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On the Formation of Degradation Products from the Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin

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ABSTRACT

Mixtures of tall oil fatty acids and kraft lignin from southern pine wood were pyrolyzed at 160 C and 280 C with or without exclusion of oxygen. In addition to fatty acids of various chain lengths and aromatic degradation products from lignin, a number of homologous *n*-alkylbenzenes were formed (ca. 1.5%) and characterized by gas chromatography-mass spectrometry. The possible ways of formation of the latter from fatty acids are discussed briefly.

INTRODUCTION

The tall oil distillation and fractionation process is carried out at temperature regions above 200 C (1). Because partially demethylated lignin is present in the tall oil distillation residue (pitch) (2), lignin, though modified, must be present in the raw tall oil before the distillation process. To determine substances which possibly could have been produced during tall oil distillation by reaction with still present lignin, similar reaction conditions to those in the technical distillation process were applied to a mixture of tall oil fatty acids and kraft lignin. By this procedure it was possible to obtain more information on possible reaction products of tall oil fatty acids and kraft lignin. The composition of the tall oil fatty acid fraction which was used in all experiments is shown in Table I (3).

EXPERIMENTAL PROCEDURES

Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin at 280 C

Kraft lignin (5 g) and tall oil fatty acids (17.5 g) were heated to 280 C and kept at this temperature for 30 min. After cooling, the mixture was shaken with chloroform and filtered. The insoluble residue was ca. 1 g. The clear solution was distilled at a maximum temperature of 265 C at 2000 Pa. The fraction distilled at this temperature was 5.2 g. One gram of the distillate was taken up in 10 ml methanol and methylated with 100 ml of a solution of freshly prepared diazomethane in ether. The solvent mixture was evaporated, and the residue was dissolved in ether and analyzed by gas chromatography-mass spectrometry. The gas chromatographic separation was performed using a 25 m OV-101 WCOT glass capillary column, and the mass spectra were recorded on a Hewlett-Packard quadrupole mass spectrometer system HP 5992A. The construction of the apparatus allowed connection of the end of the column directly to the ion source. The list of detected compounds is given in Table II.

Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin at 160 C

Kraft Lignin (5 g) and tall oil fatty acids (17.5 g) were heated to 160 C and kept at this temperature for 30 min. After cooling, the mixture was extracted with chloroform (ca. 50 ml) and filtered to yield 5.5 g insoluble residue. Additional procedures were the same as described above. The list of detected compounds is given in Table III.

Pyrolysis of Tall Oil Fatty Acids with Kraft Lignin at 280 C under Nitrogen

The same reaction procedures were used as described above. This distillation was performed at 0.1 Pa, and one part of

TABLE I

Composition of the Tall Oil Fatty Acids
Used in All Experiments

Compound	%
hexadecenoic acid	1.0
hexadecanoic acid	6.5
heptadecanoic acid	1.5
octadecatrienoic acid	0.5
octadecadienoic acid	ca. 39.0
octadecenoic acid	ca. 40.0
octadecanoic acid	2.0
other fatty acids	ca. 2.0
total fatty acids	92.5
isopimaric acid	1.5
pimaric acid	0.7
dehydroabietic acid	0.5
other diterpenoid acids (including abietic acid)	2.0
total diterpenoid acids	4.7
pinosylvin dimethylether	ca. 3.0
other unsaponifiables	ca. 1.5

the distillation mixture was collected in a trap which was cooled with liquid air. The distillation temperature was kept below 200 C, and a separation from the main components (higher fatty acids) was obtained (Table IV). This procedure was also applied to the redistillation of tall oil fatty acids (Table V).

RESULTS AND DISCUSSION

Apart from fatty acids of various chain lengths and aromatic degradation products from lignin, a number of homologous *n*-alkylbenzenes could be characterized by gas chromatography-mass spectrometry. The aromatic is always monosubstituted, and the side chain is of saturated aliphatic structure and exclusively linear. As pyrolysis of lignin itself gave no *n*-alkylbenzenes, it can be excluded as precursor. Also by the absence of any related compounds, ring cleavage of dehydroabietic acids could not be observed. Moreover no cyclic fatty acids could be detected.

