The Behavior of Resin Acids during Tall Oil Distillation[1]

BJARNE HOLMBOM, Institute of Wood Chemistry and Cellulose Technology, Åbo Akademi, SF-20500 Turku/Åbo 50, Finland

ABSTRACT

The behavior of resin acids during tall oil distillation was studied by analyzing samples from six industrial-scale processes. The same artifact resin acids were formed in all processes. However, the proportion of artifact resin acids in tall oil rosins varied from 8.3 to 18.3% of the resin acids. The lowest values were found for two processes utilizing thin-film evaporators. The yield of resin acids in the tall oil rosin fraction varied from 62 to 80% of the resin acids in the crude tall oil feeds. Dehydroabietic acid was formed in all processes, the amount in rosin being 14-44% more than in the crude tall oil feed. Of the abietic acid, only 45-82% was recovered in the tall oil rosin fraction. The distribution of various resin acids and their reaction products during distillation was determined. Major resin acid impurities in tall oil fatty acids were 8,15-pimaradien-18-oic acid and 8,15-isoprimaradien-18-oic acid, both formed chiefly during distillation, and two secodehydroabietic acid isomers common in crude tall oils. The reactions of resin acids leading to new isomers or non-acidic products are discussed.

INTRODUCTION

In a previous study made in this laboratory, the resin acid composition of Finnish tall oil rosins obtained by distillation of crude tall oil was found to differ significantly from that of corresponding crude tall oil feeds (1). Several resin acids present in the tall oil rosins had evidently been formed in the distillation processes. These distillation artifact resin acids, which altogether comprised about 15% of the resin acids in rosin, could be identified by capillary gas chromatography-mass spectrometry. Further improvements in the technique for analyzing complex mixtures of fatty and resin acids have been recently reported (2).

The reactions of resin acids during distillation can appreciably lower both the yield and quality of tall oil rosin, and can also cause undesirable effects on other distillation fractions. Therefore, it was decided to study more thoroughly the behavior of resin acids during distillation on an industrial scale. One objective was to investigate the principal reactions that resin acids undergo during distillation. Another objective was to investigate how different distillation processes influence changes in resin acids. A matter of further interest was to determine the distribution of different resin acids and their reaction products in the distillation process.

EXPERIMENTAL PROCEDURES

Samples were taken of the crude tall oil feed and of the tall oil rosin fraction from six industrial continuous distillation processes. In one case, process A, samples were also taken of all other outcoming streams and of two process streams inside the plant as shown in Figure 1. All samples were taken under steady-state process conditions. For process A, sampling was performed according to a time schedule under which consideration was taken of the hold up times in the different process steps. The yield of tall oil rosin and of other fractions relative to the feed was recorded by the process personnel at the time of sampling. The resin acid composition was analyzed by gas chromatography (GC) and combined mass spectrometry (GC-MS) with glass capillary columns as described in (2). All quantifications were made relative to heptadecanoic acid added as an internal standard.

To the samples from process A, three internal standards were added: heptadecanoic acid, heptadecanoic acid methyl ester, and squalane. The free acids were separated and analyzed by GC and GC-MS as above. The neutral fractions were saponified with a 0.5 N KOH-ethanol solution and heated for 3.5 hr. at 70 C. The saponification solution was neutralized with a Dowex 50 cation exchanger. Liberated acids and unsaponifiable compounds were separated by extracting a diethyl ether solution with 2% aqueous KOH. The liberated acids (esterified acid fraction) were methylated with diazomethane and analyzed by capillary GC in the same way as used for the free acids. The unsaponifiable compounds were dissolved in benzene. After silylation GC analysis was performed with a 25 m/0.30 mm ID SE-30 glass capillary column, temperature programmed from 160 to 280 C at 2 C/min. Hydrocarbons derived from resin acids by decarboxylation in the distillation process were identified by GC-MS.

RESULTS AND DISCUSSION

The results of the analysis of crude tall oils and tall oil rosins from the six distillation processes are presented in Table I. The results for samples of nine streams of process A are given in Table II.

