Studies on Utilization of Higher Fatty Alcohol from Sperm Whale Oil

By
Shinichi Tomiyama and Masayasu Takao

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Introduction

Sperm whale oil has been used in Japan for limited purposes such as wax, textile oil agent and detergent etc. So we studied utilization of higher fatty alcohol from sperm whale oil. Alcohol fraction from sperm whale oil was condensed with aromatic hydrocarbon to get alkyl aryl hydrocarbon, from which superior lubricating oil, hydraulic oil vacuum pump oil, cutting oil, detergent and fat splitting agent were made on an industrial scale.

Process for them and their properties are described in the following paragraphs.

1. New synthetic method of alkyl aryl hydrocarbon.

a. Condensation between saturated alcohol from hydrogenated sperm whale oil and naphthalene.

Hydrogenated sperm whale oil was used as sample, which was saponified and distilled into saturated alcohol (A.V. 0.2, S.V. 2.8, Ac. V. 190.6 and I. V. 4.7). The reaction between this alcohol and refined naphthalene using active clay as catalyst, with incessant stirring, at normal pressure let to dehydration at 160°C. There was a violent dehydration at 180° to 190°C. Then alkylation at 200°C and came up to its maximum in 30–90 minutes. The results of experiments showed that this new reaction for industrial synthesis of alkylnaphthalene was superior in the following points to previous methods using sulphric acid[2], metals haloide[3] or boron trifluoride[4] as catalyst.

1. More yield and easier operation in reaction process.

2. No need of after-treatment except removal of clay.
3. Simple equipment without special material.

By the result of the experiments on various temperatures, reaction hours, and amounts of active clay and naphthalene, the best condition to get a condensed oil principally consisting of monoalkyl naphthalene which is suitable for the diffusion pump oil, cutting oil and surface active agent as described later, was: 100 parts of higher fatty alcohol (1 mol), 103 parts of naphthalene (2 mols) and 20–25 parts of active clay, 180–200°C in reaction temperature, and 30–60 minutes in reaction hours. In this case, the yield of monoalkyl naphthalene was 57–59% of theoretical value. After various experiments, was found the best condition to obtain a condensed oil principally consisting of dialkylnaphthalene and polyalkylnaphthalene, which is used for high grade lubricating oil. That is, 100 parts of higher fatty alcohol (1 mol), 30 parts of naphthalene (0.6 mol) and 30 part of active clay, 200–210°C in reaction temperature and 90–120 minutes in reaction time. On this condition, the yield of dialkylnaphthalene and polyalkylnaphthalene was 45% of alcohol and that of monoalkylnaphthalene was 35% and the small amount of olefine dimer was obtained as by product. The above mentioned monoalkylnaphthalene is considered to consist of β alkylnaphthalene, for in the ultraviolet ray absorption spectrum photograph the maximum absorption of monoalkylnaphthalene did not coincide with that of α methyl naphthalene but with that of β methyl naphthalene. Furthermore, judging from the significantly lower solidifying point and the smaller viscosity index of monooctadecylnaphthalene than those of n-β monooctadecylnaphthalene, the alkyl in question should be not of normal chain but of isoparaffine base.

b. Condensation between olefine from saturated sperm alcohol and naphthalene and benzol.

For the synthesis of alkylaryl hydrocarbon by condensation of olefine and aromatic hydrocarbon, sulphric acid[6], metal haloide[7], phosphoric acid or boron trifluoride[8] have been hitherto used. A condensation method to use active clay as catalyst has been already patented also[9]. The following experiments were carried out to find the best condition of the reaction, for of which details have never been reported yet.

The above mentioned higher fatty alcohol from sperm whale oil was normally dehydrated with active almina at 300–350°C and distilled into olefine fraction (260–310° in distilling temperature, N_D^{20} 1.4425, I.V. 103.0 Mol. wt. 226) with a yield of 87% of alcohol.

Olefine content in this distillate was calculated 92% from molecular weight and iodine value. In the process of condensing this olefine and naphthalene in the presence of active clay, alkylation commenced at 140°C and came up to its maximum at 180–190°C. Olefine, even with half amount of active clay, led reaction easier and more sufficiently than alcohol did. The best condition was: 100 parts of olefine (1 mol) 104 parts of naphthalene (2 mols) and 11.8 parts of active clay 180–190°C in reaction temperature, 60 minutes in reaction time. In this case, the yield of monoalkylnaphthalene was 66.2% of thoretical value, showing better result than experiment (a), using alcohol.

