# ENCLOSURE (B) 12

# STUDIES ON THE SYNTHESIS OF AERO-ENGINE OIL FROM FATTY OILS

by

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# LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

Subjecting a sodium soap of cocoanut oil to dry distillation at 500°C, olefins were obtained which were distilled with 1% of metallic sodium or 10% of solid caustic soda at temperatures below 300°C. This oil was polymerized in the presence of 10% of aluminium chloride at 80°C for 8 hours, dechlorinated, and topped to get rid of light oil. The yield of aero-engine oil #120, thus obtained from cocoanut oil, was 20.5%.

Fatty oils suitable as raw materials for this method were sought and it was found that fatty oils other than cocoanut oil and palm oil must not be used without being hydrogenated. Using the above-mentioned aero-engine oil mixed with 30% of the natural mineral oil, a full size engine test was successful.

## I. INTRODUCTION

### A. History of Project

It was already known that hydrocarbons mainly composed of olefins can be produced by the dry distillation of alkali soaps of fatty acids. In Japan, the dry distillation of soaps was considered as a method for obtaining hydrocarbon fuels from fatty oils. At the beginning of this research in June 1943, it was reported from the Nakabe Laboratory in TOKYO that lubricating oils could be obtained from hydrocarbons produced by the dry distillation of sodium soaps of cocoanut oil followed by polymerization in presence of anhydrous aluminium chloride. Although this report was short and incomplete, it presented new ideas for the synthesis of lubricating oils from fatty oils.

If a yield of aero-engine oil could be obtained greater than 15% of cocoanut oil and the amount of aluminium chloride could be held to less than 10% of olefins polymerized, this method could be developed to commercial scale. In dry distillation the Knowles type coke oven was used in order to save steel materials. At that time, since cocoanut oil could be obtained, tests were mainly centered on that soap. It was found that by this method aero-engine oil can be obtained from cocoanut oil, and this work was centered on finding the best method of removing the poisonous oxygen compounds in the cracked distillate of sodium soap of fatty oil.

This method was not brought to the commercial scale because the plant which was being constructed at the Sixth Naval Fuel Depot in FORMOSA was bombed.

### B. Key Research Personnel Working on Project

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## II. DETAILED DESCRIPTION

### A. Test Procedures

Cocoanut oil was hydrolyzed by the ordinary autoclave method to

glycerine and fatty acids. The fatty acids were neutralized by sodium carbonate and completely by sodium hydroxide. Sodium soap in flake was dried to less than 10% of water content and packed in paper bags each containing 20 kg.

In the following experiments, mainly the above-mentioned soap was used. At first a glass distilling flask was used in order to observe the changes during the dry distillation. Next, a copper flask was used to facilitate operation, and then a 100 liter steel batch-still heated by gas burners was used for obtaining material balance. At last, in order to save steel parts, the Knowles type coke oven, which was composed of fire-bricks and had a $1 \cdot 2 m^2$ bed area, was tested. This apparatus is shown briefly in Figure 1(B)12, and the procedure was as follows.

200 kg of soap were charged through a sluice valve (S), and then heated slowly by gas burners. Some water was distilled at 100°C and most of the oil vapour came off at 350-400°C. At 500°C the distillation ceased. The dry-distilled oil was redistilled in an atmospheric batch still, and the distillate boiling from first drop to 300°C was subjected to polymerization.

It was agitated with 10% of aluminium chloride for 8 hours at 80°C and at the end of that time, the product was allowed to settle, the sludge was separated and the supernatant solution of the polymerized oil was mixed with the recovered oil obtained by hydrolysis of the aluminium chloride sludge. Then, active clay and calcium hydroxide were added to the mixture of polymerized oil for dechlorination and after heating at 250°C for 1 hour, the oil was filtered. This material was vacuum topped to produce a residue of the desired viscosity. Olefins prepared by the redistillation of dry distilled oil contained some oxygen compounds which poisoned the catalytic action of aluminium chloride, so that they required a large quantity of aluminium chloride for polymerization. Studying the preliminary refining method for the dry distilled oil, it was found best for the polymerization to redistill the oil with 1% of solid NaOH to dry the distilled oil.

