

# Influence of the Moisture Content on the Composition of the Liquid Smoke Produced in the Pyrolysis Process of *Fagus sylvatica* L. Wood

María D. Guillén\* and María L. Ibargoitia

Tecnología de Alimentos, Facultad de Farmacia, Universidad del País Vasco,  
Paseo de la Universidad 7, 01006 Vitoria, Spain

The pyrolysis of several samples of sawdust of *Fagus sylvatica* L. wood with different moisture contents was carried out, keeping all other smoke generation parameters constant. However, parameters such as smoke production length and maximum temperature reached were affected by the moisture content of the sample and varied in the different pyrolytic runs. The acidity and the composition of the liquid smokes obtained were determined, this latter by means of gas chromatography/mass spectrometry and gas chromatography with flame ionization detection. The acidity and composition of the liquid smoke produced were affected not only by the moisture content of the sawdust sample but also by the smoke generation length and by the temperature of the process. The highest yields in components were produced from samples with low moisture content that underwent a short pyrolytic process. Some compounds, with important properties from an organoleptic and preservative point of view, were not generated from samples with high moisture content. Equations that closely relate yield of the total components or of groups of components or of individual components with parameters such as moisture content, length of the process, and temperature were obtained; these equations predict yield data of liquid smoke components with a satisfactory degree of approximation.

**Keywords:** *Fagus sylvatica* L.; moisture content; smoke generation; liquid smoke; composition; gas chromatography/mass spectrometry; gas chromatography with flame ionization detection; relationships

## INTRODUCTION

During the pyrolysis of wood to produce smoke for food smoking, some factors have been considered as influential on the characteristics of the smoke produced (Maga, 1988). These factors include the type of vegetable material (Wasserman, 1966; Fujimaki et al., 1974; Baltes et al., 1981; Maga and Chen, 1985), the temperature of the process (Porter et al., 1965; Simon et al., 1966; Hamm and Potthast, 1976; Toth, 1980a,b; Maga and Chen, 1985), the amount of air present during the smoke generation (Wasserman and Fiddler, 1969; Daun, 1972; Maga and Chen, 1985), the wood particle size, and the moisture content.

Though it has been reported that wood moisture content affects the composition of the smoke produced, there are no studies on the effect of this variable, neither on the formation of the various smoke components nor on their proportions, both of which determine the organoleptic, antioxidant, and antimicrobial effects of the smoke on food. Some authors have found that, as the moisture content increases, the global amount of phenols, acids, and formaldehyde in smoke decreases; the volume of the smoke condensate from 100 g of sawdust was found to be highest with intermediate moisture content; that is, high (or low) moisture content produces liquid smokes with low (or high) concentration

of these smoke components (Gorbatov et al., 1971). The smoke condensates considered to have the best organoleptic properties were those obtained from wood having an intermediate moisture content. However, concentration data about individual components were not given, and it has been suggested that more research should be devoted to determine which specific compounds are best formed at various moisture levels (Maga, 1988).

Other authors have studied the influence of the moisture level on the generation of eight pyrazines from hickory wood pyrolysis. Their initial results (Maga and Chen, 1985) showed that hickory wood with low moisture content generates higher proportions of pyrazines than hickory wood with high moisture content; however, further studies (Chen and Maga, 1995) indicate that high moisture levels affect negatively or positively the formation of these pyrazines, depending on their molecular structure.

In previous papers we have found that in the pyrolysis of *Vitis vinifera* L. the composition of the liquid smoke obtained is related to the maximum temperature reached in the process (Guillén and Ibargoitia, 1996a). We have also studied the influence of the nature of some vegetable sources on the composition of the liquid smoke produced (Guillén and Ibargoitia, 1996b; Guillén and Manzanos, 1999a,b). The present paper shows the influence of the moisture content on the composition of the liquid smoke generated in the pyrolysis of *Fagus sylvatica* L. wood. Pyrolysis of sawdust samples of *F. sylvatica* L., with different moisture contents, was

\* Author to whom correspondence should be addressed (fax 34-945-130756; e-mail knpgulod@vf.ehu.es).

carried out. Parameters such as particle size, amount of oxygen present in the process, and energy supply were kept constant. The temperature and rate of the process, as well as the yield of the liquid smoke generated, its acidity, and the concentration of its main smoke components, were determined and are reported here for the first time. For this latter task, liquid smokes were extracted with dichloromethane and the extracted fraction was studied by gas chromatography/mass spectrometry (GC/MS) and by gas chromatography with flame ionization detection (GC-FID). Relationships between the yield of several components of the aqueous smoke flavoring preparations obtained and parameters such as moisture sawdust contents, length of the pyrolysis process, and maximum temperature reached were tested.

## MATERIALS AND METHODS

### Smoke Generation and Collection of Liquid Smoke.

Beech (*F. sylvatica* L.) wood sawdust, available commercially, of a particle size <2 mm was used in the smoke generation. Amounts of water of 0, 5, 10, 15, 18, 20, and 25 g were added to samples of 100 g of sawdust having 7.5% initial moisture content, and both components were mixed for 1 h and permitted to equilibrate during at least 4 h, in a closed receptacle, before smoke generation; the resulting samples contain moisture percentages of 7.50, 13.25, 15.90, 19.50, 19.50, 21.60, 22.90, and 26.00%, respectively. The smoke generation was carried out in a laboratory round-bottom flask smoke generator made of quartz. The pyrolysis was started with the use of a rheostat-controlled heating mantle. The heating mantle surface is able to reach, in 30 min, 370 °C, at 320 W, and the smoke generation was carried out by keeping the heating mantle at 320 W for 25 min. The atmospheric air and energy supplies were the same for the pyrolysis of the various samples. The temperature was measured with a Crison thermometer 639K positioned in the center of the sawdust charge. The duration of the process was considered to last from the start of the heat supply to the end of the emission of smoke.

The smoke resulting was filtered by means of a glass wool filter and collected in 150 mL of distilled water. The aqueous liquid smoke obtained was again filtered through a paper filter of pore size 30  $\mu$ m. The acidity of each smoke flavoring was determined by titration with 0.01 N sodium hydroxide.

**Extraction, GC/MS, and GC.** The extraction of the main liquid smoke components was carried out from 15 mL of liquid smoke with 30 mL of dichloromethane. This organic solvent was selected for its high effectiveness in extracting polycyclic aromatic compounds and aromatic compounds in general (Guillén et al., 1991, 1995; Guillén, 1994) and for its high volatility. The solvent was partially evaporated, under vacuum, in a rotary apparatus using mild and careful conditions to avoid the loss of very volatile compounds, until a solution volume of 1 mL was reached, and this was kept in a refrigerator for later study. Standard compounds, available from Aldrich, Fluka, and Sigma, were used for identification of some components and for the GC quantification; these are asterisked in Table 1.

The GC/MS employed a Hewlett-Packard chromatograph, Model 6890 Series II, equipped with a mass spectrometer selective detector 5973 (MS), and a Hewlett-Packard Vectra XM Pentium computer. A fused-silica capillary column (30 m, 0.25 mm, 0.25  $\mu$ m film thickness), coated with a nonpolar stationary phase (Hewlett-Packard-5, cross-linked 5% phenyl methyl silicone) was used. The temperature program began at 50 °C (0.5 min) and increased at 5 °C/min until 280 °C was reached (10 min). Helium was used as carrier gas at 1 mL/min flow rate. Injector and detector temperatures were 250 and 280 °C, respectively. The splitless injection technique was used. The volume of sample injected was close to 1  $\mu$ L. Mass spectra were recorded at an ionization energy of 70 eV.

Components were identified by their retention times, by their mass spectra, by comparing their mass spectra with those in a commercial library (Wiley, 1990), and in some cases by using standards, as in previous studies (Guillén et al., 1995).

A Hewlett-Packard gas chromatograph Model 5890 Series II, equipped with a flame ionization detector (FID) and a Vectra VL2 4/66 computer, was used for the quantitative study. A fused-silica capillary column (30 m, 0.32 mm, 0.25  $\mu$ m film thickness), coated with a nonpolar stationary phase (Hewlett-Packard-5, cross-linked 5% phenyl methyl silicone), was used. The temperature program began at 50 °C (0.5 min) with an increase of 5 °C/min until 290 °C (10 min), and nitrogen was used as carrier gas. Injector and detector temperatures were 250 and 300 °C, respectively. The injection technique used was splitless, and the volume of the sample injected was 1  $\mu$ L. All compounds asterisked in Table 1 were used as external standards for quantification, and response factors of compounds of a similar nature were used for the quantification of those compounds not commercially available.

Each stage of this experiment was performed three times to obtain accurate results.

**Statistics.** The statistical analyses were performed by means of Statview statistical software. Simple and multiple linear regressions were tested with different sets of data.

