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## ANALYSIS OF VOLATILES IN TALL OIL BY GAS CHROMATOGRAPHY, FLAME-PHOTOMETRIC DETECTION, FLAME-IONIZATION DETECTION AND MASS SPECTROMETRY

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### SUMMARY

Tall oil is a by-product obtained from the southern kraft pulping process. In order to isolate and detect the odor compounds in tall oil, we concentrated the volatiles, using a gas-phase stripping and adsorption on a thermally stable porous polymer. The volatiles were thermally desorbed onto a high-resolution capillary column. The separated compounds were detected simultaneously by flame-ionization detection and specific sulfur detection. Capillary gas chromatography–high-resolution mass spectrometry was used for positive confirmation of the eluted compounds.

More than a hundred compounds were identified, about twenty of which were sulfur-containing compounds, causing the malodor of the tall oil. The total sulfur content in tall oil was 470 ppm. Purging with inert gas at 250°C for 24 h removed only 60 ppm of the sulfur present. However, most of the bad odor was removed during the first 30 min of purging. This treatment also improved the color quality of the tall oil.

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### INTRODUCTION

Tall oil is the principal by-product of the sulfate pulping process of pine wood. Rosin acids and fatty acids represent more than 90% of tall oil, the rest being alcohols, esters, hydrocarbons and a complex mixture of other organic compounds at trace levels. This complex mixture is found in different locations in living trees<sup>1,2</sup>. In the pulping process, chipped wood is heated under pressure in the presence of sodium hydroxide and sodium sulfide. Cellulose and lignin are liberated, while fatty acids and rosin acids are changed to water-soluble soaps. This solution is known as “black liquor”. This liquor is concentrated under reduced pressure and then treated with sulfuric acid, converting it to crude tall oil.

Most of the fatty acids present in tall oil are oleic and linoleic acids, while most of the rosin acids are present as abietic-type acids plus dehydroabietic acids. The ratio of fatty acids to rosin acids depends on the species and on the geographical location of the pine trees. For example, the rosin acid content of crude tall oil from the southeastern

U.S.A. is between 40% and 50%, while further north in Virginia, it is between 30% and 35% of the total tall oil<sup>3</sup>.

About one million tons of crude tall oil are produced in the U.S.A. per year. The two principal distillable products of tall oil, tall oil fatty acids and tall oil rosin, have several applications, such as intermediates for manufacturing adhesives, inks, polyamide resins and epoxy resins. They also find use in protective coatings, soaps, flotation agents, and paper sizing. About 10% of the crude tall oil is used without fractional distillation for some specific applications, such as ore flotation and in oil well drilling muds<sup>4</sup>.

The quality of tall oil is determined basically by the concentration of the acids, the unsaponified fraction and by the odor and color qualities. The odor quality of tall oil, as well as the odor of the gaseous emissions from pulp mills, are significant and complex problems. The source of the odor produced during manufacturing and in the final product is believed to be sulfur-containing compounds.

Treating black liquor with  $H_2SO_4$  to liberate tall oil releases significant amounts of  $H_2S$  in the mill (*ca.* 0.27 lbs./ton of pulp)<sup>5</sup>. Some sulfur-containing compounds are formed during the pulping process. In the presence of sodium sulfide and sodium hydroxide, sulfide and hydrosulfide ions are formed. These ions react with methoxy groups of lignin to form methyl mercaptan<sup>6</sup> and dimethyl sulfide<sup>4</sup>. In the presence of  $O_2$ , methyl mercaptan can form dimethyl disulfide<sup>4</sup>. Other sulfur-containing compounds are probably formed, but these have not been investigated.

The types of organic sulfur-containing compound formed during Kraft pulping depend on temperature, the amount of sodium sulfide added, the pH, the design of the plant and the treatment time<sup>5</sup>. At lower temperatures, the amounts of methyl mercaptan formed exceed the amounts of dimethyl sulfide. An increase in temperature or in the amount of added sodium sulfide will cause an increase in the amount of organo-sulfur compounds liberated during the process<sup>5</sup>. Hydrogen sulfide and methyl mercaptan, being gases, are mostly removed during the pulping process. Therefore, they cannot be the major source of odor in tall oil. Other odor-causing compounds, whether they contain sulfur or not, have not been previously identified.

In this study, we developed a method for the concentration of volatiles in tall oil. Specifically, the volatiles were concentrated by gas-phase stripping, separated on a high-resolution capillary column, and detected simultaneously by flame-ionization detection (FID) and sulfur flame-photometric detection (FPD). Peaks were identified by high-resolution gas chromatography-mass spectrometry (GC-MS). We monitored the profile of volatiles released from tall oil over a period of 24 h.