Stearic acid, oleic acid and other mixed fatty acids derived from palm oil, soya bean oil and their hydrogenated oils were converted to sodium soaps and then tested in glass flasks in the same manner. Each of the above-mentioned dry distilled oils was redistilled in the presence (1%) of metallic sodium up to 300°C and then fractionated to five fractions in the presence of metallic sodium. Each fraction was polymerized with 10% of $AlCl_3$ at 80°C for 8 hours. After settling for one night, the product was separated into the supernatant polymerized oil and the aluminium chloride sludge. Each of these was treated separately, and, after dechlorination, was reduced to the desired viscosity in the same manner. The decomposed oil derived from the aluminium chloride sludge, had excellent properties and the yields were better than expected. These products had a good viscosity index and a somewhat low pour point, so that these products could be used for various purposes.

6. Experimental Results:

1. A schematic flow diagram of the processes studied, showing yields and material balance, is presented in Figure 2(B)12.

2. The physical and chemical properties of the fatty acid and distilled oils from coconut oil are shown in Table I(B)12.

3. The properties of the raw material and distilled oils are tabu-

lated in Table II(B) 12.

4. Typical compositions of the dry distilled gases and residual cokes are as follows:

Composition of Dry Distilled Gas

| Gas | Volume (%) |
|---|---|
| $CO_2$ | 11.6 |
| CO | 10.3 |
| $H_2$ | 24.2 |
| $N_2$ | 2.7 |
| $O_2$ | 0.1 |
| $C_nH_{2n}$ | 22.2 |
| $C_nH_{2n+2}$ | 28.6 |

Analysis of Residual Coke

| | |
|---|---|
| Water Insoluble Carbon Matter | 5% |
| Sodium Carbonate | 89% |
| Undecomposed soap | #6% |

5. A summary of the data showing the characteristics of polymerized oils prepared by different methods is presented in Table III (B) 12

6. The effect of the type of sodium soap used in the dry distillation on the properties of the polymerized oil is shown in Table IV (B) 12

7. A summary of the effect of the boiling range of the fraction of dry distilled oil used on the properties of the polymerized oil is shown in Table V(B) 12

## III. CONCLUSIONS

1. It was possible to operate the small Knowles type coke oven for dry distillation of soaps as a batch process but problems due to the leakage of distilled vapour through the joints of firebricks and the durability of the fire-bricks used at the bottom of the coke oven, were not solved.

2. With the Lub. oil thus produced from cocoanut oil mixed with 30% of mid Continent mineral oil, a full size engine test by the "Kasei-1' type aero-engine was carried out successfully. The results were comparable to those obtained with the aero-engine oil #120 in actual use.

3. It was better to use the dry distilled oil after redistillation up to 300°C, than to use the oil which had not been redistilled, the product of the former showed a large yield and low pour point.

4. When the quantity of $AlCl_3$ was 15% to the distillate, the yield of aero-engine oil was 15% for cocoanut oil. With 10% of $AlCl_3$, the yield of product was 10%. Thus the yield of aero-engine oil was proportional to the quantity of $AlCl_3$ used.

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5. In case the dry distilled oil was redistilled with 1% of metallic sodium, a 7.5% concentration of $AlCl_3$ was sufficient to obtain a yield of 15% of the coconut oil. However, the use of metallic sodium was difficult in practice because of limited production of metallic sodium in Japan.

6. Sodium caustic soda was tried in place of metallic sodium. The use of sodium hydroxide was successful and the quantity used was reduced from 10% to 1% with but little decrease in yield of aero-engine oil. The temperature for treating with alkali could not be lowered below 250°C. A good contact of the olefins and caustic soda was desirable.

7. In place of solid caustic soda, a 40% water solution of NaOH could be used for the preliminary refining of olefines, but to obtain the same results 6% of NaOH had to be used. The presence of water had a harmful effect on the alkali refining.

8. Sodium carbonate, calcium oxide and calcium hydroxide were not as satisfactory refining agents as sodium hydroxide.

9. In the dry-distillation of soaps, the presence of excess caustic soda gave good results, but it caused the corrosion of firebricks and the products required redistillation. Therefore this method was not practised.

10. In order to improve the oxidation stability of the synthetic product, the condensation of the dry distilled oil with aromatics was tested. Solvent naphtha obtained in coal carbonization gave the best result. The synthetic lubricating oil condensed with naphthalene did not show improved oxidation stability over the synthetic oils obtained from olefins derived from wax decomposition.