## RESULTS AND DISCUSSION

Amounts of 0, 5, 10, 15, 18, 20, and 25 g of water were added to eight samples of 100 g of beech sawdust with 7.5% initial moisture content, which were pyrolyzed using the same atmospheric air and energy supplies; the different samples were designated B0, B5, B10, B15, B15', B18, B20, and B25, respectively. Figure 1 shows the variation of the temperature in the center of the sawdust charge during the pyrolysis process of the different samples versus the duration of the smoke emission, and Table 1 also gives the moisture percentage in the initial samples (*M*), the length of the smoke emission (*L*), or the duration of the pyrolysis experiments, and the maximum temperature reached in the center of the charge in each pyrolysis experiment (*T*).

It can be observed, in Figure 1, that there is a period of time in which, despite the heating, the temperature in the center of the sawdust charge does not exceed 100 °C. This indicates that at this temperature there is an endothermic process and that this process is only slightly longer in the pyrolysis of samples with a high moisture content. After this period, the temperature increases, reaching different maximum temperatures for each sample. The process reaches a higher temperature in samples with a low moisture content (B0, B5) than in samples with a very high moisture content (B25).

In relation to the rate of the pyrolysis or the smoke production, three different types of processes can be observed in Figure 1: very fast processes, in which the length of the smoke emission is short, such as for B0 (532 °C), B5 (522 °C), and B15 (467 °C), with emission durations of 53, 60, and 66 min, respectively; processes in which the smoke is produced at an intermediate rate, such as in the pyrolysis of B10 (509 °C), B15' (593 °C), and B20 (490 °C), with emission durations of 101, 99, and 105 min; and, finally, slow pyrolysis processes such as those undergone by B18 (474 °C) and B25 (460 °C), with emission durations of 141 and 150 min. Therefore, moisture content influences not only the temperature of the process but also its rate, and these three factors together influence the composition of the smoke produced. Differences found in the pyrolysis process of samples with the same or very similar moisture contents

**Table 1. Wood Samples Used, Moisture Percentage *M* of These Samples, Length *L* of the Smoke Emission, Maximum Temperature *T* Reached in Each Pyrolysis Process, Volume and Acidity of the Liquid Smoke Produced Together with the Yield in Milligrams of the Total Smoke Components and of the Different Groups of Components and of the Several Components of Each Smoke Flavoring Dichloromethane Extract and Their Retention Times RT<sup>a</sup>**

sample	B0	B5	B10	B15	B15'	B18	B20	B25
moisture, <i>M</i> (%)	7.50	13.25	15.90	19.50	19.50	21.60	22.90	26.00
length of the smoke emission, <i>L</i> (min)	53	60	101	66	99	141	105	150
max temp, <i>T</i> (°C)	532	522	509	467	593	474	490	460
vol of the liquid smoke (mL)	177	177	188	185	179	190	185	184
acidity of the liquid smoke (acid equiv)	0.117	0.102	0.101	0.104	0.088	0.090	0.095	0.091
<b>common total compounds (mg)</b>	<b>3022.4</b>	<b>2800.9</b>	<b>2203.8</b>	<b>2642.9</b>	<b>2017.1</b>	<b>2174.0</b>	<b>2255.9</b>	<b>1756.0</b>
<b>common total carbonyl and carboxyl derivatives (mg)</b>	<b>2333.4</b>	<b>2130.3</b>	<b>1661.8</b>	<b>2070.6</b>	<b>1548.7</b>	<b>1640.3</b>	<b>1709.0</b>	<b>1429.1</b>
<b>common total phenolic derivatives (mg)</b>	<b>659.0</b>	<b>640.0</b>	<b>515.8</b>	<b>543.0</b>	<b>444.1</b>	<b>510.9</b>	<b>523.5</b>	<b>304.2</b>
<b>common total others (mg)</b>	<b>30.0</b>	<b>30.6</b>	<b>26.2</b>	<b>29.3</b>	<b>24.3</b>	<b>22.8</b>	<b>23.4</b>	<b>22.7</b>
<b>RT aldehydes</b>								
1.52 acetaldehyde*	7.6	8.3	8.2	7.3	7.8	5.0	6.2	6.8
1.70 propionaldehyde*	nd	nd	nd	nd	nd	nd	nd	nd
2.19 3-methylbutyraldehyde*	116.5	108.1	78.0	90.9	71.4	73.3	83.5	58.3
2.33 2-methylbutyraldehyde*	1.8	1.6	1.7	1.6	1.4	1.5	1.2	1.3
2.49 valeraldehyde*	3.3	7.3	12.8	12.7	5.9	3.9	6.4	3.2
3.09 2-ethylbutyraldehyde*	149.8	130.7	94.8	123.5	91.7	93.1	97.2	84.4
<b>total common aldehydes</b>	<b>279.0</b>	<b>256.1</b>	<b>195.5</b>	<b>235.9</b>	<b>178.2</b>	<b>176.8</b>	<b>194.6</b>	<b>154.1</b>
<b>ketones</b>								
1.58 2-propanone*	7.9	5.0	3.8	4.4	6.1	2.4	3.5	10.3
1.85 2-butanone*	nd	nd	nd	nd	nd	nd	nd	nd
2.38 2-pentanone*	3.1	3.0	2.6	2.8	2.4	2.5	1.9	1.7
2.92 2-methyl-3-pentanone*	12.6	13.8	11.1	16.5	8.6	7.3	11.8	8.7
3.34 3-hexanone*	7.2	25.6	24.7	35.9	17.8	10.8	22.3	16.6
3.39 cyclopentanone*	17.7	14.9	15.1	13.2	12.0	15.0	11.3	7.8
4.21 4-hydroxy-4-methyl-2-pentanone	nd	nd	nd	nd	nd	nd	nd	nd
4.47 1-acetyloxy-2-propanone	nd	nd	nd	nd	nd	nd	nd	nd
4.71 2-heptanone*	10.5	3.9	4.2	4.3	4.1	8.7	4.1	4.8
4.90 cyclohexanone*	3.2	2.2	2.2	2.2	2.0	2.1	1.2	1.7
5.22 2-methyl-2-cyclopenten-1-one*	46.2	36.7	30.2	35.9	26.8	31.1	27.6	29.4
5.94 2,5-dimethyl-2-cyclopenten-1-one	11.7	9.4	7.7	9.8	7.3	8.5	6.3	6.2
6.20 3-methylcyclohexanone*	4.1	5.7	2.5	6.4	2.5	2.5	1.5	4.1
6.59 3-methyl-2-cyclopenten-1-one*	nd	nd	nd	nd	nd	nd	nd	nd
7.30 dimethyl-2-cyclopenten-1-one	nd	nd	nd	nd	nd	nd	nd	nd
8.32 3,4,5-trimethyl-2-cyclopenten-1-one	11.5	8.2	7.0	9.1	7.2	7.7	6.1	4.7
8.40 dimethyl-2-cyclopenten-1-one	2.6	1.5	1.7	2.2	2.0	2.2	1.5	1.5
9.00 1-phenylethanone (acetophenone)*	19.6	8.4	6.8	8.1	6.8	6.7	6.8	5.9
12.34 2-ethyl-2,5-dimethylcyclopentenone	11.0	7.4	5.2	6.6	3.1	4.4	4.8	7.2
15.49 2-methylindanone*	2.6	2.6	1.6	1.9	1.0	1.6	1.6	0.5
<b>total common ketones</b>	<b>171.6</b>	<b>148.3</b>	<b>126.3</b>	<b>159.4</b>	<b>109.7</b>	<b>113.4</b>	<b>112.3</b>	<b>111.2</b>
<b>diketones and triketones</b>								
1.84 2,3-butanedione*	19.1		15.9		14.8	13.0	12.6	8.7
2.44 2,3-pentanedione*	2.8	3.3	2.0	3.1	1.6	1.5	1.9	3.0
4.95 1,4-cyclopenten-2-dione	6.2	1.6	4.5	1.9	4.9	4.8	4.0	1.7
5.55 2,5-hexanedione	36.3	42.2	22.7	39.5	17.7	22.4	23.3	15.6
6.14 1,2,4-cyclopentanetrione		3.7	13.3	6.8			11.3	2.7
6.30 2-methyl-1,3-cyclopentanedione	2.8	1.6	tr	1.3	tr	tr	tr	tr
7.75 2,4-dimethylcyclopent-4-ene-1,2-dione	9.9	5.1	7.3	6.4	7.0	6.6	6.2	4.4
8.27 3-methyl-1,2-cyclopentanedione (cyclotene)*	73.1	64.8	44.8	57.7	40.9	45.8	51.0	29.8
10.60 3-ethyl-1,2-cyclopentanedione (3-ethylcyclopentenolone)*	12.8	8.8	7.5	9.2	9.3	9.3	8.0	4.7
<b>total common diketones and triketones</b>	<b>141.1</b>	<b>125.8</b>	<b>88.7</b>	<b>117.7</b>	<b>81.2</b>	<b>90.4</b>	<b>94.4</b>	<b>59.3</b>
<b>furan and pyran derivatives</b>								
3.87 2-furancarboxaldehyde*	445.3	395.3	332.1	395.6	319.3	353.8	336.8	377.9
4.26 2-furanmethanol*	111.2	123.0	82.0	123.7	77.7	77.2	92.6	71.9
4.67 5-methyl-2(3 <i>H</i> )-furanone ( $\alpha$ -angelicalactone)*	66.2	60.5	51.5	62.0	48.4	49.0	51.3	52.7
5.28 2-ethylfuran	6.0	5.0	5.2	5.1	4.2	4.3	3.6	3.9
5.30 1-(2-furanyl)ethanone (acetyl furan)*	13.2	10.8	10.3	11.4	9.5	10.5	8.3	10.0
5.40 2(5 <i>H</i> )-furanone ( $\gamma$ -crotonolactone)*	86.9	68.6	51.0	74.5	53.2	58.4	64.3	52.0
5.49 2(3 <i>H</i> )-dihydrofuranone	91.8	89.2	53.2	77.5	48.9	53.3	53.1	45.6
5.70 5-methyl-2(5 <i>H</i> )-furanone	16.1	8.5	13.2	9.8	13.2	14.4	10.2	7.9
6.50 5-methyl-2-furancarboxaldehyde*	101.6	86.2	73.3	89.3	71.7	80.0	75.2	81.7
6.65 dimethylfuranone	8.8	3.9	6.3	4.8	6.0	6.2	4.3	3.1
6.92 3-methyl-2(5 <i>H</i> )-furanone*	22.8	19.3	15.8	20.5	14.9	16.0	15.7	12.8
7.52 1-(2-furanyl)-1-propanone	9.0	6.4	6.4	7.6	6.5	7.0	4.7	6.0
10.47 3-hydroxy-2-methyl-4 <i>H</i> -pyran-4-one (maltol)*	18.4	16.3	12.3	14.6	9.7	8.8	13.2	5.1
10.89 5-propyl-2(3 <i>H</i> )-dihydrofuranone	10.4	5.6	5.5	8.4	7.2	6.1	5.2	4.0
12.05 5-hydroxy-2-(hydroxymethyl)-4 <i>H</i> -pyran-4-one	2.7	2.6	3.3	2.8	2.5	tr	3.0	tr