## EXPERIMENTAL

The apparatus used in this work separated the volatile components by gas-phase stripping<sup>7</sup>. It consisted of a glass tube (15 × 2 cm O.D.). The bottom part of this tube was attached to 6-mm-O.D. glass tubing to allow pure helium to bubble through the tall oil. A 15-cm condenser was adapted to this glass device, and chilled water was used to cool the condenser. A sample tube (110 × 10 mm O.D.) was placed on top of the condenser via shrinkable PTFE tubing. The sample tube was filled with *ca.* 150 mg of Tenax GC, 80–100 mesh (Alltech Assoc., State College, PA, U.S.A.). Two small plugs of glass wool kept the adsorbent in place. Before use, the adsorbent (Tenax GC) was

conditioned for several hours in a specially built all-metal device at a temperature of 350°C in a stream of helium<sup>8</sup>. All glassware was silanized by standard procedures and kept in an oven at 200°C.

A nominal sample size of 10 ml of tall oil was transferred to the glass device, which was then placed in an oil bath at a controlled temperature. All samples analyzed in this work were supplied by Arizona Chemical Co. (Tuxedo, NY, U.S.A.). The heated tall oil was purged with pure helium at a rate of 30 ml/min. The purge gas continuously transferred the volatiles from the tall oil to the adsorbent. After collection, the trap was removed and placed in a thermal desorption system<sup>8</sup>.

A small section of fused-silica capillary tubing (750 × 0.32 mm O.D.) was attached to the desorber and kept at liquid nitrogen temperatures. Through this pre-column of fused silica, coated with DB-5 (J&W Scientific, Folsom, CA, U.S.A.), helium was passed at 20 ml/min for 15 min. After desorption was completed, the pre-column was removed and placed in the gas chromatograph, where it was attached to the front end of the capillary column. The analytical column was fused silica (50 m × 0.34 mm O.D.), coated with immobilized SE-30 (J&W Scientific). The column was operated at linear gas velocity of 32 cm/s. The gas chromatograph was a Varian 3700, equipped for FID and sulfur FPD. The effluent of the column was split equally between the two detectors. The chromatographic parameters were as follows: detector temperature, 300°C; temperature program, 2 min at 40°C, then 5°C/min to 170°C.

The chromatographic signals were recorded and integrated on a Hewlett-Packard 3357 data system. The GC-MS studies were performed on a Kratos MS-50 high-resolution mass spectrometer equipped with a Perkin-Elmer Sigma 3 gas chromatograph. The mass spectrometer was operated in the high-resolution mode with a resolution of 6000 and at a scan rate of 1.5 s/dec. A Data General Nova 4 computer was used for the collection of data and the subsequent calculation of exact mass.

Total sulfur analysis was carried out by combustion in a Parr oxygen bomb, followed by measurement of sulfate ion by ion chromatography<sup>9</sup>.

## RESULTS AND DISCUSSION

Gas-phase stripping is a commonly used technique for the concentration of trace compounds in liquid samples. Subsequent analysis of the enriched material by high-resolution GC and GC-MS often provides information which cannot be obtained otherwise. Typical applications of these techniques include the analysis of volatile pollutants in water and the analysis of aromatic compounds in beverages.

We investigated the effects of the stripping temperature between 20°C and 250°C, and found that the efficiency of volatile stripping was poor at low temperature. At 20°C, the chromatogram of the collected sample did not change substantially after 8 h of purging with helium. At 250°C, stripping of volatiles was greatly enhanced. Fig. 1 shows the volatiles chromatogram recorded with FID and FPD after the volatile fraction was collected at 20°C for 30 min, and Fig. 2 shows the chromatogram after the volatile fraction was collected at 250°C for 2 min. Fig. 3 shows the GC-MS analysis of a sample collected at 250°C for 20 min, and Fig. 4 shows a typical expanded portion for the first 10 min of a GC-MS analysis.