11. As the starting material, stearic acid was better than oleic acid, in regard to viscosity index and yield of products. The preliminary hydrogenation of fatty oils seemed promising for the process.

12. In the dechlorination process, the best products are obtained when an inert gas atmosphere is used.

Table I(B)12
PHYSICAL AND CHEMICAL PROPERTIES OF
RAW MATERIAL AND INTERMEDIATES

| | Dry Distilled Oil | Alkali Redistilled Oil (I.B.P. - 300°C) |
|---|---|---|
| Specific Gravity d(25/4) | 0.7787 | 0.7748 |
| Refractive Index n(25/D) | 1.4330 | 1.4260 |
| Specific Refraction r(25/d) | 0.3337 | 0.3306 |
| Acid Value | 1.20 | 0.28 |
| Saponification Value | 2.76 | 0.05 |
| Iodine Value | 115.9 | 131.4 |
| Mean Molecular Weight | 198 | 187 |
| Elemental Analysis C(%) | 82.20 | 83.75 |
| H(%) | 13.63 | 14.01 |
| (by difference)O(%) | 4.18 | 2.24 |
| Mean Molecular Formula | $C_{13.5}H_{26.6}O_{0.5}$ | $C_{13.0}H_{26.0}O_{0.3}$ |
| Distillation Test I.B.P. (°C) | 60 | 68 |
| 5% | 97 | 102 |
| 10% | 114 | 113 |
| 5% | 127 | 117 |
| 20% | 138 | 134 |
| 5% | 150 | 142 |
| 30% | 160 | 156 |
| 5% | 170 | 165 |
| 40% | 176 | 174 |
| 5% | 188 | 180 |
| 50% | 193 | 185 |
| 5% | 204 | 191 |
| 60% | 213 | 197 |
| 5% | 229 | 205 |
| 70% | 245 | 211 |
| 5% | 263 | 221 |
| 80% | 282 | 235 |
| 5% | 306 | 251 |
| 90% | | 270 |
| 5% | | 286 |

Fatty Acids From Cocoanut Oil

Specific Gravity ..... 0.8925
Iodine Value ..... 8.5
Acid Value ..... 249.3
Melting Point ..... 25

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Table II(B)12
PROPERTIES OF POLYMERIZED PRODUCTS

| | Specific Gravity ($d_4^{25}$) | Viscosity (S.U.S.) | | Viscosity Index | Oxidation Test Viscosity Ratio | Pour Point (°C) |
|---|---|---|---|---|---|---|
| | | 100°F | 210°F | | | |
| Dechlorinated Oil | 0.8507 | 374 | 63 | 125 | | |
| Distillate (240-285°C/2.5mm) | 0.8362 | 69.4 (R-1,30°C) | 49.6 (R-1,50°C) | | | |
| Residual Oil (285°C-/2.5mm) | 0.8573 | 1250 | 166 | 114 | 1.8 | -20 |

(See page 157 for Table III(B)12.)

Table IV(B)12
EFFECT OF TYPE OF SODIUM SOAPS DRY DISTILLED ON SYNTHETIC OIL

| No. | Stock | Yield for Stock (wt %) | Cutting Temp. (°C) | Viscosity S.U.S. 210°F | Viscosity Index |
|---|---|---|---|---|---|
| 1 | Cocoanut oil | 20.5 | 500- | 115.8 | 113.6 |
| 2 | Palm oil | 15.0 | 450- | 122.1 | 113.4 |
| 3 | Hydrogenated palm oil | 18.5 | 460- | 132.8 | 114.1 |
| 4 | Fatty acid produced from fish oil | 8.3 | 400- | 111.4 | 75.5 |
| 5 | Fatty acid produced from Tubaki Oil | 14.0 | 460- | 100.4 | 81.6 |
| 6 | Soya bean oil | 6.6 | 150- | 61.6 | 54.8 |
| 7 | Hydrogenated Soya bean oil | 18.4 | 450- | 146.3 | 118.3 |
| 8 | Rape oil | 15.8 | 450- | 133.7 | 77.7 |
| 9 | Castor oil | difficult to dry distill owing to foaming | | | |
| 10 | Distilled Fatty acid produced from Whale oil | 27.2 | 460- | 123.6 | 90.7 |
| 11 | Stearic acid | 24.5 | 450- | 133.6 | 112.6 |
| 12 | Oleic acid | 17.5 | 430- | 117.5 | 79.3 |

