Polyhydric Alcohol Esters of Fatty Acids from Sardine Oil

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Synopsis

By stirring a mixture of purified sardine oil and the same amount of 0.5 N 99 per cent ethanolic solution of sodium hydroxide at 25°C for two hours, a mixture of ethylesters of the fatty acids was obtained by the interesterifical reaction.

The ethylester of the saturated fatty acid boiling at lower temperature than the unsaturated one was separated from the mixed ethylester by fractional distillation under reduced pressure of 3~5 mmHg. Polyhydric alcohol ester of unsaturated fatty acid obtained by heating the ethylester with mannitol or sorbitol in the presence of some catalyst, showed excellent drying properties like as the wood oil.

I. Introduction

For utilizing effectively the components of sardine oil, lower alcohol esters of fatty acids from the oil were prepared. The product was distilled under reduced pressure, remaining the part rich in esters of unsaturated fatty acids, which was then changed into esters of polyhydric alcohols, such as mannitol or sorbitol, using catalysts. The drying properties of polyhydric alcohol esters thus obtained were examined.

II. Experiments and their results

(1) The preparation of lower alcohol esters of fatty acids from the sardine oil and their distillation.

A mixture of 1 kg of the purified sardine oil, previously treated with sodium hydroxide and Japanese acid clay (n_D^{25} 1.4834, acid value 2.18, saponification value 185.6 and iodine value 146.3), and the same amount of 0.5 N 99 percent ethanolic sodium hydroxide was stirred in a flask at 25°C.[1][2] After 3 minutes, the mixture became brown homogeneous liquor. After 30 minutes, the refractive index of the produced ethyl esters became constant. After 2 hours' stirring, the mixture was acidified with 0.1 N hydrochloric acid and washed several times with cold and hot water respectively. Taking off excess of alcohol, glycerol and sodium chloride, it was dried on water bath under reduced pressure; the yield of the ethyl estr thus obtained was 1050 grams, the properties of which being as follows: n_D^{25} 1.3658, acid value 21.43, saponification value 165.6 and iodine value 147.3.

The esters were fractionary distilled under the pressure of 3~5 mm Hg. Boiling

(1) Toyama and Tsuchiya, J. Soc. Chem. Ind. Japan, 36, (1933) 619.
(2) M. Takano, ibid., 43, (1940) 314.

began at about 170°C and the esters having iodine value of about 70 were obtained (fatty acids from the sardine oil began to boil at about 185°C under the same condition).

Fourty nine percent of the esters were distilled out until 180°C and 80 per cent until 200°C. As the esters of the saturated fatty acids were distilled quickly, iodine value of the remaining part became larger as the distillation ratio became larger; that is, the remaining ratio smaller; the results being shown in Table 1.

Table 1. Fractional distillation of ethyl esters (315g) of fatty acids from the sardine oil under reduced pressure.

Distillate	Distilling temperature (°C)	Pressure (mm)	Yield (g)	Yield percentage (%)	Iodine value (Wijs)
1	163 ~170	4.5	77.6	24.63	75.1
2	170 ~175	4.5	39.3	12.48	100.6
3	175 ~180	4.5	37.3	11.90	121.6
4	180 ~187.5	4.5	41.0	13.00	152.1
5	187.5~197.5	4.5	39.0	12.38	224.3
6	197.5~203	3.5	32.1	10.19	285.7
Residue	—		44.0	13.97	264.0
Loss	—	—	4.5	1.43	—

As will be stated in the later part, the distillation was stopped at different stages, and the interesterification of the residual part was conducted by adding polyhydric alcohols.

For the methanolysis of the acids, the sardine oil was reacted with the same amount of 0.5 N 97.3 percent methanolic solution of sodium hydroxide, obtaining the reaction ratio of 50.3, 80.7, and 95.5 percent after 7, 30, and 80 minutes.

(2) Interesterification of the ethyl esters of the fatty acids from sardine oil with polyhydric alcohols.