Figs. 2-4 are very complex. Table I lists 120 compounds which were identified by

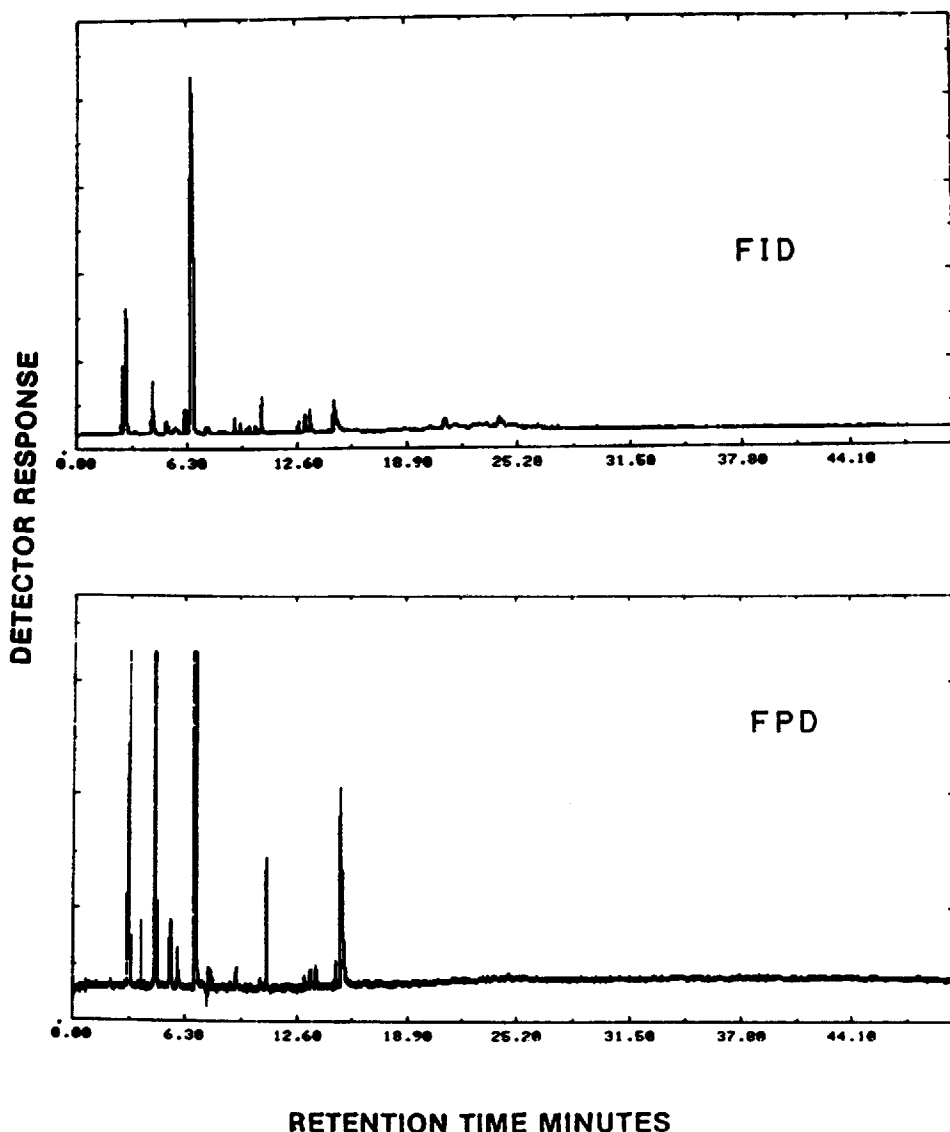


Fig. 1. Profile of tall oil volatiles, collected at 20°C for 30 min. The upper chromatogram was recorded by the flame-ionization detector and the lower chromatogram by the flame-photometric detector. For chromatographic conditions, see text.

MS from a typical volatile tall oil sample. These compounds include various hydrocarbons, sulfur-containing compounds, and oxygen-containing compounds. Identification of many of these was based on the exact measurement of molecular ions. High-resolution MS with a mass resolution of over 6000 and with mass accuracy of milli-mass units was essential for the identification of this complex mixture. In