Resin Acid Composition of Crude Tall Oils

All crude tall oils studied contained the same seven major resin acids. The proportion of these major acids was also very similar. The American oil (process F) contained less pimaric acid than isopimaric acid, but otherwise had a resin acid composition comparable to the European oils. In addition to these well-known resin acids, all oils also contained minor components, together comprising 1.3-2.0% of the resin acids. The two epimeric secodehydroabietic acids mentioned in our previous report (2) have not previously been detected in crude tall oil. They may originate from levopimaric acid, which, under alkaline conditions such as in the sulfate cook, can form secodehydroabietic acids as well as other resin acids (3). Traces of 8,15-pimaradien-

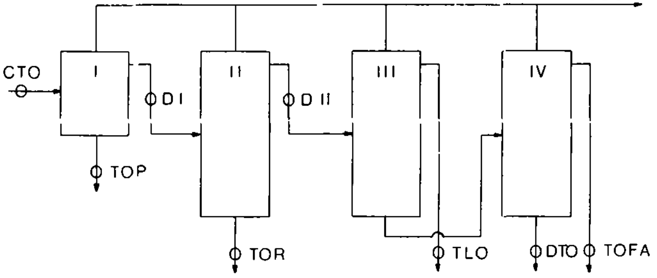

FIG. 1. Flow scheme for distillation process A. Points of sampling marked with O. Abbreviations: CTO: Crude Tall Oil, TOP: Tall Oil Pitch, D: Distillate, TOR: Tall Oil Rosin, TLO: Tall Light Oil, DTO: Distilled Tall Oil, TOFA: Tall Oil Fatty Acids.

---

[1] Some results of this work were presented at the 173rd American Chemical Society Meeting, New Orleans, March 1977.

TABLE I

Analysis of Crude Tall Oil (CTO) and Tall Oil Rosin (TOR) from Six Distillation Processes

Process	A		B		C		D		E		F	
Location	Finland		Sweden		Sweden		Austria		Holland		U.S.	
CTO origin	Finland		Sweden		Sweden		Austria		Scandinavia		Southern U.S.	
Special equipment					Thin film evaporators		Thin film evaporators		Steam addition			
Bottom temp. in rosin column, C		270						288		280		
Bottom vacuum in rosin column, Torr				17		16.5		23		134		
	CTO	TOR	CTO	TOR	CTO	TOR	CTO	TOR	CTO	TOR	CTO	TOR[a]
Acid number, mg KOH/g	134	157	146	162	as in B	173	145	173	139	155	152	157
Saponification number, mg KOH/g	163	174	165	171		183	162	182	153	168	164	173
Resin acids, %	39.9	79.2	31.2	80.4		85.9	39.5	90.2	34.4	80.1	35.3	76.3
Unsaponifiables, %	11.8	5.3	11.2	9.6		3.1	12.0	2.7	11.8	6.0	7.6	7.5
Petroleum ether insolubles, %	4.4		3.5				6.8		3.6			
Softening point, C[b]		63		59.2		64.5		71.5		68.1		46.5
Color (ASTM)				X		X		X		WW		
TOR yield, kg/ton CTO		336		231		287		314		301		316
Resin acids, kg/ton CTO												
Pimaric	33	8.0	29	4.2		10.1	37	12.2	32	10.5	23	10.4
8,15-Pimaradien-18-oic (A)	0.4	5.2	1.0	3.8		2.8	0.6	4.3	0.4	5.5	0.8	6.0
Isopimaric	26	5.5	20	5.4		11.2	18	9.3	26	9.0	24	11
Sandaracopimaric	6.8	3.5	5.3	1.1		3.4	6.4	3.7	7.0	3.2	5.9	3.9
8,15-Isopimaradien-18-oic (A)	0.4	4.0	0.7	2.3		1.6	0.5	2.0	0.4	3.1	1.0	5.4
Abietic	171	91	120	54		99	168	116	142	95	148	86
Palustric	31	21	35	14		27	28	28	46	23	53	26
Neoabietic	37	12	33	5.2		9.9	35	13	44	9.5	42	10.7
Other abietadienoic[c] (A)	---	22	---	16		9.3	---	17	---	21	---	19
Dihydroabietic[d] (A)		7.0	---	9.7		3.5	---	7.3	---	8.9	---	9.0
Dehydroabietic	58	70	43	62		51	44	56	51	58	47	58
Dehydrodehydroabietic[e] (A)	1.2	3.0	---	1.6		2.0	0.5	1.7	0.5	1.9	2.1	1.9
Secodehydroabietic[f]	4.5	1.0	3.4	0.3		0.8	3.4	0.6	3.4	1.0	3.0	1.7
Resin acids, total	369	253	290	179		232	340	271	353	250	350	250
Resin acids, yield, %		69		62		80		80		71		71
Artifact resin acids (A), %[g]		16.5		18.7		8.3		11.9		16.2		16.7
Dehydroabietic: Abietic	0.34	0.76	0.36	1.15	0.36	0.51	0.26	0.48	0.36	0.61	0.32	0.68

[a] A fraction containing most of the resin acids; not a typical U.S. tall oil rosin.