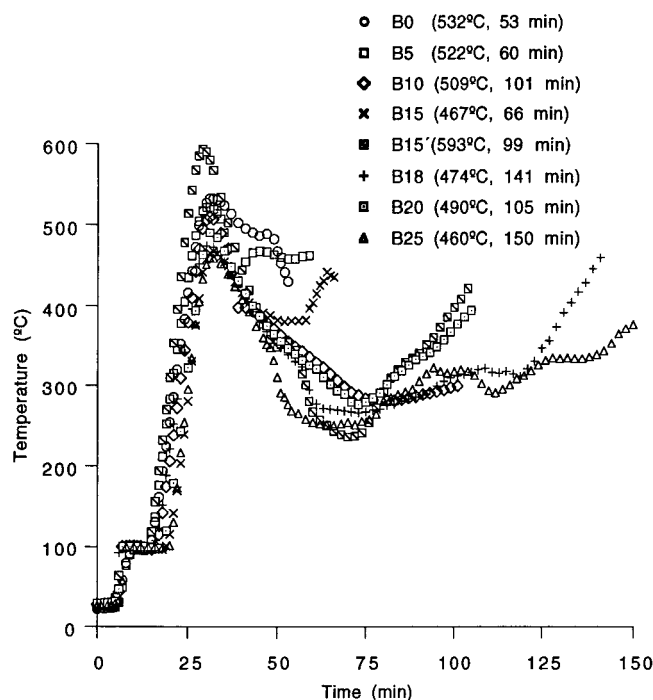
Table 1 (Continued)

RT		B0	B5	B10	B15	B15'	B18	B20	B25
13.00	4-methoxy-6-methyl-2 <i>H</i> -pyran-2-one	2.4	4.7	4.9	4.8	2.4	tr	1.0	2.9
13.67	5-hydroxymethyl-2-furancarboxaldehyde*	4.9	4.4	2.0	3.2	2.1	2.5	2.1	0.7
	<b>total common furan and pyran derivatives</b>	<b>1012.8</b>	<b>903.0</b>	<b>720.0</b>	<b>908.2</b>	<b>692.5</b>	<b>747.6</b>	<b>740.7</b>	<b>735.5</b>
	<b>acids</b>								
1.99	acetic acid*	589.8	583.1	441.3	543.7	409.4	424.3	483.8	294.7
2.62	propionic acid*	63.5	62.4	41.7	58.4	31.7	33.2	48.1	44.0
3.72	butyric acid*	5.2	26.4	5.8	26.0	4.2		3.3	19.3
3.85	2-butenic acid	11.1	2.1	9.3	2.5	8.5	8.1	8.7	1.7
6.70	tiglic acid*	5.4	4.9	3.8	5.7	3.7	3.7	2.5	5.1
10.07	levulinic acid*	15.8	12.1	3.4	11.9	4.0	4.9	4.4	9.3
10.81	heptanoic acid*	2.6	4.3	tr	4.1	tr	tr	tr	tr
16.23	nonanoic acid*		3.9		2.8				
	<b>total common acids</b>	<b>685.5</b>	<b>664.6</b>	<b>499.5</b>	<b>622.2</b>	<b>457.4</b>	<b>474.2</b>	<b>547.5</b>	<b>351.8</b>
	<b>esters</b>								
2.12	methyl propionate*	10.1	8.4	9.2	7.8	7.6	6.7	4.6	4.0
2.69	acetic anhydride*		12.7		13.7	22.7	21.8		9.9
3.56	ethyl butyrate*	6.7	5.2	5.3	5.4	5.2	4.9	4.4	3.8
3.80	methyl pentanoate*	nd	nd	nd	nd	nd	nd	nd	nd
4.18	ethylene glycol monoacetate*	8.8	3.9	5.2	3.9	4.8	3.9	3.6	1.9
5.42	ethyl pentanoate*	tr	3.4	1.6	3.5	1.5	1.2	0.6	1.7
6.75	2-furancarboxylic acid, methyl ester	3.4	2.5	5.1	3.1	tr	tr	3.4	1.9
6.99	methyl levulinate*	6.1	2.9	tr	4.0	7.3	7.6	tr	4.2
7.87	ethylene glycol diacetate*	15.7	12.0	10.5	7.7	10.2	8.5	5.3	7.0
13.39	methyl benzoate*	2.2	3.1	1.5	2.4	1.9	2.0	1.5	0.4
37.88	hexanedioic acid, dioctyl ester	tr							
	<b>total common esters</b>	<b>43.5</b>	<b>32.6</b>	<b>31.7</b>	<b>27.2</b>	<b>29.7</b>	<b>37.9</b>	<b>19.4</b>	<b>17.2</b>
	<b>phenol derivatives</b>								
7.10	phenol*	nd	nd	nd	nd	nd	nd	nd	nd
8.93	2-methylphenol*	12.7	18.8	15.3	17.7	16.2	20.5	16.5	11.6
9.53	3-methylphenol* and 4-methylphenol*	62.2	44.0	34.4	29.2	36.7	43.7	37.0	23.7
10.21	2,6-dimethylphenol*	4.0	2.0	3.4	2.5	3.8	3.8	3.4	2.4
11.15	2-ethylphenol*	2.4	2.3	1.3	3.7	1.5	1.2	1.4	0.7
11.45	2,4-dimethylphenol* and 2,5-dimethylphenol*	3.6	6.3	1.3	6.1	1.3	1.8	1.1	3.6
12.03	4-ethylphenol*	9.5	2.6	6.1	2.6	8.7	8.6	6.8	
12.21	2,3-dimethylphenol*	7.1	3.1	1.0	3.3	5.4	4.4	4.5	3.3
12.66	3,4-dimethylphenol*	0.7	3.1	0.6	2.3	2.1	2.0	0.8	
12.85	2,4,6-trimethylphenol*	0.4	2.9	0.2	2.4	1.3	1.0	0.2	0.3
13.56	2,3,6-trimethylphenol*	2.6	1.3	1.7	1.4	2.3	2.3	1.8	0.3
13.84	3-ethyl-5-methylphenol	1.1	1.5	1.6	1.6	2.6	1.9	1.3	0.8
	<b>total common phenol derivatives</b>	<b>96.1</b>	<b>82.1</b>	<b>60.2</b>	<b>68.0</b>	<b>71.0</b>	<b>80.5</b>	<b>67.1</b>	<b>46.8</b>
	<b>methoxyphenol derivatives</b>								
9.76	2-methoxyphenol (guaiacol)*	96.6	87.7	65.7	83.3	68.7	68.9	68.5	66.5
12.56	4-methyl-2-methoxyphenol (4-methylguaiacol)*	60.7	46.7	44.0	44.4	51.8	47.2	47.5	40.6
14.86	4-ethyl-2-methoxyphenol (4-ethylguaiacol)*	46.7	32.3	30.9	30.1	24.9	34.5	32.3	22.3
15.79	4-vinyl-2-methoxyphenol (4-vinylguaiacol)*	14.8	19.4	18.1	19.9	15.9	13.3	16.7	9.4
15.92	2-methyl-3-methoxyphenol	2.7	1.5	1.5	1.4	2.6	1.7	1.4	
16.99	4-(2-propenyl)-2-methoxyphenol (eugenol)*	8.6	4.8	6.6	6.3	8.1	7.8	6.9	5.0
17.17	4-propyl-2-methoxyphenol (4-propylguaiacol)*	5.5	13.1	4.8	10.6	5.2	4.2	4.7	2.2
18.12	4-hydroxy-3-methoxybenzaldehyde (vanillin)*	2.7	7.2	2.3	5.0	3.9	1.7	2.2	1.1
18.21	4-(1-propenyl)-2-methoxyphenol ( <i>trans</i> -isoeugenol)*	8.4	3.1	7.5	2.9	7.1	5.3	7.6	2.7
19.32	4-(1-propenyl)-2-methoxyphenol ( <i>cis</i> -isoeugenol)*	nd	nd	nd	nd	nd	nd	nd	nd
20.25	1-(4-hydroxy-3-methoxyphenyl)-2-ethanone (acetovanillone)*	3.3	4.2	4.0	2.5	2.9	2.4	3.8	
21.28	1-(4-hydroxy-3-methoxyphenyl)-2-propanone (2-propiovanillone)	7.9	9.7	8.8	6.9	4.0	6.5	8.8	0.8
24.08	benzeneacetic acid, 4-hydroxy-3-methoxy (vanillic acid)*	0.3	1.0	0.7	0.6		0.4	0.9	
	<b>total common methoxyphenol derivatives</b>	<b>251.8</b>	<b>224.0</b>	<b>188.7</b>	<b>209.6</b>	<b>189.4</b>	<b>189.5</b>	<b>195.3</b>	<b>150.5</b>
	<b>dimethoxyphenol derivatives</b>								
16.62	3,4-dimethoxyphenol	3.3	5.4	3.4	1.4	1.9	3.1	3.3	
16.84	2,6-dimethoxyphenol (syringol)*	120.3	120.1	94.2	92.2	60.8	79.7	92.4	38.0
17.44	3-(methoxymethyl)-4-methoxyphenol	3.0	2.4	2.2	1.8	2.5	nd	3.7	
17.65	3,5-dimethoxyphenol	5.2	1.6	4.9		1.6	nd	5.0	
19.27	4-methyl-2,6-dimethoxyphenol (4-methylsyringol)*	78.5	85.3	78.1	67.9	50.6	65.2	75.5	31.7
19.92	2,6-dimethoxyphenol acetate	2.5	0.5	1.7	0.6	3.4	1.1	1.8	0.7
21.12	4-ethyl-2,6-dimethoxyphenol (4-ethylsyringol)	29.4	31.3	27.1	26.4	17.5	25.7	26.9	10.5
22.03	4-vinyl-2,6-dimethoxyphenol (4-vinylsyringol)	1.1	1.9	8.4	8.3	4.0	9.1	10.6	1.9