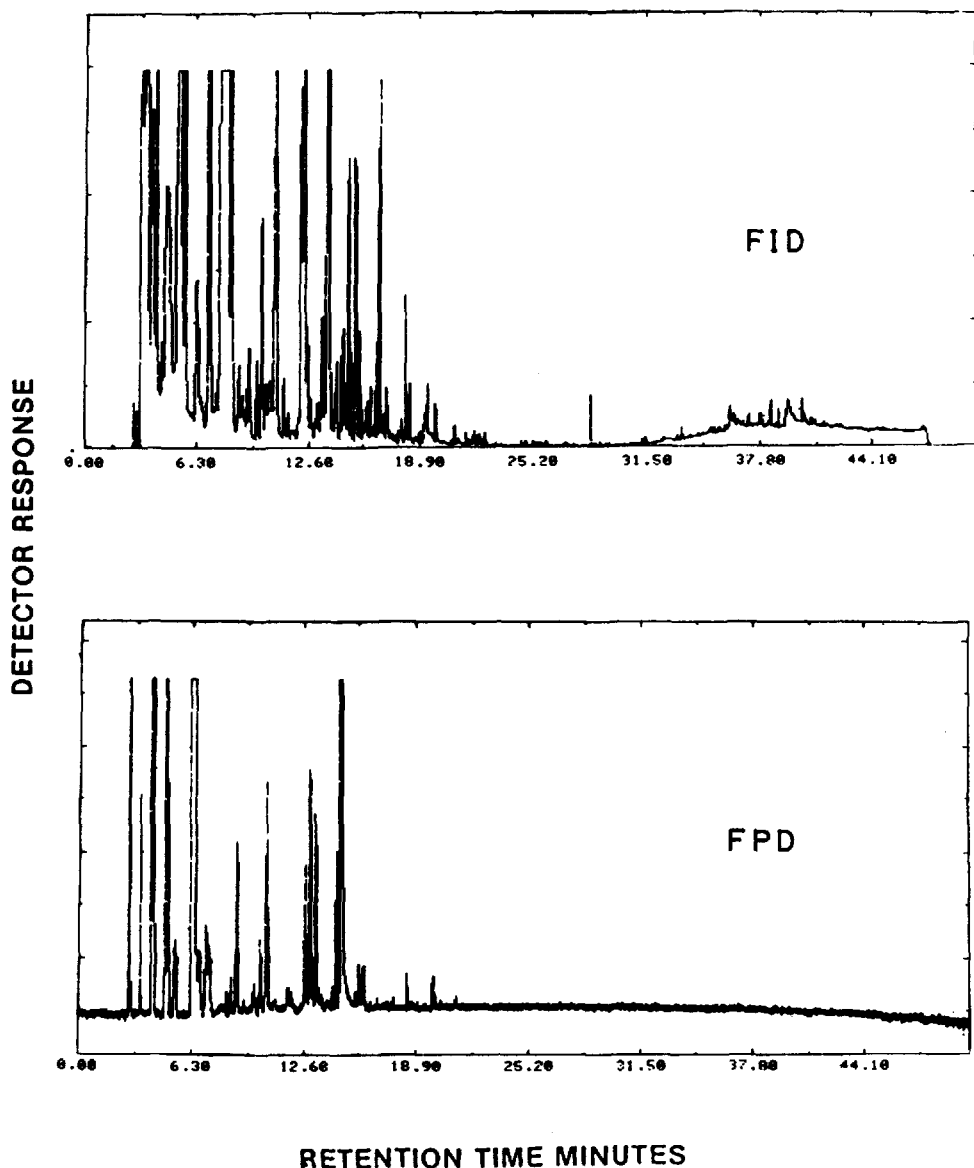


Fig. 2. Profile of tall oil volatiles, collected at 250°C for 2 min. For chromatographic conditions, see text.

addition to exact mass, the presence of  $^{34}\text{S}$  isotope ions was also used for confirmation of sulfur-containing compounds.

Major peaks in Figs. 3 and 4 are numbered according to their elution order and are listed in Table I. Peaks labeled with plain numbers are hydrocarbons. Peaks labeled with bold (underlined) numbers are sulfur-containing compounds. The majority of identified compounds are hydrocarbons, mostly with a backbone structure of *ca.*  $\text{C}_{10}$  or  $\text{C}_{20}$  (terpenes are  $\text{C}_{10}$  compounds, and rosin acids are  $\text{C}_{20}$  compounds).

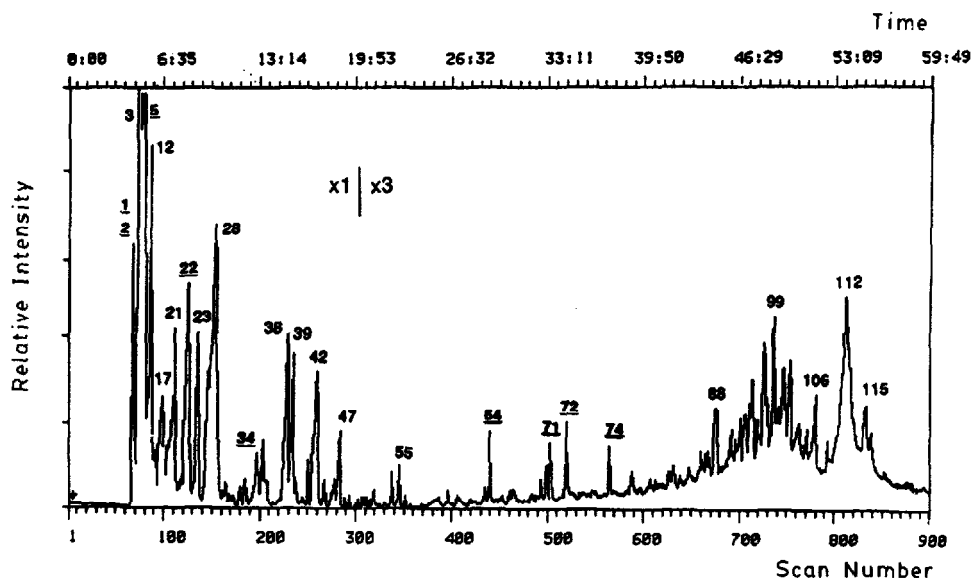


Fig. 3. GC-MS of tall oil volatiles collected at 250°C for 20 min. For chromatographic conditions, see text. Peaks labeled with plain numbers are hydrocarbons. Peaks labeled with underlined numbers are sulfur-containing compounds. Peak identifications are listed in Table I. Time in mins.

Identification of these hydrocarbons is beyond the scope of this investigation and was not attempted.

In addition to hydrogen sulfide, 22 sulfur-containing compounds were identified in the sample. The amount of hydrogen sulfide retained in tall oil is probably not significant, since most of it is released during the pulping process. About 4.5% of the volatile sulfur compounds released to the atmosphere during the pulping process is methyl mercaptan and *ca.* 0.1% is dimethyl disulfide. Both compounds were detected in tall oil<sup>4</sup>.

Other sulfur-containing compounds present in trace amounts are saturated alkyl mercaptans with carbon chains up to C<sub>10</sub>. The higher-molecular-weight mercaptans probably contribute only insignificantly to the malodor because of their relatively small concentration and low volatility. Several oxygenated compounds were detected at trace levels, but no nitrogen-containing compounds were detected. Since hydrocarbons and oxygenated compounds are generally less malodorous, it may be safe to conclude that the offending odor is caused by combinations of various mercaptans, particularly the lower-molecular-weight alkyl mercaptans.

