

ENCLOSURE (B) 14

STUDIES ON THE SYNTHESIS OF
AERO-ENGINE OIL BY CATALYTIC
CRACKING AND POLYMERIZATION
FROM FATTY OILS

by

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SUMMARY

Owing to the difficulties of importing crude oil to manufacture aero-engine oil, cracking of fatty acids to olefines with alkali-carbonate catalyst has been experimented with in some of the chemical laboratories in Japan. We have studied the cracking of fatty acids of cocconut oil with soda-carbonate, to seek the suitable conditions of temperature and space-velocity in the cracking of fatty acids to get good lubricating oil with high yield. We also wanted to know what is the best carrier of catalyst and, in conformity with the reports from other laboratories such as that of the Mitsui Chemical Company, cokes and pumice-stones were used.

This experiment has not yet been completed, but to obtain a cracked oil of good quality with high yield, it seems best to crack fatty acids at the temperature between 500°C and 525°C and space-velocity of 0.18.

I. INTRODUCTIONA. History of Project

Because of the difficulty of importing crude oil to produce aero-engine oil, its production was intended from fatty oil by cracking fatty acids to olefines and polymerizing the olefines.

Research was carried on from May, 1945.

B. Key Research Personnel Working on Project

Chem. Eng. Sub. Lt. T. SAKURA.

II. DETAILED DESCRIPTIONA. Description of Test Apparatus

Through the stopcock of a separating funnel fatty acids were dropped into a quartz tube filled with catalyst. heated in an electric furnace, the temperature being measured by a thermocouple in the catalyst zone. Cracked oil was caught at the first trap jointed to the tube, the remaining oil vapor was cooled through a spiral condenser and caught at the second trap, and the gas was discarded. Diameter of the quartz tube was 2.3cm and the length 1 meter. A simplified flow diagram is shown in Figure 1(B)14.

B. Test Procedures Details of Test Procedures and Conditions

Fatty acids were melted by the heat of the electric furnace and dropped in the tube naturally through the stopcock. Upper part of the quartz tube is filled with carrier only and through this zone fatty acids were preliminarily heated. The object of preliminary heating is only to keep the temperature of catalyst zone suitable and this doesn't effect the quality and quantity of the cracked oil. To keep the condition of catalyst constant the length of catalyst zone was fixed at 50 cm. The surface of the carrier of catalyst becomes covered with carbonized oil as the reaction proceeds and fatty acids cannot flow through and so the average dia. of every piece of carrier was fixed at 1 cm. The method of covering pumice-stone and coke with soda-carbonate is as follows:

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At first pieces of carrier are put in a saturated solution of soda-carbonate at 80°C, kept at that temperature for about two hours to make the carrier absorb the solution adequately, and then cooled. After 24 hours the carrier which is covered with crystals of salt is removed and dried. Before the experiment the tube is blown down with air at 500°C to dehydrate the catalyst. It is noticed that the catalyst becomes quickly inactive after passing 200 gm of fatty acids. Hence, for the purpose of keeping the condition of catalyst constant in every experiment, 200 gm of fatty acids are passed and the experiment is stopped.

The temperature of reaction: While the temperature necessary to crack is reported to be about 525°C, experiments were made at 450°C, 500°C, 525°C and 550°C

Volume of passing: It was noticed that the space-velocity* of 0.18 is better at 525°C and in this tube this value of S V means the passing of 60 gm of fatty acids per hour. Then we vary the volume of passing from 30 gm to 100 gm per hour to survey a good condition.

Since the diameter of the carrier is relatively large compared with the diameter of the reaction tube, we define S V as gm/hr/s where s is the total surface area of the pieces of carrier covered with catalyst expressed in cm². This value can be calculated, regarding the shape of the carrier as a tetrahedron 1cm in diameter. Correctness of the calculation can be ascertained when we measure the total surface area of several pieces of carrier.

Characteristics of cocconut oil fatty acids: density (at 50°C) 0.865

Average molecular weight 190-200 (This value is derived by the experimental formula

$$M.W. = \frac{56.11}{\text{Acid value}} \times 100$$

Acid value = 280-290

Iodine value = 2-3

Through the curve of vacuum distillation it seems that fatty acids consist mainly of Lauric acid $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ and partially of Caprylic acid $\text{CH}_3(\text{CH}_2)_6\text{COOH}$, Capric acid $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ and Myristic acid $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ etc.

C. Experimental Result

The results shown in Table I(B) 14 indicate that the yield of cracked oil boiling from room temperature to 300°C, is relatively small. This is due to the fact that the fraction of higher boiling point than 300°C is not yet cracked and contains many oxygen compounds as determined by elemental analysis. This will interfere with polymerization.