Table 1 (Continued)

RT		B0	B5	B10	B15	B15'	B18	B20	B25
22.88	4-(2-propenyl)-2,6-dimethoxyphenol (allylsyringol)*	13.3	13.3	14.4	11.3	8.3	11.3	13.4	4.3
23.03	4-propyl-2,6-dimethoxyphenol (4-propylsyringol)	5.8	5.5	6.3	5.4	4.6	6.1	6.9	3.0
24.33	4-(1-propenyl)-2,6-dimethoxyphenol ( <i>cis</i> -propenylsyringol)	2.2	1.5	5.7	4.9	3.8	6.9	6.5	1.6
24.35	4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde)*	11.0	15.1	13.1	8.9	5.5	9.3	11.6	
25.08	4-(1-propenyl)-2,6-dimethoxyphenol ( <i>trans</i> -propenylsyringol)	2.3	3.4	18.2	15.3	11.8	35.6	23.7	
25.83	1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone (acetosyringone)*	12.0	16.2	13.3	11.2	6.0	10.2	12.2	7.5
26.61	2-(4-hydroxy-3,5-dimethoxyphenyl)propanone (2-propiosyringone)	35.1	46.7	38.0	30.9	19.1	26.2	32.9	
27.74	1-(4-hydroxy-3,5-dimethoxyphenyl)propanone (1-propiosyringone)	5.6	7.3	6.1	5.2	2.9	4.9	5.8	
<b>total common dimethoxyphenol derivatives</b>		<b>265.2</b>	<b>275.6</b>	<b>249.2</b>	<b>228.2</b>	<b>159.0</b>	<b>215.4</b>	<b>246.2</b>	<b>99.3</b>
<b>polyphenol derivatives</b>									
11.83	dihydroxybenzaldehyde	6.3	1.2	3.4	1.2	3.8	4.2	3.6	
13.25	1,2-benzenediol (pyrocatechol)*	5.0	9.5	2.4	3.7	4.0	3.3	2.6	1.7
14.53	3-methyl-1,2-benzenediol (3-methylpyrocatechol)*	16.1	5.3	4.5	4.5	11.7	10.9	4.1	3.7
14.72	3-methoxy-1,2-benzenediol (3-methoxypyrocatechol)*	24.7	43.4	11.0	29.1	9.0	11.5	8.3	2.2
<b>total common polyphenol derivatives</b>		<b>45.8</b>	<b>58.2</b>	<b>17.8</b>	<b>37.2</b>	<b>24.7</b>	<b>25.6</b>	<b>15.0</b>	<b>7.6</b>
<b>alkyl aryl ethers</b>									
11.25	1,2-dimethoxybenzene*	3.4	2.1	2.1	1.5	2.7	2.2	2.1	1.4
12.13	1,4-dimethoxybenzene*	1.6	7.5	6.5	7.9	4.3	1.7	4.9	6.3
13.76	2,6-dimethoxytoluene	1.8	1.8	0.7	1.7	4.1	5.3	0.7	
16.46	1,2,3-trimethoxybenzene*	4.6	2.0	2.9	2.6	2.8	2.2	2.4	
18.09	5-methyl-1,2,3-trimethoxybenzene	3.4	2.1	2.9	1.6	3.1	2.5	1.0	
18.43	4-(1-propenyl)-1,2-dimethoxybenzene*	0.6	0.5	0.8			0.4	0.8	
<b>total common alkyl aryl ethers</b>		<b>5.0</b>	<b>9.7</b>	<b>8.6</b>	<b>9.4</b>	<b>7.1</b>	<b>3.9</b>	<b>7.0</b>	<b>7.6</b>
<b>lignin dimers</b>									
28.11	234 (100), 219 (38), 207 (33), 188 (10), 173 (25), 164 (8), 129 (15), 94 (7), 81 (22)	0.2							
31.28	254 (80), 208 (34), 194 (48), 167 (100), 151 (24), 137 (22), 125 (19), 115 (15), 91 (15)	0.7	0.8	0.8	0.6	0.5	0.6	0.8	
36.64	286 (57), 243 (14), 211 (21), 196 (13), 164 (100), 149 (37), 137 (30), 108 (11), 94 (14)	0.7	1.8	1.6	1.5	0.7	1.3	1.4	
37.39	300 (66), 219 (8), 177 (11), 164 (100), 149 (17), 128 (6)	tr							
38.23	300 (48), 164 (100), 149 (27), 131 (9), 121 (5), 103 (11), 91 (11), 77 (13)	0.5	0.5	0.1					
38.69	302 (91), 281 (29), 194 (100), 179 (20), 164 (44), 146 (17), 121 (42)	0.2	0.4	0.3	1.3	0.1		0.2	
39.84	316 (52), 194 (100), 179 (13), 164 (11), 149 (25), 135 (13)	0.3	0.3	0.3		0.6			
40.32	316 (56), 194 (100), 179 (10), 149 (23), 135 (11)	0.9	1.0	0.8	0.5	0.4		0.4	
40.76	316 (62), 194 (100), 179 (14), 164 (26), 149 (18), 135 (11)	1.0	1.1	0.6	0.4	0.3		0.5	
40.80	330 (100), 300 (13), 287 (20), 206 (15), 189 (14), 163 (64)	0.6	0.7	0.9		0.2			
41.07	330 (63), 314 (26), 208 (19), 194 (100), 177 (30), 164 (80), 150 (36)	0.5	0.6	0.5	0.4	0.1		0.2	
41.74	330 (40), 194 (100), 163 (22), 149 (11)	0.4	0.7	0.3	0.2	0.1		0.2	
41.90	330 (48), 194 (22), 179 (17), 164 (100), 150 (17), 136 (10)	tr							
42.09	330 (38), 316 (21), 194 (100), 180 (22), 163 (13), 149 (10)	tr							
42.47	344 (13), 330 (37), 194 (100), 177 (13), 163 (21)	0.2	0.3	0.6					
42.70	332 (47), 257 (10), 194 (100), 179 (9), 165 (10), 151 (17)	tr							
42.85	344 (7), 330 (26), 316 (6), 207 (17), 194 (100), 179 (15), 163 (17), 149 (8)	tr							
43.30	348 (24), 330 (18), 193 (31), 181 (100), 167 (19), 151 (13), 135 (21), 122 (12)	tr							
43.98	346 (31), 272 (10), 194 (100), 179 (15), 165 (12), 150 (11)	tr							
<b>total common lignin dimers</b>									
<b>miscellaneous</b>									
2.52	2-pentanol*	5.0	4.0			3.7	4.0	4.0	
2.78	3-methyl-1-butanol*	6.8	7.2	5.0	5.2	4.1	4.5	4.0	2.5
3.18	toluene*		3.0	3.6	4.2	2.6	2.2	2.9	1.2
8.17	benzenemethanol*	18.2	13.6	12.5	14.7	13.1	14.5	12.4	12.7
44.22	2,6,10,14,18,22-tetracosahexaene, 2,6,10,15,19,23-hexamethyl (squalene)*	tr	0.5	0.8		0.1			
26.06	210 (100), 195 (8), 166 (14), 121 (17), 116 (5), 103 (10), 91 (16)	1.4	1.1	1.6	0.9	0.2	1.3	1.6	
28.22	204 (100), 189 (82), 157 (33), 146 (20), 118 (10), 101 (16), 89 (13)	0.2	0.4	0.3		0.2	0.2	0.3	
<b>total common miscellaneous</b>		<b>25.0</b>	<b>20.9</b>	<b>17.6</b>	<b>19.9</b>	<b>17.2</b>	<b>18.9</b>	<b>16.4</b>	<b>15.1</b>