Fig. 5 shows the profile of organic volatiles released (total peak area) from tall oil over a 24-h period. For sulfur-containing compounds determined by FID, the amount of volatiles released decreased to constant but small amounts after *ca.* 1 h of purging with helium at 250°C. On the other hand, the profile of total volatiles recorded by FID initially increased, followed by a slight decrease with time.

The rapid loss of some of the sulfur-containing compounds is due to the loss of volatile sulfur-containing compounds. The persistent evolution of low levels of sulfur is due to slow decomposition of higher-molecular-weight sulfur-containing com-

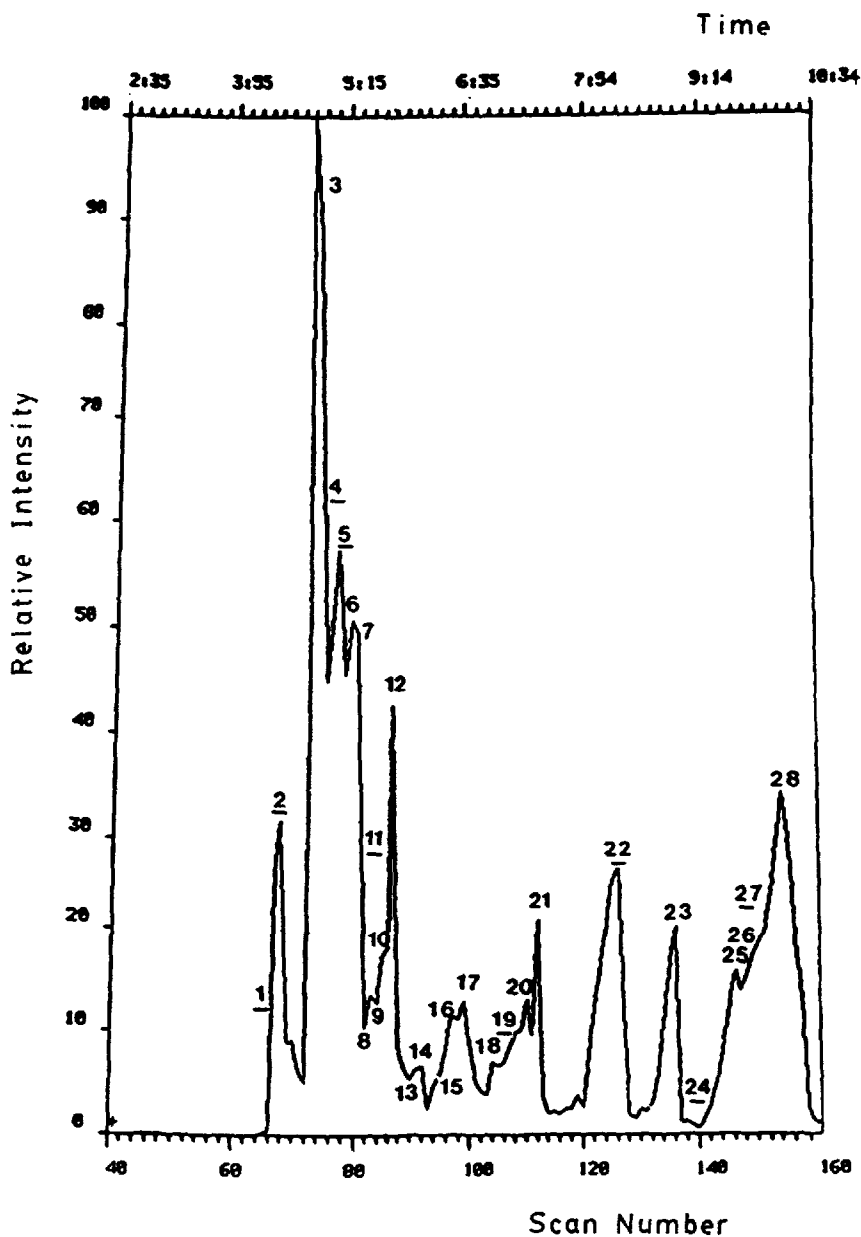


Fig. 4. Expanded 10 min of Fig. 3. Peaks labeled with underlined numbers are sulfur-containing compounds. Time in min:s.

pounds. Based on total sulfur analysis, the total sulfur of a tall oil sample was 470 ppm before purging and 410 ppm after 24 h of purging at 250°C. It is somewhat unexpected that the sulfur content of tall oil did not decrease substantially after prolonged purging at high temperature. This suggests that most sulfur-containing compounds present in