III. CONCLUSION

There appears to be no difference between coals and pumice-stone as the catalyst carrier. When volume of fatty acid charged increases the yield becomes good, but the acid value of the cracked oil increases and the iodine

*Calculation of S V: Ordinarily the meaning of S V is gm/hr/v where gm:gram put in hr:hour volume of the zone of a reaction tube filled with catalyst expressed in cm³.

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Value decreases and the cracked oil is not suitable for polymerization. This fact may mean that fatty acids could not be cracked completely and go down without being reacted. At 450°C, yield and quantity of the cracked oil is good, but from the point of view of practical application the volume of passing is too small. At 500°C and 525°C, near the volume of passing 50-70 gm/hr (S V 0.15-0.21), a cracked oil was obtained with a high Iodine Value and low Acid Value which is estimated to be good for polymerization. At 550°C fatty acids are quickly cracked to gases.

In conclusion, at 500°C and S V 0.18 the order of cracking is desirable judging from the value of S V and I.V., but when the volume of passing is large, A.V. is comparatively large and the cracked oil contains comparatively large quantity of unreacted fatty acids.

Our experiment is not yet finished. We have to investigate how to separate oxygen compounds from cracked oil or to find a method of analysis of oxygen compounds contained in olefines. For this purpose it is proposed to investigate ketones contained in the cracked oil by the ultra-red absorption spectrum.

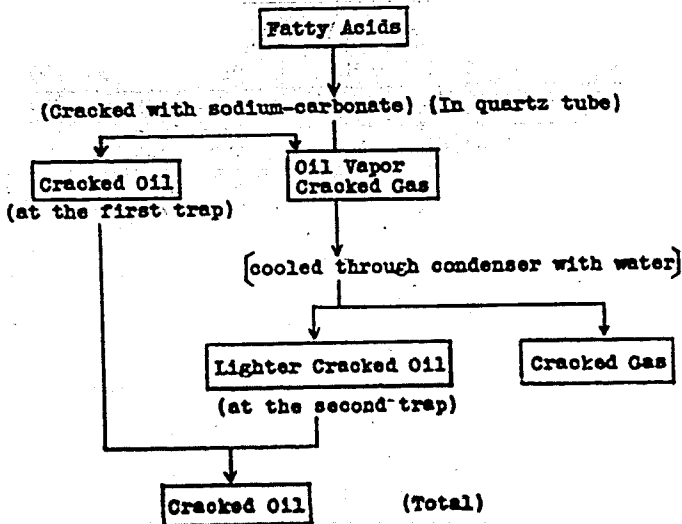


Figure 1(8)16

SIMPLIFIED FLOW DIAGRAM SHOWING FORMATION
OF OIL FROM FATTY ACIDS

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Table I(B)14
 CONDITIONS OF CRACKING AND PROPERTIES OF THEIR PRODUCTS

	Volume of pass (gm/hr)	S.V.	Yield (-300°C)	Product (Vol x% Yield)	Acid Value (A.V.)	Iodine Value (I.V.)
450°C	20	0.06	41%	820	10	146
	30	0.09	25%	750	12	122
	40	0.12	30%	1200	21	112
	50	0.15	28%	1400	36	101
500°C	30	0.09	27%	810	16	162
	40	0.12	21%	840	22	144
	50	0.15	34%	1700	20	136
	60	0.18	40%	2400	27	140
	70	0.21	32%	2240	39	118
525°C	30	0.09	29%	870	15	162
	40	0.12	24%	960	19	154
	50	0.15	31%	1550	21	147
	60	0.18	42%	2520	25	141
	70	0.21	33%	2010	37	124
	100	0.30	31%	3100	58	107
550°C	30	0.09	23%	690	19	152
	40	0.12	22%	880	21	149
	50	0.15	24%	1200	24	147
	60	0.18	29%	1740	26	136
	70	0.21	26%	1820	39	129
	100	0.30	30%	3000	61	116