[b] SCAN-T 10:69 standard method.

[c] Including 7,9(11)-abietadien-18-oic, 13β-abieta-7,9(11)-dien-18-oic,8,12-abietadienic and two unidentified acids.

[d] The sum of five peaks, according to mass spectra, apparently including 8-, 8(14)-, 7- and 13-abieten-18-oic acid isomers.

[e] 8,11,13,15-Abietatetraen-18-oic acid.

[f] The sum of two components: Seco 1 and Seco 2 as in ref. 2.

[g] The sum of all acids marked with (A) as a percentage of the resin acids in TOR.

TABLE II

Quality Data, Yields, and Contents of Resin Acids and Resin Acid Reaction Products for Crude Tall Oil and Distillation Fractions in Process A

Fraction[a]	CTO	TOP	D I	TOR	D II	TLO	TOFA	DTO
Acid number, mg KOH/g (SCAN)	134.2	20.2	177.2	157.0	174.6	136.7	194.3	159.2
Saponification number, mg KOH/g (SCAN)	162.8	100.7	178.7	174.4	177.5	141.5	197.0	180.7
Resin acids, % (Linder-Persson)	39.9	9.3	45.3	79.2	9.1	1.8	1.2	34.0
Unsaponifiables, % (SCAN)	11.8	30.3	7.4	5.3	11.2	32.2	3.2	2.5
Relative yield, kg/ton CTO	1000.0	293.0	686.0	336.0	349.0	108.0	154.0	86.0
Resin acids, kg/ton CTO								
Secodehydroabietic 1	2.7	—	2.3	0.5	1.8	—	0.4	1.3
Secodehydroabietic 2	1.8	—	1.4	0.5	0.9	—	0.2	0.9
Pimaric	33.0	0.3	28.8	8.0	5.2	0.1	0.2	2.5
8,15-Pimaradien-18-oic	0.4	—	0.8	5.2	2.4	—	0.3	3.9
Isopimaric	25.9	0.4	22.1	5.5	2.2	—	0.1	1.3
Sandaracopimaric	6.8	0.1	6.0	3.5	1.2	—	—	0.7
8,15-Isopimaradien-18-oic	0.4	—	0.8	4.0	2.3	—	0.2	2.6
Paulustric	31.0	0.9	37.2	20.9	1.7	—	0.1	0.9
Abietic	171.0	3.9	150.0	91.3	7.4	—	0.2	4.8
Neoabietic	37.0	0.6	16.3	11.6	0.5	—	—	0.4
7,9(11)-Abietadien-18-oic	—	—	0.9	5.5	0.4	—	—	0.3
13 β-Abieta-7,9(11)-dien-18-oic	—	—	0.9	8.7	0.4	—	—	0.6
Other abietadienoic[b]	—	—	1.0	8.2	0.7	—	—	1.2
Dehydroabietic	57.6	2.6	73.6	69.7	6.1	—	0.2	5.2
Dehydrodehydroabietic	1.2	0.1	1.7	3.0	0.1	—	—	0.1
Dihydroabietic[c]	—	—	1.2	7.0	0.8	—	—	0.5
Resin acids, total	368.8	8.9	345.0	253.1	34.1	0.1	1.9	27.2
Esterified resin acids	0.5	2.1	0.2	22.3	—	—	—	1.4
Hydrocarbons derived from resin acids	—	—	7.0	0.2	15.0	15.0	0.3	—

[a] Abbreviations as in Fig. 1.

[b] Including 8,12-abietadien-18-oic and two unidentified acids.

[c] The sum of five peaks.

18-oic and 8,15-isopimaradien-18-oic acids, not earlier reported in crude tall oil, were detected in all oils. Dehydrodehydroabietic acid was present in four of the oils. This acid, earlier detected in tall oil rosin (1), was found to have the 8,11,13, 15-abietatetraen-18-oic structure. The GC and MS characteristics were identical with those of a reference substance, which was prepared by dehydration of 15-hydroxydehydroabietic acid (4).