It was also found that alkylbenzol could be more easily obtained by the condensation of the above mentioned olefine and benzol than in case of experiment using naphthalene. Namely, in a rotative autoclave, olefine and benzol began to alkylate at 120°C in the presence of active clay. The reaction advanced with the ascent of temperature, amounting to 60–70% at 150–160°C, and to the maximum, over 90% at 210°C. At higher temperature, decomposition was seen with the lapse of time, the yield of alkylbenzol decreasing. The best condition for monoalkylbenzol synthesis was: 100 parts of olefine (1 mol), 321 parts of benzol (10 mol) and 10 parts of active clay, at 200–210°C, 30 minutes in reaction time, at the pressure of 10–12 kgs/cm^2. In this case, the yield of monoalkyl benzol was 81.2% of theoretical value and that of dialkylbenzol was 8.8% viz. 90% of olefine was alkylated.

2. Utilization as lubricating oil and hydraulic oil and their properties.

Tomiyama demonstrated by his patent[10] that high grade lubricating oil can be synthesized from higher alcohol and naphthalene. Among many experimental manufacturing of lubricating oil from higher fatty alcohol of sperm whale oil and naphthalene with use of active clay as catalyst, the representative result is as follows. Condensation is made on the following condition: 96 kg of alcohol, 29 kg of naphthalene and 29 kg of active clay to 205–210°C for 90 minutes in reaction time, in the 200 L condensation kettle. Average yield of crude condensed oil was 86.4 kg. The result of topping 100 kg of the above mentioned condensed oil to 300°C in the oil temperature under the vacuum of 20 mg Hg in the vacuum super steam kettle, is as shown in the following table 1.

The followlng table 2 shows the comparison of properties among lubricating oil from natural mineral oil and the other synthetic lubricating oil.

Table 1. Results of fractional distillation of crude condensed oil.

	Distillates				
	Naphthalene fraction	1st fract.	2nd fract. N.F. No. 2	3rd fract. N.F. No. 63	Residum
Boiling point C/mmHg	84-120/760	120-180/20	180-203/20	203-210/20	—
Condenced water /distilled oil	5.2	0.9	2.9	6.2	—
Yield for condensed oil in percentage	5.5	14.2	21.0	14.6	43.5
Appearance	white solid	faint yellow liquid	light yellow liquid	light brown oily	reddish yellow oily
Viscosity at 100°F U.S.S.	—	57.0	169.5	294.0	1350

Table 2. Properties of some lubricating oil.

	Japanese Navy standard	Texaco No. 120	Philip	Lubricating oil polymerized from paraffin	Lubricating oil polymerized from fatty acid	Lubricating oil condensed by our method
Acid value	under 0.1	0.08	0.06	0.02	0.02	0.03
Saponification value	under 1.5	0.10	0.12	1.41	0.38	0.28
Specific gravity D_4^{25}	under 0.9	D_4^{30} 0.8806	D_4^{30} 0.8972	D_4^{30} 0.869	D_4^{30} 0.8504	D_4^{30} 0.8785
Flash point °C	over 200	251	246	245	261	248
Solidifying point 0°C	under −5	−14	−7.6	−13	−27	−5.6
Viscosity at 210°F U.S.S.	115–125	120.0	122.0	121	123	120.0
Viscosity index	over 90	95	77	107	117	111
Conradson test carbone %	under 1.5	0.56	1.13	0.70	0.97	0.980
Stability						
Viscosity ratio	under 2.0	1.06	1.37	1.90	1.45	1.15
Conradson test (%)	under 2.5	1.64	2.22	1.71	1.59	1.49

Engine test: The result of an engine test for 2180 kg of the above mentioned lubricating oil with use of (*EI*) 1450 H.P. engine, was as follows. After eighty hour running test it was judged that this oil could be used sufficiently for the practical purpose. Thus, our lubricating oil has some properties superior to common mineral oils and polymerized lubricating oils. It is not poorer in stability than higher grade mineral oils.

The second fraction (B.P. 180–203°C under the vacuum of 20 mm) and the third one (B.P. 203–210°C in the same vacuum) were dehydrated and refined with clay into a refined oil with the following properties, which was suitable for hydraulic oil for machine tool.