As the polyhydric alcohols, mannitol (mp 166°C) and sorbitol (75 per cent sorbitol was dehydrated by heating under reduced pressure) were used, and the ethyl esters of the sardine oil fatty acids used had the following properties: acid value 15.19, saponification value 169.9 and n_D^{25} 1.4700. Although mannitol and sorbitol have six hydroxyl groups, it is difficult to esterify all the groups. Don S. Bolley[3] states that, in the case of esterification, an alcohol having six hydroxyl groups formes inner molecular ether expelling water at the reaction temperature. It is therefore proper to add 4.5 mols fatty acid to 1 mol mannitol. I. D. Bradner and his co-worker[4] conducted the esterification of fatty acids from wood oil with polyhydric alcohols, concluding the proper mol ratio of mannitol as 4.0 and of sorbitol as 4.5. The present authors conducted the experiments in the mol ratio of 4.0~4.8, the results being shown in Table 2. The two components were heated in a flask

(3) Ind. Eng. Chem., 41, (1949) 287.
(4) Ind. Eng. Chem., 37, (1945) 809.

under vigorous agitation in the current of carbon dioxide Samples were taken out time by time and their constants were measured.

Owing to small difference between the saponification values of ethyl and polyhydric alcohol esters, it was difficult to investigate exactly the grade of esterification from the change of saponification value. It was however assumed that the reaction had completed within 7~8 hours at the above mentioned method from the standpoint of reflactive index measurement.

Table 2. The interesteresterification between the fatty acid ethyl esters and the polyhydric alcohols.

Exptl No.	Ethyl ester (g)	Polyhydric alcohol (g)	Catalyst (g)	Temp. (εC)	Reaction time (hr)	Acid value	Sapon. value	n_D^{25}
1	50	M6.9 (4.0)	none	220–230	4.5 11.5	 3.06	166.9. 165.1	1.4789 1.4837
2	50	M6.9 (4.0)	do	245–250	10.5 20.5	1.71 2.24	163.7 161.2	1.4820 1.4843
3	50	M6.9 (4.0)	$CaCO_3$ 0.3	225	11.0 17.0	1.04 1.77	162.4 161.6	1.4819 1.4839
4	50	M6.9 (4.0)	$Ca(Ac)_2$0.2 $Ba(Ac)_2$0.1	225	17.0	1.58	162.3	1.4837
5	50	M6.9 (4.0)	do	250	7.5 13.0	1.95 2.44	163.6 163.4	1.4857 1.4885
6	50	S6.0 (4.6)	do	250	9.0 15.5	1.90 2.62	161.1 160.8	1.4868 1.4873
7	30	S3.6 (4.6)	NaOH 0.1	225	8.5 16.5	1.03 1.20	162.3 161.5	1.4880 1.4880
Sardine oil						2.18	185.6	1.4834
Ethyl ester						15.19	169.9	1.4700

M shows mannitol, S sorbitol and numbers in the brackets the mole ratio between polyhydric alcohols and fatty acid ethyl ester.

For comparison, the esterification of the sardine oil fatty acids with polyhydric alcohols was conducted, the results being shown in Table 3. The fatty acids were prepared by saponifying, decomposition and dehydrating the sardine oil. From the change of acid value and refractive index, the reaction was assumed to be completed in 3~5 hours. In the case of esterification of sardine oil fatty acid or its ethyl ester with polyhydric alconols, the reaction was not completed by 3~5 hours' heating without catalyst and deposited polyhydric alcohols were found on the bottom of the reaction vessel after cooling. That the refractive indexes of Table 3 were larger than those of Table 2 would due to smaller ratio between polyhydric alcohol and the fatty acid.

(3) Drying properties of the polyhydric esters.

The residual part obtained by the fractional distillation of ethyl esters of the sardine oil fatty acids was esterified with polyhydric alcohols under the condition shown in Table 4. The drying properties of the polyhydric alcohol esters thus

produced were examined, the results being shown in Table 4. The cases having more than 50 per cent residue were excepted from the table.

Table 3. Esterification of the sardine oil fatty acids with the polyhydric alcohols.