Resin Acid Composition of Tall Oil Rosins

All tall oil rosins studied contained the same resin acid components. The higher resolution of the columns used in this work made it possible to separate still more resin acid isomers formed during distillation than in the previous study of Finnish tall oil rosins (1). Five dihydroabietic acid peaks were separated. GC-MS data indicated that some of these peaks were still mixtures. Clear indications of two 8-, two 8(14)-, one 13- and two 7-abieten-18-oic acid isomers were found by comparison with the GC and MS data given by Zinkel et al. (5). All rosins gave five peaks, apparently being abietadienoic acid isomers formed during distillation. Predominant among these were the two peaks representing 7,9(11)-abietadien-18-oic and 13β-abieta-7,9(11)-dien-18-oic acids. One of the peaks had GC and MS characteristics which agreed well with 8,12-abietadien-18-oic acid (5).

Significant differences between the rosins were seen in the proportion of distillation artifact resin acids. (Table I). Altogether 13 peaks were considered. These could either not be detected at all in the crude tall oils, or had substantially increased compared with quantities found in the crude tall oils. The artifact resin acid content was particularly low in the rosins from processes C and D, 8.3 and 11.9% of the resin acids, respectively. The rosin from process B showed the highest percentage of artifact resin acid components, 18.7%.

The ratio of dehydroabietic to abietic acid in the rosins was significantly different from that in corresponding crude tall oil. The smallest change in this ratio was found for process C and the largest for process B, although both processes worked with the same crude tall oil feed. The artifact resin acid content in tall oil rosins and the change in the ratio of dehydroabietic to abietic acid between crude tall oil and tall oil rosin both provide information about the degree of change in resin acids during distillation. It is apparent from the results that the design and operation of the distillation process significantly influences the change in resin acids, and consequently both the yield and quality of the tall oil rosin fraction.

Resin Acid Reactions During Distillation

A summary of the dominant resin acid reactions during distillation is presented in Table III.

Both pimaric and abietic type acids undergo double bond isomerization. Pimaric acid had been isomerized to a considerable extent. 8,15-pimaradien-18-oic acid might have been formed from both isopimaric and sandaracopimaric acid. Five isomers, evidently of abietadienoic structure, not present in crude tall oil, were detected in the tall oil rosins. In process A the double bond isomerizations were found to take place almost exclusively in the second distillation step, in the rosin column, as very little of these artifact resin acids were present in the distillate from the depitching step (Table II).

It has previously been reported that an equilibrium of the abietadienoic acids of 81% abietic, 14% palustric and 5% neoabietic can be approached by heating for extended periods at 200 C (6). A clear change in this direction had already occurred during the depitching step of process A. In the distillate from this step, the proportion was

TABLE III

Dominating Resin Acid Reactions during Distillation

Reaction type	Reacting resin acids		Reaction products	Principal distribution of products[a]
Reactions giving other resin acids				
Double bond isomerization	Pimaric	→	8,15-Pimaradien-18-oic acid	TOR, DTO
	Isopimaric Sandaracopimaric	→	8,15-Isopimaradien-18-oic acid	TOR, DTO
	Palustric Neoabietic Abietic	→	Abietic acid an other abietadienoic isomers	TOR
Disproportionation	Abietadienoic	→	Dehydroabietic acid Dihydroabietic acid	TOR TOR
Dehydrogenation	Abietadienoic	→	Dehydroabietic acid	TOR
	Dehydroabietic	→	Dehydrodehydroabietic acid	TOR
Reactions giving losses of resin acids				
Decarboxylation	All acids (?)	→	C_{19}-hydrocarbons + HCOOH or CO_2	TLO
Dehydration	All acids	→	Resin acid anhydrides + H_2O	TOR
Polymerization	All acids, except aromatic (?)	→	Dimers, trimers, etc.	TOR, TOP

[a] Abbreviations as in Fig. 1.

74% : 18% : 8%. The proportion was substantially the same in the tall oil rosin fraction, and the isomerization equilibrium was obviously already reached during the depitching step. The proportions between these abietadienoic acids were similar for all tall oil rosins in this study and varied in the narrow range 70-74% abietic, 18-21% palustric and 7-9% neoabietic. Differences in process design and operation were thus not reflected in this isomerization equilibrium.

Substantial losses of resin acids occur during distillation. A resin acid material balance for the first two steps of process A showed a loss of 20% of the resin acids. For the whole process, the losses were 21%. The yield of resin acids in the tall oil rosin fractions was 69% for process A, and between 62 and 80% for the other processes. It appears that the losses of resin acids in the processes studied varied between ca. 10% and 25%. The lowest losses were found for processes C and D, which were equipped with thin-film evaporators for heat supply.

