Distillability of Extracted Mixed-Birch Tall Oil

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ABSTRACT

Chemical and physical properties of tall oil made in the CSR process and distillation results of three different types of distillation plants are presented. Chemically extracted, mixed-birch, tall oil differs remarkably from the normal Scandinavian crude tall oil. The extracted oil deviates from the normal, unextracted, mixed-birch tall oil with respect to the smaller unsaponifiable amount and the fatty acid esters. The amount of resin acid is small in extracted mixed-birch tall oil. The quantity of fatty acids, especially that of saturated fatty acids, is large. Distillation of extracted mixed-birch tall oil is most successful in a distillation plant where thin film evaporators are used.

INTRODUCTION

Raw material basis of the extracted mixed-birch tall oil is the following: 52% birch, 34% pine and sawmill chips, and 14% sawdust. The pure pine crude soap developing in pine cooks is used as a dispersant of birch pulp in birch cooks. The soap coming to the tall oil process is thus merely mixed soap.

Quality of mixed soap differs from the conventional Finnish pine crude soap. The properties of tall oils made of mixed soap and normal pine crude soap are unequal. The large share of neutrals in mixed soap lowers the acid number. The amount of resin acids is naturally smaller, because birch does not contain resin acids (1). The quantity of fatty acid esters is also high in mixed soap made of tall oil. Mixed-birch tall oil contains plenty of saturated fatty acids.

The high neutral matter content of mixed tall oil causes difficulties in distillation of tall oil. Pitch yield is high, the quality of rosin poor; heads contain lots of saturated fatty acids, and the amount of heads is large.

The Crude Soap Refining process has been developed to improve the quality and distillability of mixed tall oil (2) (Fig. 1). In the CSR process, neutrals are separated from the mixed soap into the hexane phase. These neutrals partly correspond to the unsaponifiable material of mixed tall oil.

Through extraction of mixed soap, it is possible to decrease the amount of unsaponifiable material of mixed tall oil. The acid number in extracted mixed tall oil rises even higher than in the normal tall oil (Table I).

EXPERIMENTAL

The extracted mixed tall oil and the distillate fractions of tall oil were analyzed in a Pye Unicam gas chromatograph. The output was made in a Hewlett-Packard 3380 integrator.

In analyzing the acids, a BDS glass capillary column was used, length 34 m, i.d. 0.3 mm. The carrier gas was helium, 1.5 ml/min. The split-ratio was 1:40. The analysis was made isothermally at 197 C. The temperatures of the detector and injector were 250 C.

In the analysis of unsaponifiables, an SE-30 glass capillary column was used, 26 m, i.d. 0.3 mm. The carrier gas was helium 1.8 ml/min; the split-ratio was 1:30. The analysis was made isothermally at 265 C. The temperatures of the detector and injector were 300 C.

The acids were analyzed as their methyl esters after esterification with diazomethane (3). Identification was done partly with the help of Holmbom's (3) literature references and partly with the help of reference samples.

The unsaponifiable samples were silylated with HMDS and TMCS (3). Identification was based on reference samples and relative retention.

The acid number, saponification number and the analysis of the amount of unsaponifiables were made according to the SCAN methods (4-6). The viscosity measurements were made with the Brookfield viscosimeter.

DISCUSSION

The Chemical Composition of Extracted Mixed Tall Oil

The composition of the fatty acid components of extracted mixed oil differs from that of the normal tall oil. The amount of saturated fatty acids, especially the quantity of palmitic acid is large. Mixed oils also contain $C_{18:0}$, $C_{20:0}$, $C_{22:0}$, and $C_{24:0}$ acids. There is relatively plenty of linoleic acid in extraced mixed-birch tall oil. There is not

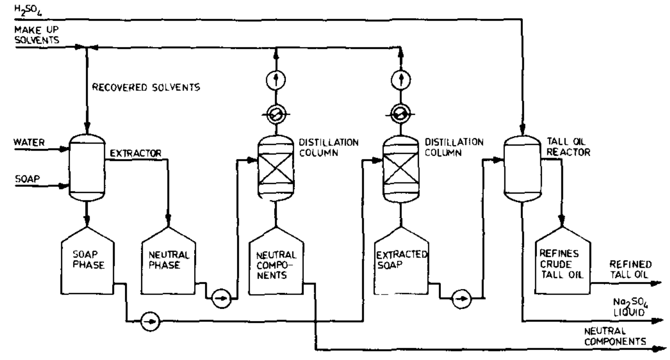

FIG. 1. CSR process.