TABLE I  
ELEMENTAL COMPOSITION AND EXACT MASSES OBTAINED BY GC-MS

| Compound <sup>a</sup> | Elemental composition                        | Measured mass | Deviation (milli-mass units) <sup>b</sup> | Compound <sup>a</sup> | Elemental composition             | Measured mass | Deviation (milli-mass units) <sup>b</sup> |
|-----------------------|--|---------------|---|-----------------------|-----------------------------------|---------------|---|
| 1                     | CH <sub>3</sub> SH                           | 48.0033       | 0.0                                       | 60                    | C <sub>11</sub> H <sub>12</sub> O | 160.0845      | -4.7                                      |
| 2                     | SO <sub>2</sub>                              | 63.9593       | -2.6                                      | 61                    | C <sub>6</sub> H <sub>12</sub> S  | 116.0653      | -0.6                                      |
| 3                     | C <sub>3</sub> H <sub>6</sub> O              | 58.0405       | -1.4                                      | 62                    | C <sub>7</sub> H <sub>16</sub> S  | 132.0957      | -1.6                                      |
| 4                     | CS <sub>2</sub>                              | 75.9447       | 0.5                                       | 63                    | C <sub>10</sub> H <sub>16</sub> O | 152.1239      | 3.7                                       |
| 5                     | C <sub>2</sub> H <sub>6</sub> S              | 62.0209       | 1.9                                       | 64                    | C <sub>7</sub> H <sub>14</sub> S  | 130.0844      | 2.8                                       |
| 6                     | CH <sub>2</sub> Cl <sub>2</sub>              | 83.9516       | -1.7                                      | 65                    | C <sub>13</sub> H <sub>12</sub> O | 184.0914      | 2.6                                       |
| 7                     | C <sub>4</sub> H <sub>8</sub> O              | 72.0583       | 0.8                                       | 66                    | C <sub>11</sub> H <sub>18</sub>   | 150.1378      | -3.1                                      |
| 8                     | C <sub>4</sub> H <sub>8</sub> O              | 72.0579       | 0.3                                       | 67                    | C <sub>10</sub> H <sub>14</sub> O | 150.1075      | 3.0                                       |
| 9                     | C <sub>4</sub> H <sub>6</sub> O              | 70.0430       | 1.2                                       | 68                    | C <sub>9</sub> H <sub>14</sub> S  | 142.0811      | -0.5                                      |
| 10                    | C <sub>4</sub> H <sub>6</sub> O              | 72.0569       | -0.6                                      | 69                    | C <sub>8</sub> H <sub>16</sub> S  | 144.0985      | 1.3                                       |
| 11                    | C <sub>2</sub> H <sub>6</sub> S              | 62.0209       | 1.9                                       | 70                    | C <sub>8</sub> H <sub>14</sub> S  | 142.0833      | 1.7                                       |
| 12                    | C <sub>5</sub> H <sub>6</sub> O              | 82.0414       | -0.5                                      | 71                    | C <sub>8</sub> H <sub>14</sub> S  | 142.0786      | -3.0                                      |
| 13                    | C <sub>6</sub> H <sub>14</sub>               | 86.1084       | -1.2                                      | 72                    | C <sub>7</sub> H <sub>14</sub> S  | 130.0837      | 2.1                                       |
| 14                    | C <sub>5</sub> H <sub>8</sub> O              | 84.0548       | -2.7                                      | 73                    | C <sub>10</sub> H <sub>18</sub> S | 170.1212      | 8.1                                       |
| 15                    | C <sub>6</sub> H <sub>10</sub>               | 82.0779       | -0.3                                      | 74                    | C <sub>8</sub> H <sub>16</sub> S  | 144.0987      | 1.5                                       |
| 16                    | C <sub>5</sub> H <sub>10</sub> O             | 86.0721       | -1.1                                      | 75                    | C <sub>19</sub> H <sub>22</sub>   | 250.1699      | -2.2                                      |
| 17                    | C <sub>6</sub> H <sub>6</sub>                | 78.0483       | 1.4                                       | 76                    | C <sub>17</sub> H <sub>30</sub>   | 234.2370      | 2.2                                       |
| 18                    | C <sub>6</sub> H <sub>10</sub>               | 82.0803       | 2.1                                       | 78                    | C <sub>17</sub> H <sub>32</sub>   | 236.3510      | 0.6                                       |
| 19                    | C <sub>4</sub> H <sub>8</sub> S              | 88.0318       | -2.9                                      | 79                    | C <sub>18</sub> H <sub>32</sub>   | 248.2474      | -3.0                                      |
| 20                    | C <sub>7</sub> H <sub>14</sub>               | 98.1110       | 1.4                                       | 80                    | C <sub>19</sub> H <sub>28</sub>   | 256.2181      | -1.0                                      |
| 21                    | C <sub>7</sub> H <sub>16</sub>               | 100.1237      | -1.5                                      | 81                    | C <sub>19</sub> H <sub>28</sub>   | 256.2185      | -0.6                                      |
| 22                    | C <sub>2</sub> H <sub>6</sub> S <sub>2</sub> | 93.9906       | -0.5                                      | 82                    | C <sub>19</sub> H <sub>28</sub>   | 256.2192      | 0.0                                       |
| 23                    | C <sub>7</sub> H <sub>8</sub>                | 92.0635       | 0.9                                       | 83                    | C <sub>20</sub> H <sub>32</sub>   | 272.2496      | -0.8                                      |
| 24                    | C <sub>5</sub> H <sub>6</sub> S              | 98.0146       | -4.4                                      | 84                    | C <sub>20</sub> H <sub>32</sub>   | 272.2489      | -1.5                                      |
| 25                    | C <sub>7</sub> H <sub>10</sub> O             | 110.0750      | 1.8                                       | 85                    | C <sub>19</sub> H <sub>28</sub>   | 256.2207      | 1.6                                       |
| 26                    | C <sub>6</sub> H <sub>10</sub>               | 82.0776       | -0.6                                      | 86                    | C <sub>15</sub> H <sub>14</sub> O | 220.1807      | -1.0                                      |
| 27                    | C <sub>5</sub> H <sub>8</sub> S              | 100.0336      | -1.1                                      | 87                    | C <sub>20</sub> H <sub>32</sub>   | 272.2504      | 0.0                                       |
| 28                    | C <sub>8</sub> H <sub>18</sub>               | 114.1394      | -1.4                                      | 88                    | C <sub>19</sub> H <sub>28</sub>   | 256.2158      | -3.3                                      |
| 29                    | C <sub>8</sub> H <sub>14</sub>               | 110.1124      | 2.8                                       | 89                    | C <sub>19</sub> H <sub>26</sub>   | 254.2034      | 0.0                                       |
| 30                    | C <sub>3</sub> H <sub>6</sub> S <sub>2</sub> | 108.0112      | 4.4                                       | 90                    | C <sub>19</sub> H <sub>26</sub>   | 254.2040      | 0.6                                       |