Table III(B)12

EFFECT OF PRELIMINARY REFINING DRY DISTILLED OIL ON PROPERTIES OF POLYMERIZED OIL

| No. | Preliminary Refining Method and Special Points | Name | Refining Agent (% Used) | $AlCl_3$ (%) | Properties of Synthetic Oils Vacuum Distilled | | |
|---|---|---|---|---|---|---|---|
| | | | | | Yield for Cocomut Oil (%) | Viscosity (S.U.S.) 210°F | Viscosity Index |
| 1 | Not treated | | | 15 | 11.8 | 149.8 | 103.6 |
| 2 | Redistilled up to 300°C | | | 15 | 15.6 | 117.6 | 101.3 |
| 3 | Redistilled up to 300°C and $AlCl_3$ decreased | | | 10 | 8.9 | 132.4 | 106.3 |
| 4 | Redistilled with metallic sodium, $AlCl_3$ decreased | Na | 1 | 7.5 | 17.7 | 110.1 | 114.9 |
| 5 | Redistilled with solid caustic soda | NaOH | 10 | 10 | 20.5 | 115.8 | 113.6 |
| 6 | Redistilled with solid caustic soda and then condensed with solvent naphtha* | NaOH | 10 | 10 | 22.4 | 118.2 | 108.8 |
| 7 | Redistilled with solid caustic soda and then condensed with naphthalene | NaOH | 10 | 10 | 12.6 | 115.7 | 100.3 |
| 8 | Redistilled with solid caustic soda and then condensed with benzene | NaOH | 10 | 10 | 17.9 | 97.5 | 102.4 |
| 9 | Redistilled with caustic soda decreased NaOH | NaOH | 1 | 10 | 16.4 | 115.3 | 107.0 |
| 10 | Redistilled with 40% water solution of NaOH each 2% and repeated 3 times | NaOH water solution | 6 | 10 | 18.1 | 130.0 | 115.7 |
| 11 | Alkali steaming redistilled | NaOH water solution | 2.5 | 10 | 10.6 | 134.2 | 108.2 |
| 12 | Redistilled with solid sodium carbonate | $Na_2CO_3$ | 10 | 10 | 10.6 | 112.2 | 107.4 |
| 13 | Redistilled with calcium oxide | CaO | 10 | 10 | 9.3 | 130.8 | 114.7 |
| 14 | Redistilled with calcium hydroxide | $Ca(OH)_2$ | 10 | 10 | 5.4 | 118.3 | 102.4 |
| 15 | Dry distilled in presence of excess caustic soda | NaOH | 20 | 10 | 16.4 | 142.6 | 108.3 |
| 16 | Dry distilled in presence of excess caustic soda and NaOH quantity decreased | NaOH | 15 | 10 | 15.4 | 104.7 | 107.7 |
| 17 | Dry distilled in presence of excess sodium carbonate | $Na_2CO_3$ | 20 | 10 | 4.6 | 166.4 | 112.2 |

* Properties of Solvent naphtha

Specific gravity ($d_4^{15}$) ..... 0.866
Vapour Pressure (Reid, kg/cm²) ..... below 0.02
Octane Number (0.1%$(C_2H_5)_4Pb$ ..... 102

Composition (Vol.%)

Aromatic ..... 99.5
Unsaturate ..... 0.4
Sulphur ..... 0.015

Distillation Test of Solvent Naphtha (°C)

I.B.P. ..... 132
10% ..... 139
20% ..... 140
30% ..... 142
40% ..... 143
50% ..... 145
60% ..... 147
70% ..... 149
80% ..... 152
90% ..... 158
97% ..... 166
Dry Point ..... 171