To show that fatty acids are precursors of the *n*-alkylbenzenes pure fatty acids (99.5%) like oleic and linoleic acids were pyrolyzed under the same conditions. The formation of *n*-alkylbenzenes was proved (H. Traitler, E. Lorbeer, and K. Kratzl, unpublished results). Most probably the generation of these substances results from a thermal cyclization, aromatization, and decarboxylation of long chain fatty acids with the aid of lignin. Disubstituted cyclic compounds (cyclic fatty acids) have been detected and identified in tall oil (4). Also, hydrogen transfer and disproportionation and isomerization have been discussed (5). In addition to the most abundant compound octadecenoic acid, all saturated fatty acids from hexanoic up to eicosanoic acid are present. Aliphatic hydrocarbon compounds C14, C15, and C16 could also be detected and identified.

Pinosylvin dimethylether (3,5-dimethoxystilbene) and its hydrogenation product are both present. A series of lignin degradation products like 4-hydroxy-3-methoxytoluene and other mono- and dihydroxy aromatics could be identified. Of course, different diterpenoid acids are also present, as in the original tall oil fatty acid (6,7). Polycarboxy compounds were detected which could not be further identified by mass spectrometry (Table II).

To prove the absence of *n*-alkylbenzenes in the original tall oil fatty acids, a high vacuum distillation after pyrolysis under the same conditions and the absence of lignin was performed (< .1 Pa, 280 C), and the distillate was collected in two fractions: one water cooled, the other in a liquid air-cooled trap. The water-cooled fraction was simply

TABLE II

Detected and Identified Compounds of the 280 C-Run[a]

Retention time (min)	Compound	%
—	methyl hexanoate	0.1
4.4	methyl-6-heptenoate	0.3
4.6	methyl heptanoate	1.2
5.4	*n*-butylbenzene	0.2
6.1 mixture	methyloctenoate methoxy-ethylbenzene	0.2
6.4	methyl octanoate	0.9
6.5	1,2-dimethoxybenzene	0.7
7.3	*n*-pentylbenzene	0.5
8.3	methyl nonenoate	0.2
8.6 mixture	3,4-dimethoxytoluene methylnonanoate	1.7
9.6	*n*-hexylbenzene	0.2
10.6 mixture	3,4-dimethoxyethylbenzene methyl decenoate	1.2
10.9	methyl decanoate	3.0
12.0	*n*-heptylbenzene	0.2
13.1 mixture	methyl undecenoate $C_{14}H_{30}$ hydrocarbon	0.2
13.3	methyl undecanoate (branched)	0.7
14.4	*n*-octylbenzene	0.2
14.9	$C_{15}H_{30}$ hydrocarbon	0.4
15.3	$C_{15}H_{32}$ hydrocarbon	0.5
15.5	methyl dodecanoate	0.5
16.9	3,4-dimethoxyacetophenone	0.6
17.8 mixture	methyltridecanoate $C_{16}H_{32}$	1.3
19.8 mixture	hexadecanol + unidentified	2.4
21.6	methyl pentadecanoate	0.4
23.0	*methyl hexadecenoate	1.2
23.6	*methyl hexadecanoate	7.2
24.5	1-(3,5-dimethoxyphenyl)-2-phenylethane	1.2
24.7	methyl heptadecanoate (branched)	5.1
25.2	*methyl heptadecanoate	1.5
25.7	*methyl octadecatrienoate	1.3
27.3	*methyl octadecenoate	30.4
27.4	*methyl octadecanoate	7.1
28.1	*methyl octadecadienoate	7.6
28.9 mixture	*pinosylvin dimethylether	2.6
29.4	*methyl diterpenoate	1.1
31.2	*methyl eicosanoate	0.1
31.6	*methyl dehydroabietate	0.6

[a]GC conditions: 25 m OV-101 glass capillary column, (WCOT), oven temperature 90 C, 5 min iso, 6 C/min up to 270 C, injection port 250 C, flow rate 1.5 ml He/min. Compounds marked with an asterisk were originally present in tall oil as acids or ethers.