|    |   |          |      |     |  |          |      |
|----|---|----------|------|-----|--|----------|------|
| 31 | C <sub>8</sub> H <sub>7</sub> O               | 106.0765 | -1.7 | 91  | C <sub>20</sub> H <sub>32</sub>                | 272.2529 | 2.5  |
| 32 | C <sub>8</sub> H <sub>10</sub>                | 106.0811 | 2.9  | 92  | C <sub>20</sub> H <sub>32</sub>                | 272.2465 | 3.9  |
| 33 | C <sub>8</sub> H <sub>12</sub> O              | 124.0896 | 0.8  | 93  | C <sub>19</sub> H <sub>26</sub>                | 254.2049 | 1.5  |
| 34 | C <sub>4</sub> H <sub>10</sub> S <sub>2</sub> | 122.0225 | 0.1  | 94  | C <sub>20</sub> H <sub>32</sub>                | 272.2507 | 0.3  |
| 35 | C <sub>7</sub> H <sub>12</sub>                | 96.0947  | 0.8  | 95  | C <sub>19</sub> H <sub>28</sub>                | 256.2174 | -1.7 |
| 36 | C <sub>3</sub> H <sub>10</sub> O              | 86.0768  | 3.0  | 96  | C <sub>20</sub> H <sub>32</sub>                | 272.2497 | -0.7 |
| 37 | C <sub>6</sub> H <sub>8</sub> O               | 96.0596  | 2.0  | 97  | C <sub>19</sub> H <sub>28</sub>                | 256.2163 | -2.8 |
| 38 | C <sub>10</sub> H <sub>16</sub>               | 131.240  | -1.1 | 98  | C <sub>20</sub> H <sub>32</sub>                | 272.2480 | -2.4 |
| 39 | C <sub>6</sub> H <sub>12</sub>                | 120.0921 | -1.8 | 99  | C <sub>19</sub> H <sub>26</sub>                | 254.2028 | -0.8 |
| 40 | C <sub>10</sub> H <sub>14</sub>               | 134.1104 | 0.9  | 100 | C <sub>19</sub> H <sub>28</sub>                | 256.2158 | -3.3 |
| 41 | C <sub>10</sub> H <sub>14</sub>               | 136.1266 | 1.4  | 101 | C <sub>19</sub> H <sub>26</sub>                | 254.2013 | -2.1 |
| 42 | C <sub>9</sub> H <sub>14</sub> O              | 138.1031 | 1.4  | 102 | C <sub>20</sub> H <sub>32</sub>                | 272.2504 | 0.0  |
| 43 | C <sub>10</sub> H <sub>16</sub>               | 136.1242 | -0.8 | 103 | C <sub>19</sub> H <sub>28</sub>                | 256.2168 | -2.3 |
| 44 | C <sub>10</sub> H <sub>16</sub>               | 136.1277 | 2.5  | 104 | C <sub>19</sub> H <sub>24</sub>                | 252.1879 | 0.1  |
| 45 | C <sub>10</sub> H <sub>14</sub>               | 134.1103 | 0.7  | 105 | C <sub>20</sub> H <sub>28</sub>                | 262.2177 | -1.4 |
| 46 | C <sub>10</sub> H <sub>14</sub>               | 134.1088 | -0.8 | 106 | C <sub>19</sub> H <sub>26</sub>                | 254.2061 | 2.7  |
| 47 | C <sub>10</sub> H <sub>16</sub>               | 136.1242 | -1.0 | 107 | C <sub>19</sub> H <sub>24</sub>                | 252.1853 | -2.5 |
| 48 | C <sub>10</sub> H <sub>16</sub>               | 136.1277 | 2.5  | 108 | C <sub>19</sub> H <sub>28</sub>                | 256.2205 | 1.4  |
| 49 | C <sub>10</sub> H <sub>16</sub>               | 136.1225 | -2.7 | 109 | C <sub>20</sub> H <sub>28</sub>                | 268.2188 | -0.3 |
| 50 | C <sub>10</sub> H <sub>14</sub>               | 134.1092 | -0.4 | 110 | C <sub>20</sub> H <sub>28</sub>                | 268.2214 | 2.3  |
| 51 | C <sub>10</sub> H <sub>12</sub>               | 132.0931 | -0.8 | 111 | C <sub>19</sub> H <sub>26</sub>                | 254.2064 | 3.0  |
| 52 | C <sub>10</sub> H <sub>14</sub>               | 134.1121 | 2.6  | 112 | C <sub>18</sub> H <sub>28</sub>                | 244.2175 | -1.6 |
| 53 | C <sub>6</sub> H <sub>10</sub> O              | 98.0705  | -2.7 | 113 | C <sub>20</sub> H <sub>28</sub>                | 268.2188 | -0.3 |
| 54 | C <sub>10</sub> H <sub>16</sub>               | 136.1257 | 0.5  | 114 | C <sub>20</sub> H <sub>28</sub>                | 268.2166 | -2.5 |
| 55 | C <sub>10</sub> H <sub>16</sub>               | 136.1253 | 0.1  | 115 | C <sub>18</sub> H <sub>32</sub> O              | 264.2461 | 0.8  |
| 56 | C <sub>11</sub> H <sub>16</sub>               | 148.1270 | 1.8  | 116 | C <sub>18</sub> H <sub>32</sub> O              | 264.2451 | -0.2 |
| 57 | C <sub>7</sub> H <sub>16</sub> S              | 132.0986 | 1.3  | 117 | C <sub>16</sub> H <sub>16</sub> O <sub>2</sub> | 240.1167 | 1.7  |
| 58 | C <sub>7</sub> H <sub>14</sub> S              | 130.0781 | -3.5 | 118 | C <sub>20</sub> H <sub>28</sub>                | 268.2190 | 0.0  |
| 59 | C <sub>7</sub> H <sub>16</sub> S              | 132.0944 | 0.5  | 119 | C <sub>20</sub> H <sub>26</sub>                | 266.2009 | -2.5 |