TABLE I

Properties of Mixed, Normal and CSR-Treated Mixed Crude Tall Oil at the Production

	Mixed birch-tall oil	Normal Finnish tall oil	CSR-treated mixed tall oil
Acid value	132	153	165
Saponification value	165	170	170
Unsaponifiables	20%	12%	8%
Resin acids	23%	40%	25%

TABLE II

The Yields of Mixed-Birch Tall Oil Fractions at the Normal Foster-Wheeler Distillation Plant

The quality of crude tall oil	
Acid value	115
Resin acids	21 %
Esters	16 %
Unsaponifiables	23 %
Water	1.5%
Yields	
Resin acids	28.0%
CFA I	13.6%
CFA II	6.3%
Heads	12.5%
Pitch	35.0%
Loss	3.6%
Water	1.0%

TABLE III

The Gas Chromatographic Analysis of the Main Components of the Mixed CSR-Treated Crude Tall Oil Acids

Saturated fatty acids %		
Palmitic	$C_{16:0}$	4.6
Stearic	$C_{18:0}$	1.8
Arachidic	$C_{20:0}$	1.4
Behenic	$C_{22:0}$	0.6
Lignoceric	$C_{24:0}$	0.2
Unsaturated fatty acids %		
Oleic	$C_{18:1}$	15.0
Linoleic	$C_{18:2}$	28.3
Pinolenic	$C_{18:3}$	2.3
Linolenic	$C_{18:3}$	0.2
Conjugated	$C_{18:2}$	5.1
Resin acids %		
Abietic		15.7
Dehydroabietic		5.6
Neobietic		0.3
Palustric		0.4
Pimaric		3.1
Sandracopimaric		0.2
Isopimaric		0.4

TABLE IV

The Analysis of CTO Feed in Distillation Trials

Acid value	146 - 148
Saponification value	164 - 166
Unsaponifiables	9 - 10%
Resin acids	24 - 25%

TABLE V

The Yields of CSR-Treated Mixed Oil Fractions at Different Distillation Plants

	Linder (%)	Foster-Wheeler (%)	Luwa (%)
Heads	5	8	10
Fatty acids	30	41	32
Resin acids	13	15	20
Pitch	35	36	30
Distilled tall oil	17		8

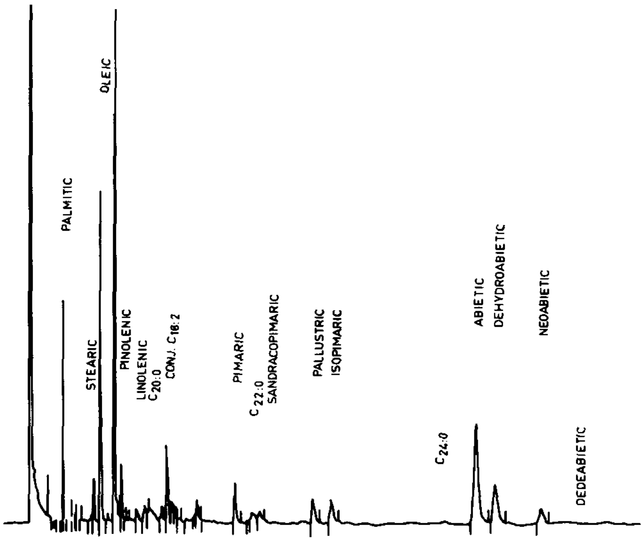

FIG. 2. Gas chromatogram GCR-treated CTO.