<sup>a</sup> Asterisked compounds were used as standard for identification and quantitation. nd, not determined. tr, compounds in very small proportion.



**Figure 1.** Maximum temperature reached in each pyrolytic run versus length of the process.

could be due to the difficulty of having composition samples, which are totally homogeneous, or to an irregular distribution of the moisture content; both aspects may be present in the production of smoke flavorings.

The smoke produced by each sample, after filtration, was collected in distilled water and filtered again. Table 1 gives the amount of liquid smoke obtained in each case; it can be observed that there is no simple relationship between the moisture content of the sample to be pyrolyzed and the volume of liquid smoke obtained. Not only the moisture content of the sample but also the temperature and the length of the process influence the volume of the liquid smoke obtained, even though the main component of these liquid smokes is water. Samples with low moisture contents (B0 and B5) produced smaller volumes of liquid smoke than samples with very high moisture contents (B25 or B20), and the highest amount of liquid smoke was produced by samples with intermediate moisture contents (B10 and B18). These results are in agreement with the results of Gorbato et al. (1971).

The acidity of the liquid smokes, expressed as acid equivalents, is given in Table 1. It is evident that samples with low moisture contents produce higher amounts of acids than samples with high moisture contents, also in agreement with the results of Gorbato et al. (1971).

A part of each smoke flavoring preparation was extracted with  $\text{CH}_2\text{Cl}_2$  to identify and quantify its components by means of GC/MS and GC-FID techniques. Table 1 gives the retention times and the yields in milligrams of the 148 detected components in the liquid smoke dichloromethane extracts. Although compounds such as formaldehyde (Gorbato et al., 1971; Toth and Potthast, 1984), formic acid (Shafizadeh, 1984; Alén et al., 1996), ethanedial (Shafizadeh, 1984), propenal (Shafizadeh, 1984), 2-ketopropanaldehyde, or hydroxyacetaldehyde (Jakab et al., 1997) can be formed during wood pyrolysis, they were not detected in the

liquid smokes. This could be due to different causes, such as the tendency of most of these compounds to give polymers (Windholz, 1983), their poor solubility in dichloromethane (Weast, 1985), or the overlapping of their peaks with the dichloromethane peak during gas chromatography. The difficulty of separating smoke components of low molecular weights by on-line GC/MS has been shown by Jakab et al. (1997). Aldehydes, ketones, diketones, furan and pyran derivatives, acids, esters, phenol, guaiacol, syringol, and their derivatives, as well as pyrocatechol derivatives, alkyl-aryl ethers, some lignin dimers, and other compounds, were identified and quantified. Some compounds, for which the chromatographic separation was not good enough, were not quantified and are indicated in Table 1 as "nd".

The data in Table 1 are arranged in increasing moisture content. It can be observed that the highest yield in total compounds was obtained from samples with low moisture content which underwent short pyrolysis processes [samples B0 (532 °C, 53 min), B5 (522 °C, 60 min), and B15 (467 °C, 66 min)]. Intermediate yields in total compounds were obtained from samples with intermediate moisture content that underwent longer pyrolysis processes [samples B10 (509 °C, 101 min), B15' (593 °C, 99 min), B18 (474 °C, 141 min), and B20 (490 °C, 105 min)]. The high temperature at which sample B15' underwent the pyrolysis process could be the cause of the smaller yield obtained, in agreement with previous results (Guillén and Ibargoitia, 1996a). Finally, the smallest yield in total compounds was obtained from the sample with the highest moisture content, which underwent the slowest pyrolysis process and at the lowest temperature [B25 (460 °C, 150 min)]. Previous results have shown that processes at both high or low temperatures, with the same moisture content, lead to low yields and that the highest yields are obtained at intermediate temperatures (Guillén and Ibargoitia, 1996a).

The yield of total carbonyl and carboxyl derivatives, as well as of total phenolic derivatives and of other compounds from several samples, are also given in Table 1 and follow the same trend.

It can also be observed in Table 1 that the same aldehydes, ketones, and diketones were formed in the pyrolysis of different samples and that the yield of these different groups of compounds was higher in samples B0, B5, and B15 and that the smallest yield was obtained from B25. However, the decrease in yield as the moisture content increases is more noticeable in the aldehyde and diketone groups than in the ketones. Therefore, the moisture content of the sample and the conditions of the several pyrolysis experiments do not affect, to the same extent, the formation of these three groups. The yield in ketones is the least affected. In relation to individual components, some of their yields do not suffer a great variation in the several pyrolysis experiments and can be considered as constants; an example is acetaldehyde. In other cases, the yield varies in the same way as the yield of total compounds above, and usually this trend is observed in the main components, such as 3-methylbutyraldehyde, 2-ethylbutyraldehyde, and cyclopentadiene; there are also cases in which the yield was higher at intermediate moisture than at low or high moisture content, such as valeraldehyde and 3-hexanone; finally, there are other compounds for which the yields are not apparently related, either to the moisture content or to the pyrolysis conditions.

The decrease in yield of furan and pyran derivatives, as the moisture content increases, is very low, showing that the moisture content of the sample does not greatly affect the formation of these derivatives. The variation of the yield of some of the most significant components of this group, such as 2-furanmethanol,  $\alpha$ -angelicalactone,  $\gamma$ -crotonolactone, 2(3*H*)-dihydrofuranone, 5-methylfuranicarboxaldehyde, 3-methyl-2(5*H*)furanone, maltol, and 5-hydroxymethyl-2-furanicarboxaldehyde, follows the same trend observed in the variation of the yield of the total compounds.

The total yield in acids was also higher in samples B0, B5, and B15, and the smallest yield was obtained from sample B25. It must be noticed that not all acids and esters detected have been found in the eight liquid smokes. The different conditions in which the pyrolysis was produced as a consequence of the different moisture content of the samples not only diminish the generation of some phenolic derivatives but also hinder the formation of others, especially in sample B25. It is noteworthy that specific phenolic derivatives such as 2-methylphenol, 4-vinylguaiacol, 4-vinylsyringol, *cis*-propenylsyringol, and *trans*-propenylsyringol were produced in highest yields from samples with intermediate moisture contents (samples B10, B15, B15', B18, and B20).

The yield of pyrocatechol derivatives as well as of alkyl-aryl ethers was also higher in samples B0, B5, and B15, and it is significant that the formation of these compounds was prevented in the sample with the highest moisture content. Smoke can also contain lignans or lignin oligomers (Guillén and Ibargoitia, 1998). Some of these compounds have been identified in the liquid smokes obtained; the generation of these compounds is highly affected by the moisture content of the sample. As can be observed in Table 1, none of these compounds were obtained from sample B25, and the liquid smoke from sample B0 contained the highest number of lignin dimers.