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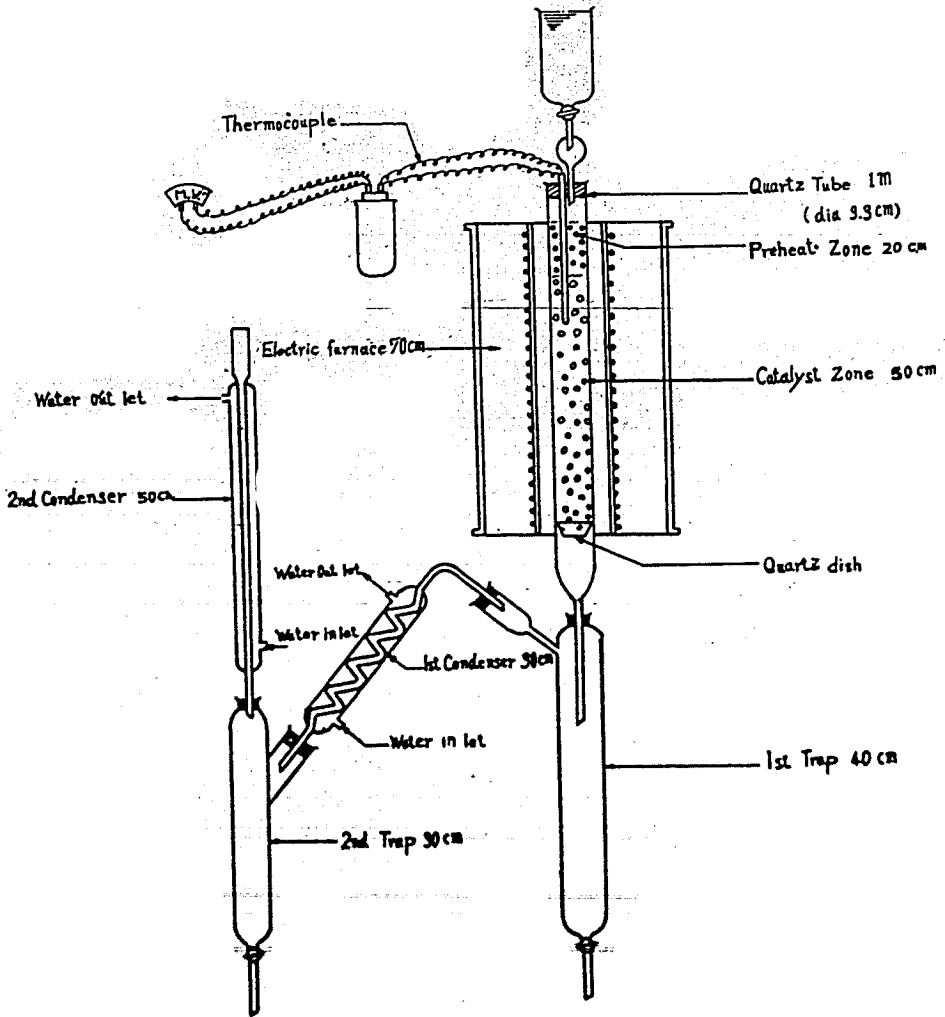


Figure 2(r)14
DRAWING OF APPARATUS

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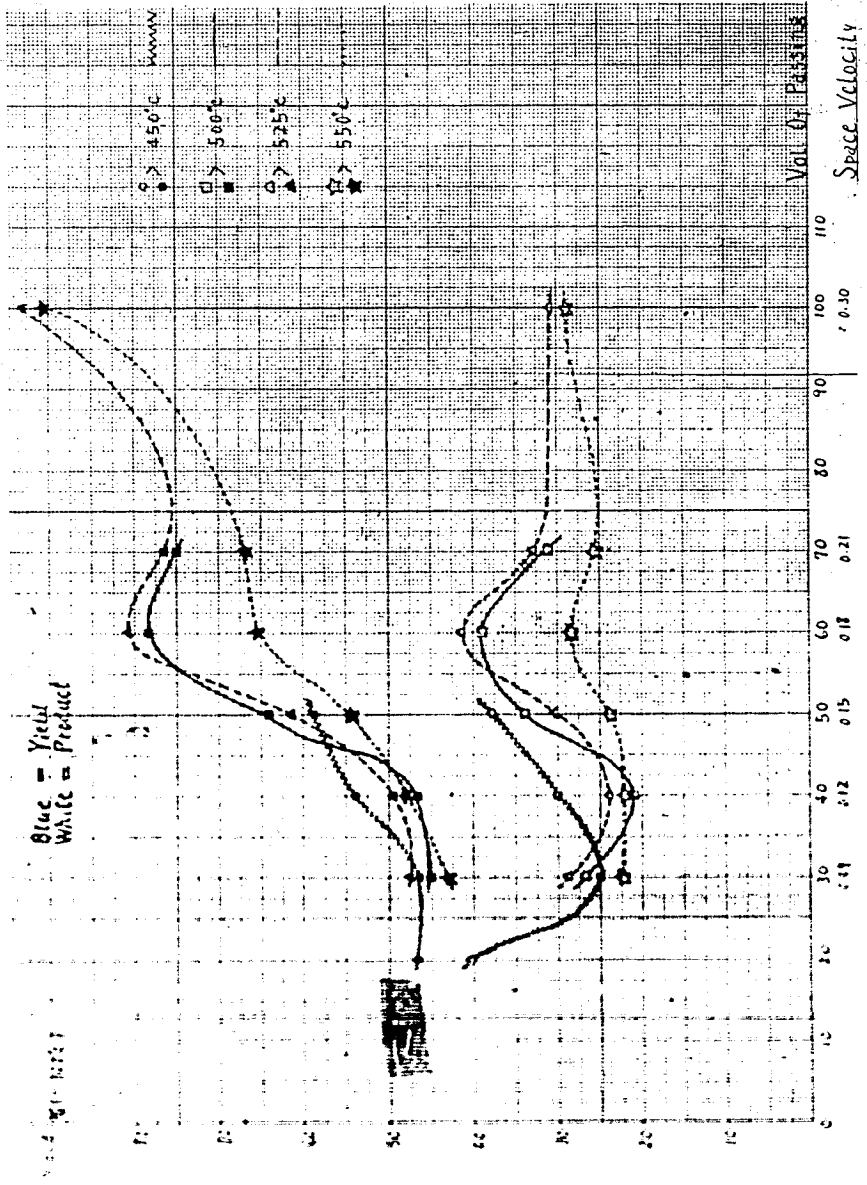