Table 3. General properties of NF 20 and NF 63

	Sample NF No. 2	NF No. 63
Specific gravity D_4^{20}	0.8883	0.8805
Index of refraction n_D^{20}	1.5092	1.5030
Flash point °C	152	
Solidifying point °C	−22	−16
Viscosity at 100°F U.S.S.	169.5	294.0
Viscosity at 210°F	45.1	54.0
Viscosity index	107.8	115.0
Molecular weight (by freezing point method)	420	590
Acid value	0.03	0.04
Saponification value	0.15	0.21
Iodine value	4.69	4.69
Oxidation test: at 100°C, for 12 hrs. air blown 6 L/min/40 gr		
Viscosity at 100°F	171.8	300.5
Viscosity ratio	1.01	1.02
Acid value	0.37	0.41
Increases in acid value	0.34	0.37

The comparative test between previously used Tycol Heavy Medium and the oil NF No. 2 was made about the effect on the velocity of reciprocating table of T 81 automatic internal grinder No. 502, made by the Toyo Kogyo Co. Ltd. During it, the pressure was 10 kg/cm^2 and the temperature was kept at 40°, 60° and 80°C by electric heater. The result is shown in the Tables 4 and 5.

Table 4.

	Tycol Heavy Medium	NF. No. 2
Flash point °C	221	152
Solidifying point °C	−12	−22
Viscosity at 30°C Red sec	380	192
〃 50°C	140	96.7
〃 80°C	61	50.8
〃 m	3.85	3.50

This result showed that the oil NF No. 2 had a smaller velocity change by temperature change than Tycol Heavy Medium, which was previously of the highest grade. As shown by the result of the

Table 5.

	Tycol Heavy Medium			NF No. 2		
	40°C mm/min	60°C mm/min	80°C mm/min	40°C mm/min	60°C mm/min	80°C mm/min
1/8	1,708,188	1,746,708	1,531,915	533,333	620,690	562,500
2/8	4,376,898	4,298,508	4,298,507	2,796,117	2,868,526	2,818,500
3/8	7,024,392	6,889,950	5,760,000	5,647,059	5,559,846	5,517,241
4/8	8,674,698	8,275,860	7,600,002	8,228,572	7,912,088	8,044,693
5/8	9,473,682	9,056,604	7,756,908	9,290,323	9,330,769	9,056,104
6/8	9,863,016	9,350,652	8,056,908	10,000,000	9,664,430	9,600,000
7/8	10,069,932	9,473,682	8,000,016	10,359,703	10,000,000	9,795,918
8/8	10,140,846	9,536,424	8,111,730	10,866,668	10,434,783	9,931,034

experiments, our condensation method made out a new lubricating oil with a large yield from higher fatty alcohol from sperm whale oil. This oil showing high viscosity index and a good stability for oxydation is superior to previously used synthetic lubricating oils and is equal to natural lubricating oils.

In addition, hydraulic oil for machine tool which is better than hydraulic oil from natural mineral oils hitherto used, was obtained from lower temperature fraction.

3. Utilization as vacuum pump oil and its property.

The authors have already reported that alkylnaphthalene has a good adaptability for a diffusion pump oil. Experiments were carried on by the various kinds of distilling methods for the purpose of obtaining a diffusion pump oil from the forementioned condensed oil. The result showed that method to obtain monoalkylnaphthalene fraction by the fractional distillation under the vacuum of 1.0–0.01 mm Hg with use of a rectifier, was the best one. After a distillation, the yield of the diffusion pump oil for the vacuum of 4×10^{-6} mm Hg was 54.2% of alcohol. After triplicate distillation, the yield of the diffusion pump oil for the vacuum of 6×10^{-7} mm Hg was 35.3%.

On the basis of these experiments, refined condensed oil was obtained in the average yield of 55 kg, from 50 kg saturated sperm whale alcohol and 51.5 kg of naphthalene. These materials condensed with 12.5 kg of active clay at 180–190°C, for 60 minutes in a 200 L iron-made condensation kettle. By steam distillation of this condensed oil, excess naphthalene was distilled out. The average yield of the dehydrated and refined condensed oil was 55 kg for these materials.

25 kg of this refined condensed oil was rectified again in a 50 L iron-made rectifier, 20 cm in diameter and 100 cm in height, which was pached with rectifying tower full of porcelain berl saddle in it. The condition was as follows: vacuum was 0.2–0.4 mm Hg, reflex ratio was 2 and distillating velocity was 1.5–20 L/hr. After rectification, the yield of the diffusion pump oil for $2\text{–}4 \times 10^{-6}$ mm Hg was 51–53% of the alcohol. After double rectification, superior diffusion pump oil was obtained with the yield of 38–40% of the alcohol. Properties of this oil was as follows.

Specific gravity D_4^{30}		0.9038
Index of refranction n_D^{30}		1.5224
Viscosity	80°F U.S.S.	224
	100° 〃	130
	130° 〃	74
Solidifying point		−45°C
Molecular weight		345
Maximum vacuum		6×10^{-7} mmHg

The results show there is a possibility that the excellent diffusion pump oil is produced on the industrial scale from the saturated alcohol of sperm whale oil.