Table V(B)12

EFFECT OF BOILING RANGE OF DRY DISTILLED OIL FROM SODIUM SOAP OF COCONUT OIL ON SYNTHETIC OIL

| | | Number | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| | Temperature (°C) | I.B.P. (56)-160 | 160-200 | 200-230 | 230-260 | 260-300 | 300 |
| Distilled Fraction | Yield, wt(%)* | 10.8 | 8.8 | 7.7 | 2.6 | 3.4 | 12.5 |
| | Density At room temp. | 0.718 | 0.751 | 0.763 | 0.784 | 0.80 | |
| | Iodine Value | 163.1 | 140.0 | 134.0 | 119.8 | 107.2 | |
| | Pour Point (°C) | 70 | -50 | -35 | -25 | -15 | |
| Supernatant Polymerised Oil | Yield, wt(%)** | 66.5 | 67.0 | 60.0 | 60.0 | 61.3 | |
| | Yield, wt(%)* | 6.7 | 5.9 | 4.6 | 1.5 | 2.0 | |
| Dechlorinated Oil (220°C-) | Yield, wt(%)# | 57.8 | 71.2 | 87.5 | 89.5 | 91.0 | |
| | Yield, wt(%)* | 3.9 | 4.7 | 4.0 | 1.3 | 1.8 | |
| | Viscosity S.U.S. at 100°F | 233.3 | 187.0 | 148 | 159.5 | 128.0 | |
| | 210°F | 52.3 | 55.2 | 47.0 | 47.6 | 44.5 | |
| | Viscosity Index | 128.0 | 159.7 | 150.1 | 145.0 | 149.9 | |
| | Pour Point (°C) | -51 | -41 | -31 | -20 | -12 | |
| Distillate (220-330°C) | Yield, wt(%)## | 61.0 | 48.6 | 51.3 | 50.0 | 62.1 | |
| | Yield, wt(%)* | 2.4 | 2.0 | 2.1 | 0.7 | 1.2 | |
| | Viscosity Index 100°F | 142.3 | | | | | |
| | 210°F | 92.5 | 53.2 | 44.1 | 46.4 | 55.9 | |
| | | 40.6 | 35.3 | | | | |
| Residual Oils (330°C-) | Yield, wt(%)## | 37.0 | 50.0 | 48.3 | 49.4 | 37.3 | |
| | Yield, wt(%)* | 1.4 | 2.1 | 1.9 | 0.6 | 0.7 | |
| | Yield, wt(%)** | 14.1 | 23.8 | 25.4 | 26.4 | 20.8 | |
| | Viscosity Index | 110.9 | 118.7 | 120.4 | 118.5 | 111.2 | |
| | 100°F | 1919.6 | 1391.4 | 1210.4 | 1549.2 | 1697.1 | |
| | 210°F | 149.2 | 132.8 | 125.2 | 142.9 | 138.0 | |
| | Pour Point (°C) | -25 | -34 | -30 | -20 | -14 | |
| Decomposed Oil From Sludge | Yield, wt(%)** | 27.5 | 31.0 | 34.0 | 35.0 | 33.7 | |
| | Yield, wt(%)* | 2.8 | 2.7 | 2.6 | 2.7 | 1.1 | |
| Dechlorinated Oil (260°C-) | Yield, wt(%)@ | 72.7 | 53.2 | 88.2 | 87.5 | 96.3 | |
| | Yield, wt(%)* | 2.0 | 1.4 | 2.3 | 2.4 | 1.1 | |
| | Viscosity Index | 104.4 | 116.0 | 136.1 | 126.3 | 127.2 | |
| | 100°F | 757.5 | 583.3 | 303.4 | 359.7 | 335.8 | |
| | 210°F | 80.2 | 74.9 | 60.6 | 63.1 | 60.6 | |
| Residual Oil (470°C-) | Yield, wt(%)## | 75.7 | 76.8 | 72.7 | 70.0 | 66.7 | |
| | Yield, wt(%)* | 1.5 | 1.1 | 1.7 | 1.7 | 0.7 | |
| | Yield, wt(%)** | 15.1 | 12.7 | 21.8 | 21.5 | 21.7 | |
| | Specific Gravity 60/60 | 0.8740 | 0.8704 | 0.8632 | 0.8770 | 0.8763 | |
| | Viscosity Index | 97.7 | 104.4 | 118.6 | 110.7 | 109.5 | |
| | 100°F | 2435.2 | 1938.5 | 1345.8 | 1724.8 | 1716.0 | |
| | 210°F | 150.9 | 139.6 | 129.4 | 138.6 | 136.3 | |
| | Carbon Residue (%) | 0.66 | 0.75 | 0.53 | 1.09 | 1.39 | |

