-2,6-dimethoxyphenol	(3)	4		x			
46	2-methoxy-pyrocatechol	(3)	4		x			
47	4-methyl-2-methoxy-pyrocatechol	(3)	4		x			
48	Formic acid	0.4	1,5	x				

TABLE 2. *Continued.*

Num- ber	Compound	Yield vs dry wood	Number of the analytical column used	Mass spectra		Gi- nard's deriv- lytic oils	Found in cellu- lose pyro- lytic oils
				"R" (1)	"S" (2)		
49	Acetic acid	10.14	1,2,5	x			
50	Propionic acid	0.36	1,2,5	x			
51	Butyric acid	0.2	2,5	x			
52	Isobutyric acid	0.2	2,5	x			
53	Valeric acid	0.3	2,5	x			
54	Isovaleric acid	0.2	2,5	x			
55	Acrylic acid	0.2	2,5	x			
56	Crotonic acid	0.4	2,5	x			
57	Levogluconan	1.15	3				
		77.06					

Although xylan is not the sole component of hemicellulose fraction, it is the main component in the case of beech wood. Therefore the xylan was considered as typical of the whole hemicellulose fraction.

Chromatographic and mass-spectrometric analysis

Chromatographic analyses were performed on a Girdel 3000 chromatograph equipped with a double flame detector and a catharometer.

Table 1 gives analysis parameters, characteristics of columns, and their application range.

Spectrometric identifications were achieved by coupling the same columns to a Varian CH7 spectrometer. The analysis and identification of phenol compounds required a capillary column coupled to a Ribert quadrupolar spectrometer.

Quantitative analysis was carried out by GPC with internal standard. Concentrations of four phenolics were measured by this technique, and the concentration of the others was estimated by the height of each peak.

RESULTS

Table 2 shows the nature of identified compounds and the yields of formation on a dry wood basis. The nature of the columns that permitted their identification is indicated. The identification by mass-spectrometry is also indicated by an "R" or an "S," meaning that the spectrum was compared with the reference spectrum of an authentic sample of the same chemicals. "S" means that the identification was supported only by the examination of the spectrum (when the authentic chemical was not available).

Comparison of retention volumes is sufficient for identification of the lightest compounds. Spectra of middle weight compounds of the neutral fraction and acids were interpreted by comparison with literature data.

Spectra of phenolics are not available in literature, but the identification work was here considerably facilitated by the studies of Kovacic et al. (1969), on fragmentation of lignin model compounds.

Three examples of chromatograms are presented in Figs. 3, 4, and 5. Peaks are identified by the number of the compounds in Table 2.

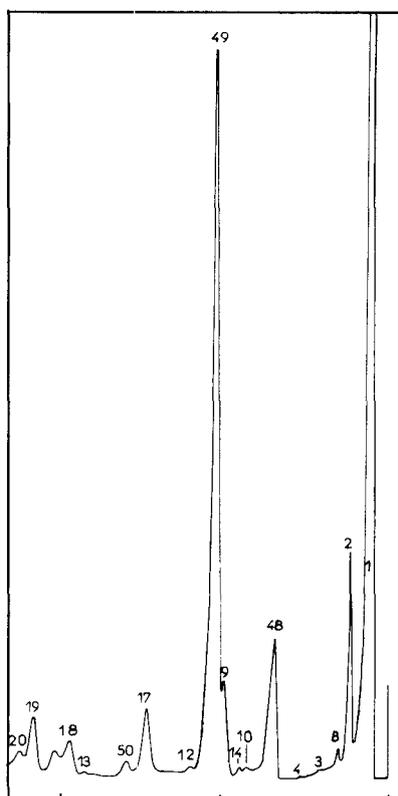


FIG. 3. Crude Pyrolytic Oil Analysis by GPC on Column Number 1. (Identification Numbers of each Peak refer to Table 2.)

DISCUSSION

By our "extractive" flash pyrolysis method, water is obtained in relatively low quantity, compared to the classical slow pyrolysis of massive pieces of wood. In this case, 50 to 60% of the water is found in the pyrolytic oils. (Consequently, the pyrolytic oil prepared in our pyrolysis unit is monophasic.) By extractive pyrolysis, the dehydration of the products is less complete. This is due to the fine granulometry of the wood that allows an easy escape of the volatiles and to the dilution of these volatiles in the inert sweeping gas, which leads them rapidly out of the hot zone. The identified proportion of the pyrolytic oil accounts for 77% of the mass. What is the nature of the other 23%?

According to the liquid-liquid extraction procedure, these remaining products are the water-soluble products that are not extracted by ether (Fig. 1). They are probably closely related to lactones and levoglucosan and should be carbohydrates more or less polymerized or degraded, too heavy to be subjected to GPC analysis. Further work for their identification should use high performance liquid chromatography. These carbohydrates are not very volatile, and their presence in the pyrolytic oils is due to the extractive method. When the pyrolysis is different, they are destroyed, and char and water are formed.