4. Utilization as cutting oil and its property.

By distilling out naphthalene, 113 parts of refined condensed oil was obtained from the above mentioned condenced oil which had been made of 100 parts of saturated alcohol from sperm whale oil. For this oil, friction coefficient between steel and steel with a load of 10 kg/mm² at room temperature were measured with the pendulum oiliness tester. The result is shown in the following table:

	Crude condensed oil	Soya bean oil	Spindle oil
Specific gravity D_4^{30}	0.8978	0.9197	0.8940
Index of refraction n_D^{30}	1.5138	1.4733	—
Viscosity 50°C centistokes	26.3	24.6	8.19
Acid value	0.04	0.9	0.08
Friction coeffieient	0.078	0.100	0.305

Thus the refined condensed oil, of which the principal ingredient is monoalkylnaphthalene, has an excellent oiliness. The following tables show the results of adaptability test of this condensed oil which is blended in turbine oil as oiliness accelerator, and the results of comparative test of utility among turbine oil, soya bean oil and this condensed oil.

No. of cutting oil	No. 3	No. 4	No. 8
Constituent of samples			
Turbine oil	100	80	80
Soya bean oil	—	20	—
Condensed oil	—	—	20
Viscosity 30°C Redwood sec.	425	294	333
50°C 〃	146	114	122
Acid valte	0.2	0.7	0.1
Saponification value	—	39.2	—
Friction Coefficient (μ)	0.167	0.131	0.136

Conditions in cutting

Machine used	Hobbing machine
Cutting material	Hard steel (0.55 C)
Hardness of cutting material	39-41° (shore's)
Cutting speed	17 m/min.
Cutting depth	Rough cutting 10.75 mm finish 0.4 mm
Cutting feed.	0.56 mm/rev.
Hobb	All ground hobb
Oiling capacity	6 *l*/min.

The result is shown in the following figure. The amount of friction, when No. 8 oil was used, of hobb at two gear cutting, was 1/4 of that when No. 3 oil was used and was 1/3 of that when No. 4 oil was used. In case of No. 3 oil, hobb had to be repolished after only two gear cutting. In case of No. 8, it was not so, even after 4 gear cutting. It was thus found that our condensed oil shows a very good oiliness exactly suitable for gear cutting oil.

5. Utilization as detergents and fat splitting agent and their properties.

Monoalkyl benzol was made of the above mentioned olefine which was obtained from sperm whale oil. To 1 mol of this monoalkyl benzol, 3 mols of 20% fuming sulphric acid was dropped at 30°C. This sulfonic acid was dissolved into alcohol and neutralized with caustic soda, then produced sodium sulfate was removed by filteration. To this alcoholic solution, petroleum ether was added so as to extract out the oil which remained not reacted. By further distillation of alcohol, alkyl benzol sodium sulfonate was obtained. Its yield and surface activity in 0.5% water solution are compared as follows, with those of sulphric ester soda salt which is normally made from saturated alcohol from sperm whale oil.

Yield for higher fatty alcohol		Monoalkylbenzol sulphonic acid soda salt	Alcoholic sulfuric acid ester-soda salt
From sperm whale oil in percentage		128	105
Sulphonation ratio in percentage		95	75
Forming (at 40°C)	1 min.	1655	1275
Loss & Milrs methods	10 min.	1620	1205
Surface tension dyn/cm^2		31.05	35.81
Interfacial tension 〃		4.21	7.05

The above results show that monoalkyl benzol-sodium sulfonate obtained by the method of condensing olefine and benzene, have the better foaming and better interfacial tension than those of sulfuric acid soda salt of alcohol. In addition, to 100 parts of the above mentioned refined condensed oil, 100 parts of 20% fuming sulpfric acid was dropped at 30°C and then a little water was added. After standing to remove the waste acid, fat splitting agent of which 80% was alkylnaphthalene sulphonic acid was obtained with a yield of 156% for alcohol, raw material.

The comparative splitting test against palm oil was made between this splitting agent and the previous one mainly consisting of dibutylnaphthalene sulphonic acid. A mixture of 100 parts of palm oil, 50 parts of water and 1.5 parts of fat splitting agent was splitted with stirring for 4 hours at 95°C. Neutralization value of fatty acid produced by our fat splitting agent was 186.0 and that of fatty acid by the previous one was 156.9. For the industrial products by this method the fat splitting test with use of the above mentioned palm oil showed that they had so good a splitting power as 96–98%.

As the result of the above experiments showed, from saturated alcohol from sperm whale we could produce with a large yield a powerful agent, which mainly consists of alkylnaphthalene sulphonic acid and has better splitting power than the previously used dibutylnaphtalene sulphonic acid.

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