* For cement oil
** For distilled fraction
\# For polymerised oil
\#\# For dechlorinated oil
@For decomposed oil

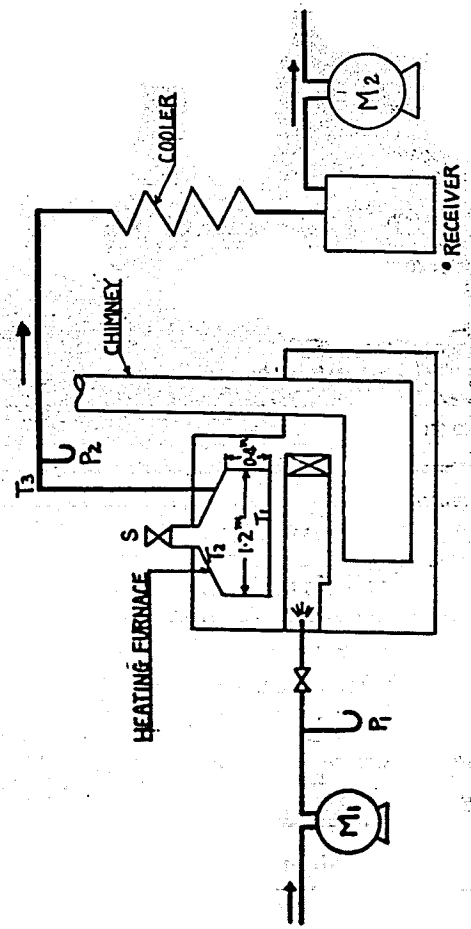
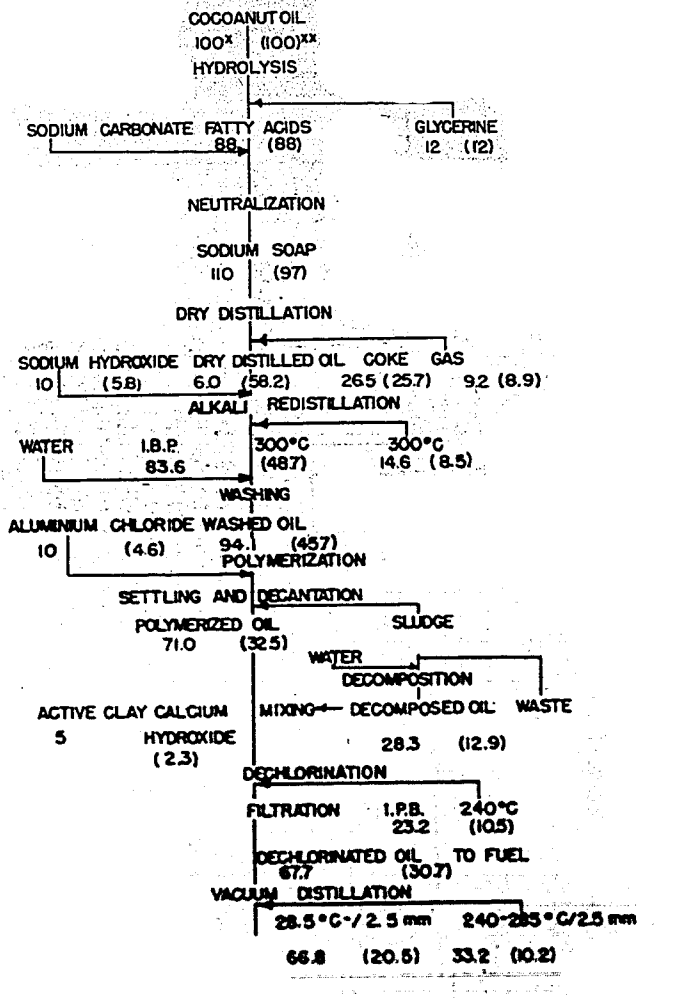



Figure 1(B)12

DIAGRAM OF SOAP DRY DISTILLATION APPARATUS

ENCLOSURE (B) 12




X LEFT NOTED FIGURES INDICATE YIELD WT.% FOR TREATED MATERIAL.

XX RIGHT NOTED( )FIGURES INDICATE YIELD WT.% FOR COCOANUT OIL.

*Figure 2(B)12*

*SCHEMATIC FLOW DIAGRAM OF YIELDS AND MATERIAL BALANCE*