TABLE III

List of Detected and Identified Compounds of the 160 C-Run[a]

Retention time (min)	Compound	%
5.3	methyl hexanoate	0.3
7.5	methyl heptenoate	0.1
7.8	methyl heptanoate	1.5
10.3	methyl octenoate	0.1
10.6	methyl octanoate	1.3
11.8	*n*-pentylbenzene	0.2
12.3	1,1-dimethoxyalkane (MW 160)	0.1
13.4	methyl nonanoate	1.1
14.9	1,1-dimethoxyalkane (MW 174)	0.2
15.6	methyl decenoate	1.8
16.0	methyl decanoate	5.6
17.6	1,2-dimethoxy-*n*-propylbenzene	0.1
18.3	methyl undecanoate	0.3
19.1	dimethoxyalkane (MW 188)	0.1
19.9	$C_{15}H_{30}$ hydrocarbon	0.1
20.2	$C_{15}H_{32}$ hydrocarbon	0.2
20.3	methyl dodecanoate	0.1
21.5	dimethoxyalkane (MW 202)	0.2
22.4 mixture	methyl tridecanoate	2.2
23.5	$C_{17}H_{34}$ hydrocarbon	0.9
23.6	$C_{17}H_{36}$ hydrocarbon	0.4
24.1	methyl tetradecanoate	0.1
25.3	methyl pentadecanoate (branched)	0.2
25.5	methyl pentadecenoate	0.3
25.8	methyl pentadecanoate	0.2
27.0	*methyl hexadecenoate	0.4
27.5	*methyl hexadecanoate	7.8
28.5	methyl heptadecanoate (branched)	1.1
28.6	methyl heptadecenoate	2.1
29.0	*methyl heptadecanoate	0.5
29.5	*methyl octadecatrienoate	0.5
29.6	*methyl octadecadienoate	0.5
30.4	*methyl octadecenoate	27.4
30.6	*methyl octadecanoate	4.2
30.8	*methyl octadecadienoate	6.7
31.3	*methyl octadecadienoate	6.6
31.4	*methyl diterpenoate	1.0
31.6	methyl nonadecenoate	0.8
31.8	*pinosylvin dimethylether	3.3
31.9	methyl nonadecanoate	0.7
32.0	*methyl-8,15-pimaradien-18-oate	1.4
32.3	*methyl sandaracopimarate	0.5
33.3 mixture	*methyl dehydroabietate *methyl eicosanoate	1.2
34.3	polycarboxymethyl compound (MW ?)	0.3

[a] GC conditions: 25 m OV-101 glass capillary column (WCOT), oven temperature 80 C, 5 min iso, 4 C/min up to 270 C, injection port 250 C, flow rate 1.5 ml He/min. Compounds marked with an asterisk were originally present in tall oil as acids or ethers.

TABLE IV

List of Volatile Compounds of the Nitrogen-280 C-Run of a High Vacuum Distillation Collected in a Liquid Air-Cooled Trap Which Could Be Identified by Mass Spectrometry[a]

Retention time (min)	Compound	%
11.8	*guaiacol	2.3
13.4	*n*-pentylbenzene	6.7
13.8	*4-hydroxy-3-methoxytoluene	6.9
15.3	*n*-hexylbenzene	5.0
15.4	*ethylguaiacol	5.8
17.1	*n*-heptylbenzene	6.7
18.8	*n*-octylbenzene	1.0

[a] GC conditions: 20 m SE-30 glass capillary column (WCOT), oven temperature 30 C, 5 min iso, 8 C/min, injection port 250 C, flow rate ca. 1.5 ml He/min. *Present in original tall oil.