Figure 3(B)14
CORRELATION CURVE 1

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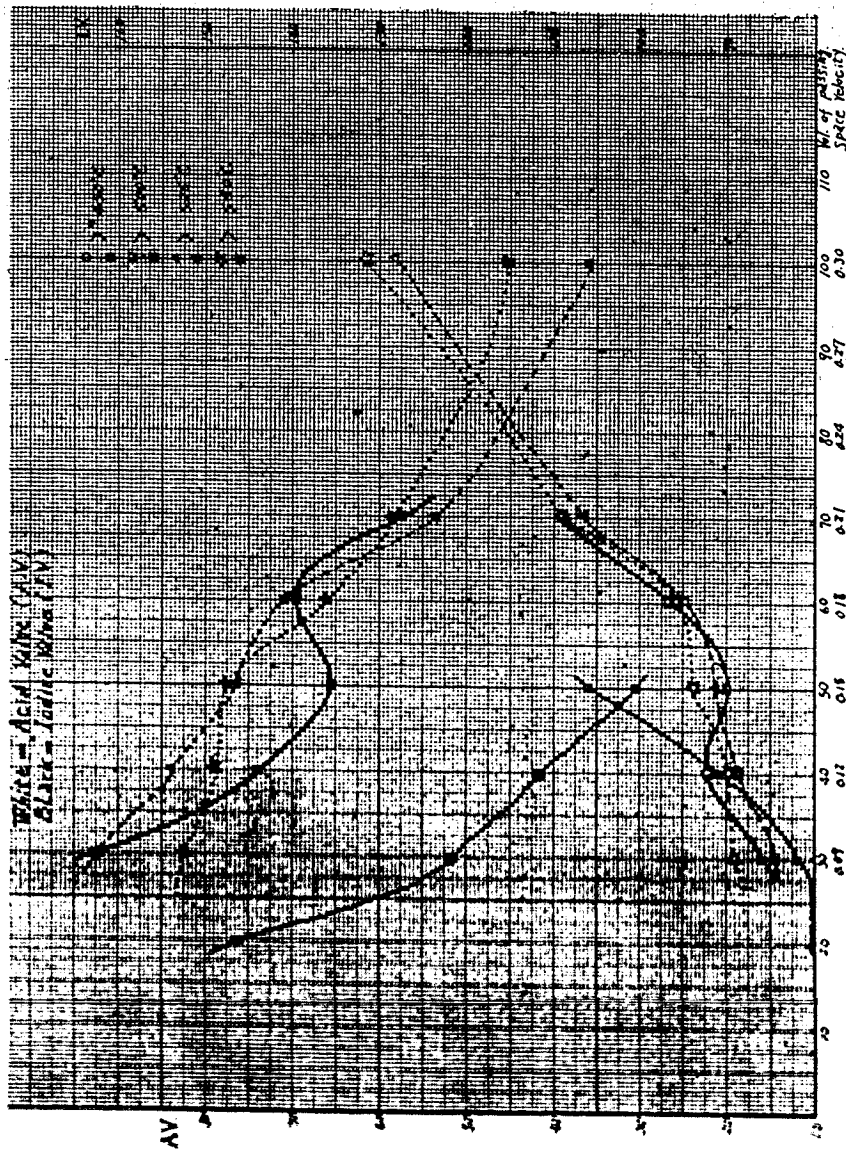


Figure 4(H)10
CORRELATION CURVE 2