<sup>a</sup> Numbers of sulfur-containing compounds are printed in italics.

<sup>b</sup> Deviation = (measured mass - theoretical mass) × 1000.

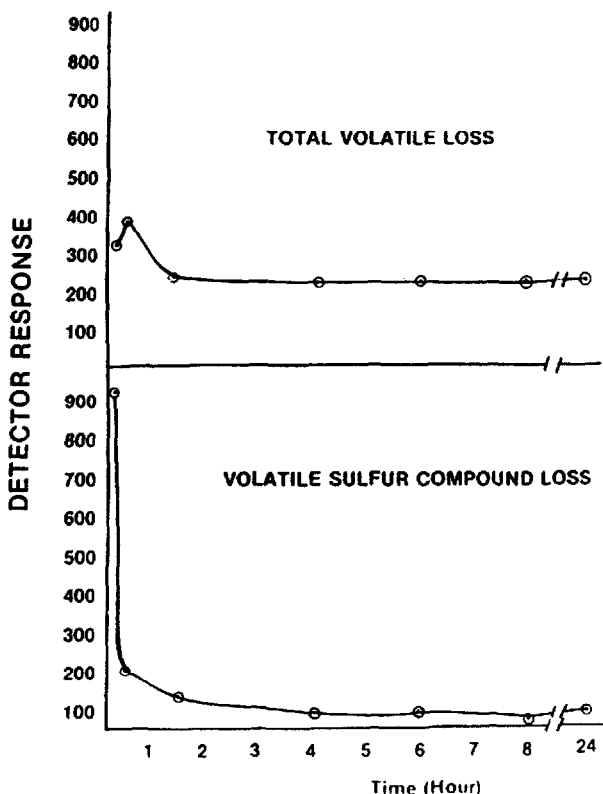


Fig. 5. Loss of total volatiles with time as tall oil was purged with helium at 250°C. The upper figure is for total volatiles measured by FID, the lower figure is for total volatiles measured by FPD.

tall oil have a low volatility. They probably are alkyl mercaptan adducts of fatty acids or rosin acids, which have molecular weights in excess of 300 and boiling points higher than that of tall oil. Prolonged heating could possibly result in scission of the carbon-sulfur bond, producing a sulfur-containing alkyl radical, which could subsequently form some mercaptans.

The continuous conversion of low-volatility sulfur compounds to higher-volatility sulfur compounds at an elevated temperature explains the persistent evolution of traces of sulfur-containing compounds, especially dimethyl disulfide, after 24 h of purging at 250°C. Such a conversion is an extremely slow process, particularly at ambient temperature. When a tall oil sample was purged at 250°C for 6 h, then cooled at 20°C, and subsequently purged with helium for 20 min at 20°C, no further release of sulfur compounds was detected.

We also noticed a correlation between the degree of removal of volatile sulfur and the color quality. The crude tall oil has a color of 13-14 on the Gardner color scale. After 1 h of purging with helium at 250°C, the color became 11-12, but continuous purging of up to 24 h did not improve the color beyond that.

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