TABLE V

List of Volatile Compounds of Tall Oil Fatty Acids of a High-Vacuum Distillation Collected in a Liquid Air-Cooled Trap Which Could Be Identified by Mass Spectrometry

Retention time (min)	Compound	%
4.5	*isobutanol	0.9
5.2	*butanol	4.0
8.6	*formic acid	51.4
9.4	*acetic acid	6.4
10.2	*2-methylbutanol	4.0
16.8	*benzaldehyde	5.4
17.9	*octanoic acid	1.7
18.1	*octanoic acid	2.5
18.3	*o-cresol	6.5
18.8	*guaiacol	6.8
19.0	*4-hydroxy-3-methoxytoluene	3.1
20.0	*methoxybenzaldehyde[b]	2.7

[a] GC conditions: 20 m SE-30 glass capillary column (WCOT), oven temperature 30 C, 1 C/min, injection port 250 C, flow rate ca. 1.5 ml He/min. Present in original tall oil.

[b] Total amount of this fraction is less than 0.5% of tall oil fatty acids.

redistilled tall oil, whereas the liquid air-cooled trap contained a number of substances not commonly found in tall oil fatty acids, like lower MW carboxylic acids (formic, acetic, octanoic acids), benzaldehyde, and, of course, guaiacol. All these compounds were present in less than 0.5% of the total fatty acids (Table V).

To elucidate the generation of the degradation products under these particular conditions, other reaction conditions were also applied. Thus the reaction of a mixture of tall oil fatty acids and kraft lignin with the same tall oil/lignin ratio as before was performed at 160 C. The composition of the reaction products differs from the reaction products composition of the 280 C-run quantitatively as well as qualitatively. The only *n*-alkylbenzene which could be detected in this run was *n*-pentylbenzene. Obviously the temperature is not high enough to give much cyclization and aromatization. Table III gives a list of the compounds which have been detected and identified in the tall oil/lignin 160 C-run. The reaction mixture was treated the same way as described for the 280 C-run.

Apart from the absence of *n*-alkylbenzenes in the original tall oil fatty acids, there are other significant differences of composition of the various reaction mixtures. In tall oil fatty acids the amount of stearic acid is only ca. 2%, whereas in the pyrolysis reaction with kraft lignin it rises to 4% in the 160 C-run and to over 7% in the 280 C-run. All calculations are based on the integration of the total ion chromatograms and are correlatable with integrated FID-chromatograms including the consideration of different molar responses of various compounds (8). In the original tall oil fatty acids and in the 160 C-run, no hydrogenated pinosylvin dimethylether could be detected, whereas in the 280 C-run over 1% of this compound is present. The high amount of the C-10 saturated fatty acid in the 160 C-run (5.6%, compare: 3% in the 280 C-run) indicates a possible intermediate for further degradation or rearrangement at higher temperatures.

Another effort to elucidate possible reactions during the pyrolysis of tall oil fatty acids with kraft lignin was undertaken by performing the whole procedure under nitrogen instead of air. *n*-Alkylbenzenes were formed, but the amount of stearic acid was unchanged and no hydrogenated pinosylvin dimethylether could be detected. It seems that the formation of *n*-alkylbenzenes is mainly due to the temperature of the pyrolysis reaction. Table IV gives a list of those substances collected in a liquid air-cooled trap which could be detected and identified in the nitrogen 280 C-run of the pyrolysis of tall oil fatty acids with kraft lignin.

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Polyamine-Koch Acid Amides As Dispersants for Two-cycle Engine Oils

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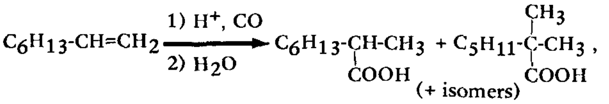
ABSTRACT

New ashless dispersants for two-cycle engine oils were developed from tetraethylenepentamine and C_{19}-C_{25} Koch acids. Engine tests showed these amides are excellent substitutions for the conventional isostearic acid-derived compounds.