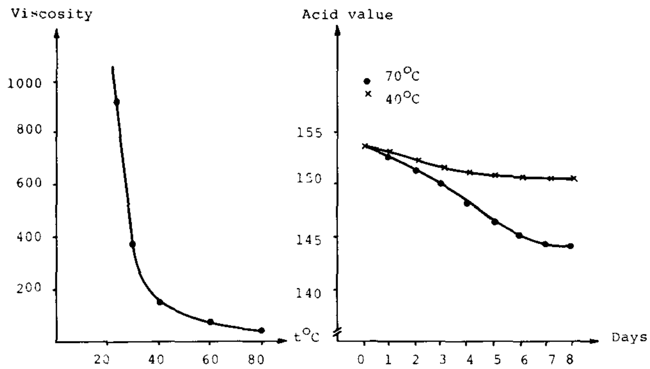

FIG. 3. The viscosity of extracted crude tall oil (left); the decrease of acid value at different temperatures.

much pinolenic acid, (5, 9, 12 -$C_{18:3}$)-acid, and hardly any linolenic acid (9, 12, 15 -$C_{18:3}$). The extracted mixed oil contains the normal amount of conjugated $C_{18:2}$ acids. The amount of saturated fatty acids is higher than that in the normal Scandinavian mixed oil.

The amount of resin acids in mixed-birch tall oil does not differ from that of the resin acids of normal tall oil. The total amount of resin acids is small, only about 20% of the total acids.

The chemical composition of unsaponifiables differ most from the normal Finnish tall oil. The share of fatty alcohols is high, as the triterpene alcohols and sterols mostly have been extracted out in the CSR process. Arachidic, behenic and lignocerylic alcohols are the main components in the neutrals of extracted tall oil. Diterpenealcohols and aldehydes are also found. In unextracted tall oil, sterols and triterpene alcohols are the main components of unsaponifiables.

On the basis of the GC analyses, it is possible to predict something on the distillability of extracted mixed-birch tall oil. The high palmitic acid content in mixed-birch tall oil means that in distillation there will be a great amount of heads available. A small amount of resin acids in crude, mixed-birch tall oil may cause some difficulties in separating rosin and fatty acids. There is the possibility of part of the saturated fatty acids ($C_{22:0}$ - $C_{24:0}$) staying in the rosin fraction. Fatty acids easily esterify with fatty alcohols, which are relatively abundant in extracted mixed-birch tall oil (Fig. 2). The analysis of the feed shows (Table IV) that there are rather large amounts of esters in crude

TABLE VI

Linder

	Pitch	Rosin	FA	Heads
$C_{16:0}$	0.3	0.3	0.6	37.7
$C_{18:0}$	---	---	2.9	0.5
$C_{20:0}$	1.1	1.3	1.2	0.2
$C_{22:0}$	4.7	4.9	0.1	---
$C_{24:0}$	1.1	1.7	0.1	---
$C_{18:1}$ oleic	3.0	0.1	28.0	8.8
$C_{18:2}$ linoleic	5.0	0.1	41.0	10.9
$C_{18:3}$ pinolenic	---	---	4.3	1.4
Conj. $C_{18:2}$				
abietic	32.3	26.5	---	---
dehydroabietic	29.4	32.3	---	---
pimaric	3.4	1.7	1.1	1.4
palustric	3.8	0.7	0.3	0.4
sandracopimaric	0.9	2.2	---	0.1
isopimaric	1.8	3.0	---	0.2

Foster-Wheeler

	Pitch	Rosin	FA	Heads
$C_{16:0}$	5.4	0.1	3.6	34.9
$C_{18:0}$	1.9	---	2.2	1.1
$C_{20:0}$	1.7	0.6	4.3	0.4
$C_{22:0}$	0.5	3.3	0.2	0.2
$C_{24:0}$	---	1.5	0.1	0.1
$C_{18:1}$ oleic	13.4	0.1	20.1	7.3
$C_{18:2}$ linoleic	20.8	0.1	37.6	13.5
$C_{18:3}$ pinolenic	1.7	---	4.0	1.8
Conj. $C_{18:2}$	2.5	0.4	5.5	6.5
abietic	22.2	27.9	0.4	---
dehydraobietic	14.0	33.5	0.8	---
pimaric	2.0	1.1	1.8	1.4
palustric	2.6	0.8	0.2	0.2
sandracopimaric	0.5	2.4	0.1	0.1
isopimaric	0.7	3.2	0.1	0.1