The acid fraction is composed essentially of acetic acid, but with a notable

TABLE 3. Percentages of basic patterns of lignin in wood and in pyroligneous substance.

Basic unit	% in beech wood	% in pyroligneous substance
Phenyl	5	0
Guaïacyl	46	30
Syringyl	49	70

percentage of ethylenic acids. Quantitatively, the third product is the hydroxy-1-propanone-2 and the fifth is hydroxy-1-butanone-2. These two alcohols are partly esterified by acetic acid. In classical slow pyrolysis, these two products are not found in so great a quantity because of their low stability. To test the stability, we pyrolyzed pure hydroxy-propanone at 200 and 450 C. At 200 C, the product is converted to acetic acid in a proportion of about one half after about 10 min. At 450 C, it is deeply decomposed with formation of more than ten different chemicals. The presence of these two hydroxy ketones in high quantity is an interesting new result.

The fourth product in quantity is methanol, and the sixth is 2-furaldehyde. These are the two classical products of wood distillation, but they are obtained in relatively small quantity.

Three cyclic oxygenated chemicals are obtained with more than 1% yield: furfurylic alcohol, 2-hydroxy-3-methyl-2-cyclopentene-1-one, and α -angelilactone. Phenolics account for 7% with predominancy of the more substituted. Levoglucosan (1, 15%) is the only carbohydrate that could be identified in the oil.

Origin of pyrolytic products

Comparison between chemical structures in wood—xylan and cellulose and pyrolysis products—leads to the understanding of the origin of each component. Phenolics derive from lignin by cracking of phenyl-propane units of the macromolecule lattice. As a matter of fact, these phenolic derivatives are not found in the cellulose and xylene pyroligneous substances. It is interesting to compare the proportions of the three basic patterns of lignin (according to Freudenberg 1966), to the proportions in the pyroligneous substance (see Table 3).

Pyrolysis seems to produce the most substituted phenols on a selective basis. This phenomenon can be explained by the fact that the syringyl-propane units are not so linked to the lignin skeleton as the less substituted units: gaiacyl-propane and phenyl-propane. As the aromatic rings of lignin are substituted only at carbons 1, 2, 4 and 6, the syringyle units encounter three sites that are already occupied (1, 2 and 6); so they can be linked to the lattice only by the propane chain in position 4. On the other hand, the gaiacyl-propane and above all phenyl-propane units can be linked at two points. During carbonization, these two products will yield coal selectively, whereas the former will escape more easily.

Degradation of xylan yields eight main products: water, methanol, formic, acetic, and propionic acids, hydroxy-1-propanone, hydroxy-1-butanone and 2-furfuraldehyde (but not furfurylic alcohol). These results do agree with those of Shafizadeh (1976) and can be related with accuracy to the chemical structure of the xylan, described by Timell (1967) as the 4-*O*-methyl-3-*O*-acetyl-glucuronoxylan:

Water is formed by dehydration.

Acetic acid comes from the elimination of acetyl groups originally linked to the xylose unit.

Furfural is formed by dehydration of the xylose unit.

Formic acid proceeds from carboxylic groups of uronic acid.

Methanol arises from methoxyl groups of uronic acid.

Pyrolysis of cellulose provides a pyrolytic oil composed of water, methanol, ethanol, 1-hydroxy-2-propanone, very little 1-hydroxy-2-butanone, furfural, furfurylic alcohol and 2-hydroxy-3-methyl-2-cyclopentene-1-one. The main product is α -angelilactone. Acetic acid is found only in very small amounts. The tar fraction contains one carbohydrate-levoglucosan. This product is found in oils of vacuum pyrolysis of cellulose with yields as high as 30% (Shafizadeh and Fu 1973). However in oils of atmospheric pyrolysis, this compound has not been isolated yet: because of its heavy molecular weight, levoglucosan cannot be drawn out of the hot pyrolysis vessel before being cracked unless the vessel is swept strongly by an inert gas flow as it is in our experimental setup.

CONCLUSION

The qualitative and quantitative composition of the most volatile part of pyrolytic oil from flash pyrolysis is described. It differs strongly from that of classical pyrolysis performed slowly with massive pieces of wood. The extractive pyrolysis unit used for this study allows a recovery of fragile compounds such as 1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 2-hydroxy-3-methyl-2-cyclopentene-1-one, α -angelilactone and levoglucosan with yields higher than 1%. The pyrolysis of cellulose and xylan under the same conditions indicates the origin of the pyrolytic products. Identification of pyrolytic products could not be completed especially in the family of heavy carbohydrates, and subsequent work would be necessary with appropriate techniques.

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