Over 30% of the resin acids lost in process A were found as esterified acids, mainly in the rosin fraction. These acids occurred principally as anhydrides, as reported earlier, for a similar tall oil rosin quality (7). Only small quantities of esterified resin acids were present in the pitch of process A. Similar low values were obtained in a recent study of a wide range of pitch samples (8). It may be concluded that anhydride formation takes place principally in the rosin column, and that this reaction may cause considerable losses of free resin acids. It appears that all resin acids have a similar tendency to take part in anhydride formation since the composition of esterified resin acids in the rosin of process A was practically identical with that of the free resin acids.

Decarboxylation of resin acids, known to occur during distillation, results in a complex mixture of C_{19} hydrocarbons. The main components formed in process A had molecular weights of 256 and 258, indicating loss of formic acid or carbon dioxide. The formation of formic acid during distillation was recently proved (9). This acid may be the main cause of the corrosion problems in tall oil distillation equipment. From the results obtained in process A (Table II), it appears that decarboxylation occurred not only in the first but also in the second distillation step. About 20% of the resin acid losses that occurred in process A seems to be due to decarboxylation.

Conjugated dienoic resin acids may form dimers, trimers, etc., through Diels-Alder condensation. Evidence of the presence of resin acid dimers in tall oil pitch and also in tall oil rosin has been found in our laboratory (8). Most reactions of resin acids during distillation must be considered undesirable, but particularly the reactions leading to losses of resin acids. The degree of resin acid reactions is certainly principally dependent on the time that the heat-sensitive resin acids are exposed to high temperatures. Thus, short residence times in the hottest zones of a distillation system are essential. This was also demonstrated in the present investigation, since less isomerization and loss reactions were found for processes C and D utilizing thin-film technology for heat supply.

Effective vacuum systems and the use of stripping steam are utilized in distillation process design to lower maximum temperatures. The use of stripping steam may have an additional positive effect in preventing the formation of resin acid anhydrides.

The Distillative Distribution of Resin Acids

An evaluation of the relative volatility of different resin acids could be made from their distribution in the rosin fraction (TOR) and the distillate from the rosin column (DII) in process A (Table II). Only 22% of secodehydroabietic acid 1 (Seco 1) was distributed in the rosin fraction, 36% of Seco 2, 61% of pimaric acid, 63% of 8,15-isopimaric acid, 68% of 8,15-pimaric acid, 71% of isopimaric acid, 74% of sandaracopimaric acid, and 83% of dihydroabietic acid. In the case of all abietadienoic acids, and also dehydroabietic and dehydrodehydroabietic acid, 90-97% were distributed in the tall oil rosin. As a consequence, the secodehydroabietic acids, which were only trace components in crude tall oil, were, together with the pimaric and isopimaric acids, the main resin acid impurities in the tall oil fatty acid fraction. On the other hand, dehydroabietic and abietic acid were the dominating resin acids left in the pitch fraction.

ACKNOWLEDGMENT

This work was supported by the National Research Council of Technical Sciences, Academy of Finalnd. Mass spectra were recorded by M. Reunanen. Some of the companies which generously delivered the samples for this study aided by performing the standard tall oil determinations.

REFERENCES

1. Holmbom, B., E. Avela, and S. Pekkala, JAOCS 51:397 (1974).
2. Holmbom, B., Ibid. 54:289 (1977).
3. Takeda, H., W.H., Schuller, R.V. Lawrence, and D. Rosebrook, J. Org. Chem. 34:1459 (1969).
4. Ekman, R., Personal communication.
5. Zinkel, D.F., L.C. Zank, and M.F. Wesolowski, "Diterpene Resin Acids," USDA, Forest Service, Forest Products Laboratory, Madison WI, 1971.
6. Takeda, H., W.H. Schuller, and R.V. Lawrence, J.Org. Chem. 33:1683 (1968).
7. Lehtinen, T., E. Elomaa, J. Alhojärvi, and H.H. Bruun, Suom. Kemistil. B 37:202 (1964).
8. Holmbom, B., and V. Erä. JAOCS 55:342 (1978).
9. Kudriavceva, T.S., M.L. Molochnikov, T.S. Tolstova, and V.B. Kogan, Gidroliz. Lesokhim. Prom. No. 2:9 (1975).

[Received March 13, 1978]