Luwa

	Pitch	Rosin	FA	Heads
$C_{16:0}$	0.8	---	4.1	35.9
$C_{18:0}$	0.4	---	2.0	1.9
$C_{20:0}$	0.5	0.2	0.8	0.5
$C_{22:0}$	2.9	1.6	0.1	0.7
$C_{24:0}$	2.9	1.7	0.1	---
$C_{18:1}$ oleic	4.2	0.1	29.2	4.4
$C_{18:2}$ linoleic	6.1	0.2	46.0	10.6
$C_{18:3}$ pinolenic	1.0	---	5.8	0.4
Conj. $C_{18:2}$	2.0	0.1	5.9	6.2
abietic	38.4	43.4	---	---
dehydroabietic	18.5	22.5	---	---
pimaric	1.5	5.0	0.1	---
palustric	7.9	2.0	0.1	---
sandracopimaric	0.1	0.4	---	---
isopimaric	36	3.0	---	---

TABLE VII

The Quality of Extracted Mixed Oil Resin Acid Fraction at Different Distillation Plants

	Linder	Foster-Wheeler	Luwa
Acid value	154	142	170
Saponification value	166	159	179
Resin acids	75%	68%	88%
Unsaponofiables	8%	9%	4%
Fatty acids (free)	9%	7%	5%

mixed-birch tall oil. It is likely that part of the esterified material is also found in distillation fractions. Yield of fatty acids is higher than normal.

The viscosity of extracted birch tall oil is lower than that of the normal Scandinavian tall oil (Fig. 3). Thus, transport of mixed oil can be accomplished at low temperatures.

On the Properties of Extracted Mixed Oil Distillates

Distillation trials were carried out with extracted mixed oil in three different distillation plants: Linder, Foster-Wheeler, and Luwa. With respect to yields, major differences occurred between the different plants. The quality of distillation fractions was best in the Luwa distillation plant.

The amount of head fraction was remarkably higher than normal in all plants. The heads obtained from extracted, mixed oil deviated from the normal head fraction with respect to the large amount of saturated fatty acids, especially palmitic acid. There were differences also between the relative amounts of oleic and linoleic acids.

The quantity of fatty acid fraction was higher than normal in all distillation plants. Also, in the fatty acid fraction the amount of saturated fatty acids was higher than normal. Arachidic acid $C_{20:0}$ seemed to be enriched in the CFA fraction, and behenic acid $C_{22:0}$ and lignocerylic acid $C_{24:0}$ were enriched in the rosin fraction, especially in the Linder and Foster-Wheeler distillation plants. In the Luwa distillation plant, the saturated fatty acids were separated satisfactorily from the rosin fraction.

The fatty acid fraction of the Linder distillation plant contained the most saturated fatty acids. As expected, the best fatty acid fraction was developed in the Luwa distillation plant. It is very difficult to say anything about the Foster-Wheeler distillation plant, because the CFA fraction was not distilled separately. Thus, only with respect to rosin and pitch fractions are the results comparable with those of the Linder and Luwa distillation results.

The rosin made in the Luwa distillation plant is qualitatively fairly good. The color of the rosin is not good, but its other properties make it quite practicable (8).

The yield of resin acids was also satisfactorily in the

TABLE VIII

The GC Analysis of the Unsaponifiables of Different Crude Tall Oils

	Normal Scand. CTO (7)%	Extracted mixed CTO %
β-sitosterol, β-sitostanol, Campesterol	42	6
Fatty alcohols		
α-sitosterol	9	5
Di- and triterpene alcohols	25	56
Diterpenealdehydes	12	18
Others	12	15

Luwa distillation plant. The qualitatively poorest rosin was developed in the Foster-Wheeler distillation plant. The yield of resin acids was poorest in the Linder distillation plant. The large amount of fatty acid esters certainly is one reason for the poor quality and color of the rosin of the Linder and Foster-Wheeler distillation plants. Instead, the rosin of the Luwa distillation plant did not contain "more than normal" esters. The color may be due to the relatively large amount of the abietic acid group and to the fact that abietic acid tends to crystallize in rosin. Some $C_{20:0}$, $C_{22:0}$, and $C_{24:0}$ fatty acids also remain in the rosin of the Luwa distillation plant. The total content of fatty acids in the rosin does not, however, deviate from the normal. The amount of dehydroabietic acid has remarkably increased especially in the rosin of the Linder distillation plant.

Pitch yields were high in all distillation plants. This is partly due to the easy formation of esters in mixed-birch tall oil, and the esters mainly remain in the pitch during distillation. On the other hand, to improve the quality of rosin, it is necessary also to have some esters and saturated fatty acids in the pitch.

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