

ENCLOSURE (B) 2

STUDIES ON THE SYNTHESIS
OF HIGH CETANE FUEL BY HIGH PRESSURE
HYDROGENATION OF FATTY OIL

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SUMMARY

It was the object of this project to compare catalyst behavior and activity in the hydrogenation of fatty oils using methyl laurate as a sample. Nickel oxide, copper chrome oxide and molybdenum sulphide were taken as catalysts and it was recognized that methyl laurate changes directly into hydrocarbon of C₁₁ under nickel catalyst and into the hydrocarbon of C₁₂ passing the corresponding alcohol as an intermediate under copper chrome catalyst and into hydrocarbon of C₁₂ under molybdenum catalyst.

I. DETAILED DESCRIPTIONA. Nickel Oxide-Clay Catalyst

Eighty grams of methyl laurate and eight grams of catalyst were taken in a autoclave which had 240 cc of inner volume, and after charging the hydrogen pressure up to 100 atmospheres, it was heated to each reaction temperature for one hour. Reaction products had properties according to the reaction temperature as shown in Table I(B)2.

The reaction product at 350°C was fractionated under reduced pressure of 15mm Hg as follows:

| <u>Distilling Temp. °C</u> | <u>Yield %</u> |
|----------------------------|----------------|
| 72.5 - 80 | 6.05 |
| 80 - 82 | 18.77 |
| 82 - 83 | 14.15 |
| 83 - 84 | 19.88 |
| 84 - 86 | 14.41 |
| 86 - 88 | 6.19 |
| 88 - 89 | 13.82 |
| residue | 2.01 |

The 83 - 84°C fraction has following physical properties and it may be considered to be n-undecane, C₁₁H₂₄

$$d_4^{20} = 0.7401$$

$$n_D^{20} = 1.4188$$

B. Copper-chrome Oxide Catalyst

The same experiments were undertaken using copper chrome oxide as catalyst and the following results (Table II(B)2) were obtained:

The reaction product at 400°C was fractionated under reduced pressure of 15mm Hg as follows:

| <u>Distilling Temp. °C</u> | <u>Yield %</u> |
|----------------------------|----------------|
| 15 - 50 | 3.76 |
| 50 - 80 | 5.59 |
| 80 - 90 | 6.93 |
| 90 - 92 | 4.33 |
| 92 - 94 | 5.99 |
| 94 - 95 | 5.46 |
| 95 - 96 | 17.72 |
| 96 - 96.5 | 21.49 |
| 96.5 - 97 | 4.00 |
| 97 - 100 | 2.76 |

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The fraction boiling between 96-96.5°C contained some unsaturates but after washing with sulfuric acid its physical properties agreed well with those of dodecane, C₁₂H₂₆.

C. Molybdenum Sulphide Catalyst

The same experiments were undertaken using molybdenum sulphide as catalyst and the following results Table III(B)3 were obtained:

The reaction product at 350°C was fractionated under reduced pressure of 15mm Hg as follows:

| <u>Distilling Temp. °C</u> | <u>Yield %</u> |
|----------------------------|----------------|
| 89.5 - 95.0 | 1.67 |
| 95 - 96 | 35.87 |
| 96 | 54.92 |
| 96 - 98 | 3.24 |

The fraction boiling at 96°C has the following physical properties and may be considered as n-dodecane, C₁₂H₂₆

$$d_{4}^{20} = 0.7493$$

$$n_D^{20} = 1.4220$$

II. CONCLUSIONS

In order to get pure n-hydrocarbons by the hydrogenation of the corresponding fatty oils it is desirable to use a molybdenum sulphide catalyst.

Table I(B)2.
REACTION PRODUCT PROPERTIES
CLAY CATALYST

| Reaction Temperature (°C) | 300 | 350 | 400 |
|---------------------------------------|--------|--------|--------|
| Final Hydrogen Pressure (atm) | 78.3 | 44.5 | 49.6 |
| Density of Product (20/4) | 0.8224 | 0.7415 | 0.7416 |
| Index of Refraction of Product (20/D) | 1.4359 | 1.4184 | 1.4187 |
| Saponification Value | 122.3 | 8.2 | 0.0 |
| Iodine Value | 5.0 | | |

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Table II(B)2
REACTION PRODUCT PROPERTIES - COPPER CATALYST

| Reaction Temperature (°C) | 250 | 300 | 350 | 400 |
|---------------------------------------|--------|--------|--------|--------|
| Final Hydrogen Pressure (atm) | 78.6 | 79.0 | 81.5 | 73.1 |
| Density of Product (20/4) | 0.8299 | 0.8229 | 0.7889 | 0.7496 |
| Index of Refraction of Product (20/D) | 1.4337 | | 1.4325 | 1.4241 |
| Acid Value of Product | 0 | 0.1 | 0.3 | 0.3 |
| Saponification Value of Product | 52.9 | 12.9 | 4.0 | 1.7 |
| Hydroxyl Value of Product | 232.2 | 274.9 | 115.3 | 12.9 |
| Iodine Value of Product | 1.9 | 0.3 | 0.3 | 6.9 |

Table III(B)2
REACTION PRODUCT PROPERTIES - MOLYBDENUM CATALYST

| Reaction Temperature (°C) | 300 | 350 | 400 |
|-------------------------------|--------|--------|--------|
| Final Hydrogen Pressure (atm) | 79.7 | 61.7 | 61.1 |
| Density of Products (20/4) | 0.8369 | 0.7479 | 0.7452 |
| Index of Refraction (20/D) | 1.4409 | 1.4219 | 1.4214 |
| Acid Value | 46.6 | 0.3 | 0.1 |
| Saponification Value | 247.4 | 3.7 | 3.6 |
| Hydroxyl Value | 28.8 | 3.1 | 0.9 |
| Iodine Value | 26.3 | 0.7 | 0.8 |