However, as has been commented above, not only moisture content of the sample *M* but also the length of the smoke emission *L* and temperature of the process *T* were different in the various pyrolysis experiments, and these two latter parameters can also affect the result of the process. To study the influence of these parameters on the formation of the different smoke components in a quantitative way, relationships between yield *Y* of the smoke components obtained and the parameters above cited were tested. It must be taken into account that pyrolysis is a very complex process which involves endothermic and exothermic reactions that can take place simultaneously or successively, including depolymerizations, dehydrations, fissions, condensations, oxidations, decompositions, and so forth, as well as formation of carbonyl, carboxyl, and hydroperoxide groups and also decarbonylation and decarboxylation processes. For these reasons, no simple relationships between the variable parameters during the pyrolysis process and yield of the liquid smoke components could be expected. It must also be taken into account that, in studies of quantitative relationships, any small variations in the pyrolysis process, the collection of smoke, the extraction of smoke components, the chromatographic run, and the subsequent quantification of the smoke components may decisively influence the results.

The fitting of the yield data (*Y*) for the eight experiments to the parameters mentioned (*L*, *M*, and *T*), using single linear relationships, shows that the first two parameters, moisture content and process length, are apparently much more closely related to the total yield, to the yield of different groups of compounds, and to the yield of many of the individual components than the maximum temperature reached in the process. Correlation coefficients of these single linear relationships are given in Table 2. Correlation coefficients between yield and moisture content of the sample or between yield and length of the process often exceed 0.8 or 0.9, showing that both parameters very decisively influence the formation of many of the smoke components and that this influence is quite well represented by a simple linear function. From correlation coefficients of biparametric linear relationships, between yield *Y* and parameters *M* and *L*, shown in Table 2, it can be deduced that compounds whose formation is more closely influenced by the moisture content of the sample, and by the length or rate of the process, are, among aldehydes, ketones, and diketones, 3-methylbutyraldehyde, 2-ethylbutyraldehyde, 2-methyl-3-pentanone, and cyclotene; among furan and pyran derivatives, 2-furanmethanol, maltol, and 5-hydroxymethyl-2-furanicarboxaldehyde; and among acids, esters, and other compounds, acetic acid, methyl propionate, ethyl butyrate, and 3-methyl-1-butanol.

However, correlation coefficients between yield *Y* and maximum temperature reached in the process, *T*, are very small, showing that there are no simple relationships between them. In a previous paper we have reported that, keeping all other parameters which may affect the pyrolytic process constant, the yield of the smoke components depends on the maximum temperature reached in the process. This dependence is well represented by a second-degree polynomial equation such as

$$Y = a + bT + cT^2 \quad (1)$$

where *Y* is yield, *a*, *b*, and *c* are the regression coefficients, and *T* is the temperature. For this reason, equations including moisture content *M*, process length *L*, temperature *T*, and *T*<sup>2</sup>, such as

$$Y = a + bL + cM + dT + eT^2 \quad (2)$$

were tested. The correlation coefficients *R* of the equations obtained are also given in Table 2. It can be observed that these coefficients are often very close to 1, showing the importance of temperature in the formation of many smoke components. From the improvement in the correlation coefficients due to the inclusion of temperature in the equations, it can be deduced that its influence is especially noteworthy in the formation of aldehydes (such as 2-methylbutyraldehyde, 3-methylbutyraldehyde, and 2-ethylbutyraldehyde), of branched and cyclic ketones (such as 2-methyl-3-pentanone, cyclohexanone, 2-methyl-2-cyclopenten-1-one, 2,5-dimethyl-2-cyclopenten-1-one, 3,4,5-trimethyl-2-cyclopenten-1-one, and 2-methylindanone), of diketones (such as 2,5-hexanedione and cyclotene), of many of the main furan and pyran derivatives [such as 2-furanmethanol,  $\alpha$ -angelicalactone, 2-ethylfuran, acetylfuran, 2(3*H*)-dihydrofuranone, 5-methyl-2-furanicarboxaldehyde, 3-methyl-2(5*H*)-furanone, 1-(2-furanyl)-1-propanone, and maltol],



**Table 2. Correlation Coefficients  $R$  between Various Yield Data  $Y$  and Parameters such as Sawdust Moisture Content  $M$ , Length of the Smoke Emission  $L$ , Temperature of the Process  $T$ , and Other Related Parameters Using Single, Biparametric, or Multiple Linear Regressions<sup>a</sup>**

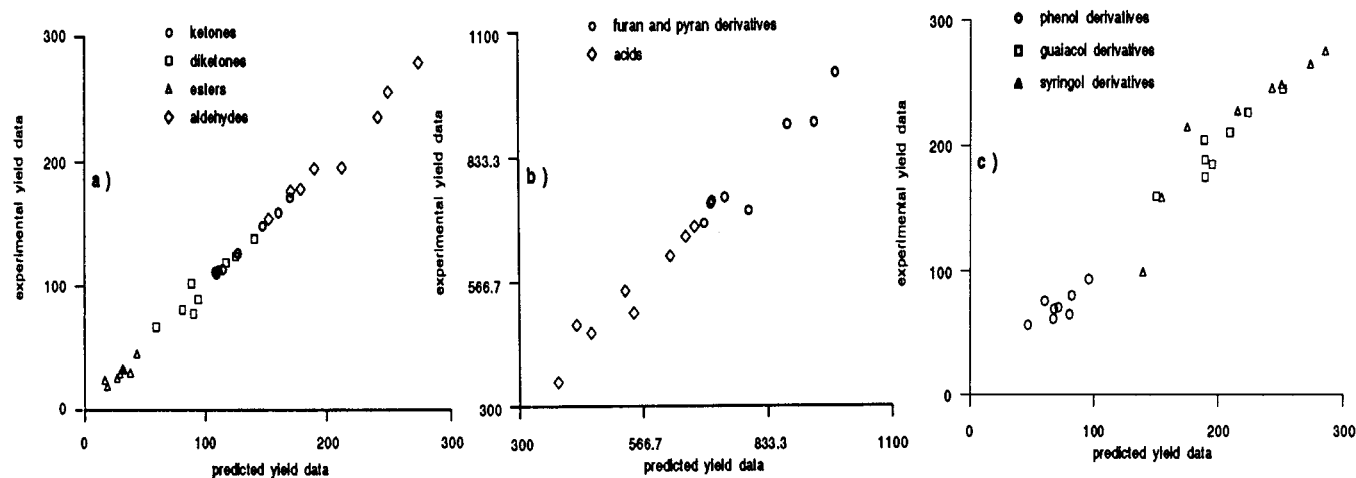
yield	correlation coefficients $R$					
	$M$	$L$	$T$	$M, L$	$M, L, T, T^2$	$M, T, M \cdot T, T^2$
<b>common total compounds</b>	0.84	0.90*	0.14	0.92*	0.97*	0.91
<b>common total carbonyl and carboxyl derivatives</b>	0.82	0.90*	0.10	0.91*	0.97*	0.90
<b>common total phenol derivatives</b>	0.83	0.83	0.24	0.87	0.92*	0.92*
<b>common total others</b>	0.81	0.93*	0.19	0.94*	0.97*	0.88
<b>acidity of the liquid smoke</b>	0.84	0.80	0.03	0.87	0.96*	0.94
<b>total common aldehydes</b>	0.87	0.93*	0.19	0.95*	0.98*	0.91
acetaldehyde	0.57	0.65	0.54	0.65	0.72	0.65
3-methylbutyraldehyde	0.87	0.90*	0.23	0.93*	0.96*	0.90
2-methylbutyraldehyde	0.86	0.63	0.18	0.86	0.93*	0.95*
valeraldehyde	0.07	0.35	0.09	0.51	0.55	0.82
2-ethylbutyraldehyde	0.84	0.89	0.16	0.91*	0.97*	0.91
<b>total common ketones</b>	0.79	0.86	0.02	0.87	1.00*	0.94
2-propanone	0.02	0.07	0.07	0.15	0.49	0.91*
2-pentanone	0.88	0.81	0.33	0.89	0.91*	0.97*
2-methyl-3-pentanone	0.43	0.81	0.13	0.90*	0.99*	0.69
3-hexanone	0.19	0.30	0.22	0.80	0.83	0.72
cyclopentanone	0.86	0.63	0.29	0.87	0.89	0.93*
2-heptanone	0.46	0.06	0.03	0.70	0.82	0.69
cyclohexanone	0.86	0.59	0.29	0.88	1.00*	0.97
2-methyl-2-cyclopenten-1-one	0.82	0.71	0.03	0.83	0.97*	0.98*
2,5-dimethyl-2-cyclopenten-1-one	0.84	0.74	0.14	0.85	0.97*	0.97*
3-methylcyclohexanone	0.29	0.53	0.22	0.59	0.85	0.73
3,4,5-trimethyl-2-cyclopenten-1-one	0.85	0.79	0.27	0.87	0.94*	0.94*
dimethyl-2-cyclopenten-1-one	0.51	0.35	0.18	0.51	0.82	0.81
1-phenylethanone (acetophenone)	0.82	0.63	0.26	0.82	0.87	0.93*
2-ethyl-2,5-dimethylcyclopentenone	0.63	0.51	0.15	0.63	0.84	0.97*
2-methylindanone	0.83	0.83	0.13	0.87	0.94*	0.92
<b>total common diketones and triketones</b>	0.84	0.90*	0.17	0.92*	0.95*	0.90
2,3-pentanedione	0.28	0.48	0.29	0.51	0.74	0.65
1,4-cyclopenten-2-dione	0.42	0.06	0.49	0.64	0.72	0.55
2,5-hexanedione	0.66	0.86	0.03	0.86	0.95*	0.83
2,4-dimethylcyclopent-4-ene-1,2-dione	0.72	0.48	0.43	0.74	0.77	0.75
3-methyl-1,2-cyclopentanedione (cyclotene)	0.84	0.88	0.18	0.91*	0.94*	0.88
3-ethyl-1,2-cyclopentanedione (3-ethylcyclopentenolone)	0.78	0.69	0.45	0.79	0.82	0.83
<b>total common furan and pyran derivatives</b>	0.74	0.79	0.03	0.81	0.95*	0.90
2-furancarboxaldehyde	0.59	0.55	0.19	0.60	0.89	0.95*
2-furanmethanol	0.58	0.88	0.02	0.91*	0.97*	0.74
5-methyl-2(3 <i>H</i> )-furanone ( $\alpha$ -angelicalactone)	0.70	0.80	0.06	0.81	0.96*	0.88
2-ethylfuran	0.90*	0.74	0.20	0.90*	0.97*	0.98*
1-(2-furanyl)-ethanone (acetyl furan)	0.75	0.57	0.02	0.76	1.00*	0.99
2(5 <i>H</i> )-furanone ( $\gamma$ -crotonolactone)	0.67	0.77	0.00	0.78	0.88	0.80
2(3 <i>H</i> )-dihydrofuranone	0.80	0.88	0.11	0.89	0.95*	0.88
5-methyl-2(5 <i>H</i> )-furanone	0.52	0.14	0.42	0.72	0.77	0.57
5-methyl-2-furancarboxaldehyde	0.63	0.58	0.15	0.64	0.91*	0.95*
dimethylfuranone	0.71	0.37	0.44	0.79	0.83	0.74
3-methyl-2(5 <i>H</i> )-furanone	0.81	0.88	0.11	0.90*	0.97*	0.92
1-(2-furanyl)-1-propanone	0.69	0.51	0.15	0.70	0.99*	0.97
3-hydroxy-2-methyl-4 <i>H</i> -pyran-4-one (maltol)	0.84	0.94*	0.25	0.95*	0.98*	0.89
5-propyl-2(3 <i>H</i> )-dihydrofuranone	0.70	0.70	0.35	0.74	0.89	0.88
5-hydroxymethyl-2-furancarboxaldehyde	0.87	0.86	0.28	0.91*	0.92*	0.89
<b>total common acids</b>	0.79	0.92*	0.17	0.93*	0.96*	0.86
acetic acid		0.78	0.92*	0.20	0.92*	0.95*
propionic acid	0.60	0.78	0.14	0.78	0.92*	0.77
2-butenic acid	0.38	0.07	0.45	0.56	0.68	0.56
tiglic acid		0.37	0.42	0.18	0.42	0.90*
levulinic acid	0.68	0.75	0.01	0.76	0.92*	0.88
	0.80	0.46	0.37	0.86	0.89	0.83
<b>total common esters</b>						
methyl propionate	0.91*	0.74	0.49	0.91*	0.92*	0.97*
ethyl butyrate	0.92*	0.78	0.46	0.92*	0.95*	0.97*
ethylene glycol monoacetate	0.88	0.63	0.50	0.89	0.91*	0.89
ethylene glycol diacetate	0.42	0.00	0.12	0.73	0.77	0.46
methyl benzoate	0.63	0.77	0.32	0.77	0.77	0.81
<b>total common phenol derivatives</b>	0.77	0.62	0.39	0.77	0.78	0.78
2-methylphenol	0.08	0.06	0.05	0.22	0.31	0.75
3-methylphenol and 4-methylphenol	0.82	0.53	0.40	0.85	0.85	0.85
2,6-dimethylphenol	0.22	0.10	0.41	0.51	0.63	0.42
2-ethylphenol	0.46	0.81	0.06	0.88	0.97*	0.84
2,4-dimethylphenol and 2,5-dimethylphenol	0.28	0.54	0.25	0.60	0.81	0.65