Exptl No.	Fatty acids (g)	Polyhydric alcohols (g)	Catalyst (g)	Temp. (°C)	Reaction time (hr)	Acid value	n_D^{25}
1	40	M5.5 (4.4)	$Ca(Ac)_2$ 0.2 $Ba(Ac)_2$ 0.1	240–250	2.0	14.4	1.4877
					5.5	3.95	1.4905
					9.0	2.82	1.4907
2	40	M5.5 (4.4)	NaOH 0.1	240–250	1.0	18.4	1.4837
					4.5	7.76	1.4906
					8.0	3.31	1.4907
3	30	S4.6 (4.8)	NaOH 0.1	230	3.0	8.74	1.4853
					5.0	5.34	1.4904
					8.0	3.56	1.4904
4	40	M5.5 (4.4)	$CaCO_3$ 0.2 $BaCO_3$ 0.2	250	3.0	5.23	1.4898
					5.0	3.24	1.4907
					8.0	2.89	1.4907
Sardine oil						2.18	1.4834
Fatty acids						158.0	1.4778

M Shows mannitol, S Sorbitol and numbers in the brackets the mole ratio between the polyhydric alcohols and the fatty acids.

III. Summary

From the table the following conclusions were resulted.

(i) The drying property was increased as the residual ratio was decreased.

(ii) The proper reaction temperature was 240~250°C (It was probable to lower the temperature below 230°C, when proper catalyst was used). At 260~270°C, polymerising reaction predominated, producing gummy substance. At 240~250°C, polymerisation occured to a certain extent, producing polybasic acid radical, which gave good effect on the drying property. T. F. Bardley(5) pointed out that there were two cases in improved drying oil, one had polyhydric alcohol radical as alcoholic one and the other polybasic acid radical as fatty one.

When diluted with mineral spirit, the sample had the same drying properties. The sample 3, 11, and 13, gelatinized by polymerisation, had supperior properties, when diluted with four times solvent. As drying test, samples were painted on a glass plate, and kept in a thermostat of 20°C. After a definite time, they were qualitatively tested by touching with a finger.

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(5) Ind. Eng. Chem., 41, (1949) 310.

Table 4. Drying properties of the polyhydric alcohol esters of the sardine oil fatty acids.

Exptl No.	Ethyl ester or fatty acid (g)	Residual ratio (%)	Polyhydric alcohol (g)	Temp. (°C)	Time (min)	Catalyst (g)	Property	Drying test (20°C)			mixed with mineral spirit			
								3 days	5 days	8 days	dilution ratio	12 hrs	24 hrs	5 days
1	ester 10	15.0	M 1.35	200–220	60	NaOH 0.5	gelatinous	slightly dry	dry	—	—	—	—	—
2	acid 10	18.0	M 1.5	250–260	180	none	—	almost dry	dry	—	×2	sticky	almost dry	dry
3	acid 10	18.0	M 1.5	250–265	300	PbO 0.5	polymerised to gummy solid	—	—	—	×4	dry	—	—
4	ester 10	25.0	M 1.35	250–260	180	Na_2CO_3 0.5	viscous oil	almost dry	dry	—	×2	sticky	almost dry	dry
5	ester 10	25.0	M 1.35	240–250	400	PbO 0.5	viscous oil	sticky	almost dry	dry	×2	sticky	almost dry	dry
6	ester 10	30.0	M 1.35	255–260	120	ZnO 0.3	—	slightly sticky	almost dry	dry	×2	—	dry	—
7	acid 10	30.6	S 1.5	250–260	60	PbO 0.5	—	do	do	do	do	almost dry	do	—
8	ester 10	35.0	M 1.35	200	120	ZnO 0.5	—	—	—	—	—	—	—	—
9	ester 10	35.0	M 1.35	250	150	ZnO 0.5	viscous oil	—	—	—	×2	sticky	slightly sticky	dry
10	acid 10	48.8	M 1.5	260–270	200	none	viscous oil	sticky	sticky	slightly sticky	—	—	—	—
11	acid 10	30.6	S 1.5	260–270	200	none	gelatinous	—	—	—	×4	dry	—	—
12	ester 10	51.2	S 1.35	260–270	200	none	viscous oil	sticky	sticdy	sticky	—	—	—	—
13	ester 10	30.0	M 1.35	260–270	200	none	gelatinous	—	—	—	×4	dry	—	—

M shows mannitol and S sorbitol.