INTRODUCTION

Prompted by a fluctuating supply of naturally derived isostearic acid, we have developed a product which can be used in its place in automotive applications. The route chosen to produce liquid isofatty acids in the C_{19} to C_{25} carbon number range involved the Koch reaction (1). These products are odd carbon number acids,



$$C_6H_{13}\text{-}CH{=}CH_2 \xrightarrow[2)\ H_2O]{1)\ H^+,\ CO} C_6H_{13}\text{-}\underset{\displaystyle COOH}{\underset{|}{C}}H\text{-}CH_3 + C_5H_{11}\text{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle COOH}{|}}{C}}}\text{-}CH_3 \quad (+\ \text{isomers}), \qquad [I]$$

in contrast to the even numbered species from natural sources. Although most of the individual isomers of alkanecarboxylic acids in the C_{19} range and above are solids, a surprising liquid mixture of isomers is formed in the Koch reaction. Koch acids produced from higher olefins are mixtures of approximately equal amounts of secondary and tertiary alkanecarboxylic acids. With a C_{18} olefin feed, based on studies with model compounds, the product was expected to contain a total of 16 isomers. Secondary acids include x-carboxyoctadecanes, where x = 2-9; tertiary acids include x-methyl-x-carboxyheptadecanes, where x = 2-9. Isostearic acid, on the other hand, is believed to be an isomeric mixture of alkanecarboxylic acids with methyl group branching in the alkane chain, some *n*-alkanecarboxylic acids and smaller amounts of unsaturated acids. The average molecular weight (MW) of the mixture corresponds to a C_{18} carboxylic acid. Koch acids can replace isostearic acid in many applications. This paper describes the production of ashless dispersants for two-cycle engine oils from these new products (2).

EXPERIMENTAL

Apparatus and Analytical

Carbonylations were done in a 1-ℓ, 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie, PA). The autoclave was equipped with a cooling coil and was connected to a cylinder of CO, as well as temperature and pressure controllers and recording instruments. Olefins were introduced into the autoclave through the top using Milroy pumps. With solid olefins, C_{20} (mp 28.5 C) and C_{20}-C_{24} (mp 42-44 C), the addition lines were traced with steam lines. Product acids were analyzed by gas liquid chromatography (GLC) according to group types as trimethylsilyl (TMS) derivatives on a 2.5 ft x 1/8-in., 3% OV-1 column, programmed from 100-240 C at 4 C/min. *tert*-Carboxylic acids were the first to emerge from the column, followed by secondary acids. Olefins used were commercial samples. The carbon number distribution of internal C_{18} olefin was: C_{12}, 0.3%; C_{13}, 1.1%; C_{14}, 1.2%; C_{15}, 2.3%; C_{16}, 1.6%, C_{17}, 7.8%; C_{18}, 85.3%; and C_{19}, 0.4%; ave. MW = 247. Similarly, the composition of C_{20}-C_{24} α-olefin fraction was: C_{18}, 3.3%; C_{20}, 51.0%; C_{22}, 37.9%; and C_{24}, 7.8%; ave. MW = 295.

Carbonylation of 1-Octadecene.

In a typical experiment, the autoclave was charged with 97% sulfuric acid (440 g) and pressured with CO to 92 atm. Temperature was kept at 15-20 C while 1-octadecene (222 g) was added to the autoclave over 3 hr; the reaction was continued for an additional 30 min. The product was hydrolyzed by adding reaction mixture to wet ice (1500 g) and the organic layer that formed upon standing was transferred to a separatory funnel and washed three times with an almost equivalent volume of hot 15% sodium chloride solution. Distillation using a 12 in x 3/4-in od column packed with stainless steel rings produced 199.2 g of acids, bp 200-205 C at 1.5 mm of Hg, neq = 312. "Vacuum distillation at 10 mm Hg (% distilled at temperature C): IBP, 221; 5-20, 222; 30-50, 223; 60-80, 224; 90, 226; end, 227." Reactions with other feeds were carried out under comparable conditions.