Table 2 (Continued)

yield	correlation coefficients $R$					
	$M$	$L$	$T$	$M, L$	$M, L, T, T^2$	$M, T, M \cdot T, T^2$
2,3-dimethylphenol	0.31	0.23	0.39	0.31	0.54	0.67
2,4,6-trimethylphenol	0.18	0.50	0.09	0.64	0.66	0.59
2,3,6-trimethylphenol	0.52	0.33	0.55	0.55	0.65	0.67
3-ethyl-5-methylphenol	0.03	0.03	0.63	0.09	0.74	0.94*
<b>total common methoxyphenol derivatives</b>	0.89	0.89	0.34	0.94*	0.94*	0.91
2-methoxyphenol (guaiacol)	0.80	0.84	0.15	0.86	0.93*	0.88
4-methyl-2-methoxyphenol (4-methylguaiacol)	0.73	0.54	0.61	0.73	0.81	0.83
4-ethyl-2-methoxyphenol (4-ethylguaiacol)	0.78	0.55	0.09	0.80	0.86	0.85
4-vinyl-2-methoxyphenol (4-vinylguaiacol)	0.42	0.74	0.23	0.80	0.86	0.91*
4-(2-propenyl)-2-methoxyphenol (eugenol)	0.32	0.10	0.45	0.42	0.59	0.51
4-propyl-2-methoxyphenol (4-propylguaiacol)	0.42	0.74	0.10	0.80	0.82	0.66
4-hydroxy-3-methoxybenzaldehyde (vanillin)	0.41	0.73	0.32	0.78	0.80	0.62
4-(1-propenyl)-2-methoxyphenol ( <i>trans</i> -isoeugenol)	0.39	0.14	0.53	0.49	0.71	0.66
1-(4-hydroxy-3-methoxyphenyl)-2-propanone (2-propiovanillone)	0.59	0.63	0.10	0.65	0.92*	0.97*
<b>total common dimethoxyphenol derivatives</b>	0.70	0.71	0.10	0.74	0.92*	0.96*
2,6-dimethoxyphenol (syringol)	0.82	0.82	0.16	0.86	0.97*	0.95
4-methyl-2,6-dimethoxyphenol (4-methylsyringol)	0.69	0.69	0.13	0.72	0.93*	0.97*
2,6-dimethoxyphenol acetate	0.27	0.12	0.81	0.31	0.85	0.83
4-ethyl-2,6-dimethoxyphenol (4-ethylsyringol)	0.68	0.69	0.06	0.72	0.89	0.95*
4-vinyl-2,6-dimethoxyphenol (4-vinylsyringol)	0.43	0.27	0.37	0.45	0.62	0.88
4-(2-propenyl)-2,6-dimethoxyphenol (allylsyringol)	0.62	0.60	0.12	0.64	0.88	0.97*
4-propyl-2,6-dimethoxyphenol (4-propylsyringol)	0.35	0.34	0.02	0.36	0.73	0.86
4-(1-propenyl)-2,6-dimethoxyphenol ( <i>cis</i> -propenylsyringol)	0.34	0.31	0.23	0.35	0.47	0.76
1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone (acetosyringone)	0.54	0.56	0.16	0.58	0.96*	0.95
<b>total common diphenol derivatives</b>	0.76	0.82	0.29	0.84	0.85	0.80
1,2-benzenediol (pyrocatechol)	0.60	0.66	0.36	0.67	0.69	0.62
3-methyl-1,2-benzenediol (3-methylpyrocatechol)	0.56	0.66	0.55	0.67	0.85	0.78
3-methoxy-1,2-benzenediol (3-methoxypyrocatechol)	0.64	0.81	0.10	0.81	0.85	0.75
<b>total common others</b>	0.81	0.93*	0.19	0.94*	0.97*	0.88
1,2-dimethoxybenzene	0.73	0.43	0.71	0.78	0.89	0.87
1,4-dimethoxybenzene	0.23	0.17	0.23	0.64	0.68	0.44
3-methyl-1-butanol	0.90*	0.86	0.30	0.93*	0.94*	0.94*
benzenemethanol	0.71	0.53	0.10	0.71	0.90*	0.90*

<sup>a</sup> Asterisks indicate significant correlation coefficients.



**Figure 2.** Experimental yield data of different groups of liquid smoke components versus predicted yield data from eq 2: (a) aldehydes, ketones, diketones, and esters; (b) furan and pyran derivatives and acids; (c) phenol, guaiacol, and syringol derivatives.

of all acids (except 2-butenic acid), and of some phenolic derivatives (such as 2-ethylphenol, guaiacol, 2-propiovanillone, syringol, 4-methylsyringol, and acetosyringone). To form these cyclic compounds, cyclation and oxidation reactions must be carried out, which are probably favored by a certain temperature range; guaiacol and syringol come from thermal lignin degradation, and obviously temperature plays an important role in the formation of these compounds, as well as in the formation of ketones derived from them.

As most of the components above are main compo-

nents of smoke, fitting of yield of total smoke components or yield of groups of compounds to  $L$ ,  $M$ ,  $T$ , and  $T^2$  parameters through multiple linear regression also gives equations such as eq 2 with correlation coefficients very close to 1, as can be observed in Table 2. Figure 2 gives representations of experimental yield data of the different groups of compounds versus predicted yield data from the corresponding eq 2. It can be observed that, in most of the cases, there is a great concordance between both sets of data, showing that eq 2 represents, with a high degree of approximation, the influence of

the several parameters on the formation of the different groups of compounds.

Even though the formation of most of the main components is well represented by eq 2, there are other compounds having yields that do not closely fit it. This may be due to many of the smoke components being formed in secondary or tertiary reactions, and conditions that favor the formation of some of them may hinder the generation of others; for this reason the same approach may not be appropriate for relating yields of all smoke components and parameters of the process. With this idea in mind, other approaches have been tested and close relationships have been found between yield of some compounds, most of them different from those above-mentioned, and parameters such as  $M$ ,  $MT$ ,  $T$ , and  $T^2$  through equations

$$Y = a + bM + cT + dMT + eT^2 \quad (3)$$

Correlation coefficients of the equations obtained are also given in Table 2. It can be observed that compounds for which the yield is well predicted by this equation are 2-methylbutyraldehyde among aldehydes; 2-propanone, 2-pentanone, cyclopentanone, acetophenone, and 2-ethyl-2,5-dimethylcyclopentenone among ketones; 2-furancarboxaldehyde and 5-methyl-2-furancarboxaldehyde among furan derivatives; methyl propionate among esters; and 3-ethyl-5-methylphenol, 4-vinylguaiacol, 2-propiovanillone, 4-methylsyringol, 4-ethylsyringol, and allylsyringol among phenolic derivatives.

In conclusion, the moisture content of the sawdust sample modifies some parameters of the pyrolysis process, such as the length of the process and the temperature reached, and in their turn the three parameters influence the composition of the smoke produced. Low moisture content produces, in general, greater amounts of most smoke components than high; the formation of some smoke components is hindered if the moisture content of the sample is very high. The yield in smoke components is closely related to the three parameters above and it can be predicted, with a high degree of approximation, from equations that include these parameters.

#### ABBREVIATIONS USED

$M$ , moisture percentage in the initial samples;  $L$ , length of the smoke emission or the duration of the pyrolysis experiments;  $T$ , maximum temperature reached in the center of the charge in each pyrolysis experiment;  $Y$ , yield of total smoke flavoring components or of groups of components or of individual components;  $RT$ , retention times.

#### LITERATURE CITED

- Alén, R.; Kuoppala, E.; Oesch, P. Formation of the main degradation compound groups from wood and its components during pyrolysis. *J. Anal. Appl. Pyrolysis* **1996**, *36*, 137–148.
- Baltes, W.; Wittkowski, R.; Sochtig, I.; Block, H.; Toth, L. Ingredients of smoke and smoke flavour preparation. In *The Quality of Food and Beverages*; Charalambous, G., Inglett, G., Eds.; Academic Press: New York, 1981; Vol. 2, Chapter 1, pp 1–19.
- Chen, Z.; Maga, J. A. Pyrazine composition as influenced by the smoking conditions of hickory sawdust. In *Food Flavors: Generation, Analysis and Process Influence, Proceedings of the 8th International Flavor Conference*; Charalambous, G., Ed.; Elsevier: Amsterdam, The Netherlands, 1995; pp 1025–1029.
- Daun, H. Sensory properties of phenolic compounds isolated from curing smoke as influenced by its generation parameters. *Lebensm. Wiss. Technol.* **1972**, *5*, 102–105.
- Fujimaki, M.; Kim, K.; Kurata, T. Analysis and comparison of flavor constituents in aqueous smoke condensates from various woods. *Agric. Biol. Chem.* **1974**, *38*, 45–52.
- Gorbatov, V. M.; Krylova, N. N.; Volovinskaya, V. P.; Lyaskovskaya, Y. N.; Bazarova, K. Y.; Khlamova, R. Y.; Yakovleva, G. Y. Liquid smokes for use in cure meats. *Food Technol.* **1971**, *25*, 71–77.
- Guillén, M. D. Polycyclic aromatic hydrocarbons: extraction and determination in food. *Food Addit. Contam.* **1994**, *11*, 669–684.
- Guillén, M. D.; Ibargoitia, M. L. Relationships between the maximum temperature reached in the smoke generation processes from *Vitis vinifera* L shoot sawdust and composition of the aqueous smoke flavoring preparations obtained. *J. Agric. Food Chem.* **1996a**, *44*, 1302–1307.
- Guillén, M. D.; Ibargoitia, M. L. Volatile components of aqueous liquid smokes from *Vitis vinifera* L shoots and *Fagus sylvatica* L wood. *J. Sci. Food Agric.* **1996b**, *72*, 104–110.
- Guillén, M. D.; Ibargoitia, M. L. New components with potential antioxidant and organoleptic properties, detected for the first time in liquid smoke flavoring preparations. *J. Agric. Food Chem.* **1998**, *46*, 1276–1285.
- Guillén, M. D.; Manzanos, M. J. Smoke and liquid smoke. Study of an aqueous smoke flavouring from the aromatic plant *Thymus vulgaris* L. *J. Sci. Food Agric.* **1999a**, *79*, 1–8.
- Guillén, M. D.; Manzanos, M. J. Extractable components of the aerial parts of *Salvia lavandulifolia* and the composition of the liquid smoke flavoring obtained from them. *J. Agric. Food Chem.* **1999b**, *47*, 3016–3027.
- Guillén, M. D.; Blanco, J.; Canga, J. S.; Blanco, C. G. Study of the effectiveness of 27 organic solvents in the extraction of coal tar pitches. *Energy Fuels* **1991**, *5*, 188–192.
- Guillén, M. D.; Manzanos, M. J.; Zabala, L. Study of a commercial liquid smoke flavouring by means of GC/MS and FTIR. *J. Agric. Food Chem.* **1995**, *43*, 463–468.
- Hamm, R.; Potthast, K. Einfluss verschiedener Techniken des Räucherns und der Anwendung von Räuchermitteln an cancerogenen Kohlenwasserstoffen, Phenolen und anderen Rauchbestandteilen. Final Report, Research Project Ha 517/6, Ha 517/11, Ha 517/14 of the Deutsche Forschungsgemeinschaft, 1976.
- Jakab, E.; Liu, K.; Meuzelaar, H. L. C. Thermal decomposition of wood and cellulose in the presence of solvent vapors. *Ind. Eng. Chem. Res.* **1997**, *36*, 2087–2095.
- Maga, J. A. In *Smoke in Food Processing*; CRC Press: Boca Raton, FL, 1988.
- Maga, J. A.; Chen, Z. Pyrazine composition of wood smoke as influenced by wood source and smoke generation variables. *Flavour Fragrance J.* **1985**, *1*, 37–42.
- Porter, R. W.; Bratzler, L. J.; Pearson, A. M. Fractionation and study of compounds in wood smoke. *J. Food Sci.* **1965**, *30*, 615–619.
- Shafizadeh, F. The chemistry of pyrolysis and combustion. In *The Chemistry of Solid Wood*; Rowell, R., Eds.; American Chemical Society: Washington, DC, 1984; Chapter 13.
- Simon, S.; Rypinski, A. A.; Tauber, F. W. Water-filled cellulose casings as model absorbents for wood smoke. *Food Technol.* **1966**, *20*, 1494–1498.
- Toth, L. Präparative Gewinnung und Analyse von Phenolfractionen aus Räucherrauch II. Mitt.: Gewinnung, Reinigung und Analyse von Phenolfractionen. *Fleischwirtschaft* **1980a**, *60*, 728–736.
- Toth, L. Einfluss der Räuchertechnologie auf die Phenole des Rauches. *Fleischwirtschaft* **1980b**, *60*, 1472–1477.
- Toth, L.; Potthast, K. Chemical aspects of the smoking of meat and meat products. *Adv. Food Res.* **1984**, *29*, 87–158.

- Wasserman, A. E. Organoleptic evaluation of tree phenols present in wood smoke. *J. Food Sci.* **1966**, *31*, 1005–1010.
- Wasserman, A. E.; Fiddler, W. Natural smoke: composition and properties. *Proceedings of Meat Industry Research Conference*, Chicago, IL; 1969; p 163.
- Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1985.
- Wiley. *Wiley 138K, Mass Spectral Database*; Chichester, U.K., 1990.

Windholz, M., Ed. *The Merck Index*, 3rd ed.; Merck & Co., Inc.: Rahway, NJ, 1983.

Received for review February 8, 1999. Revised manuscript received June 15, 1999. Accepted June 28, 1999. This work has been supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT, ALI97-1095).

JF990122E