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CRACKING OF VEGETABLE OILS.

BY N. M. DALAL AND T. N. MEHTA.

DEPARTMENT OF CHEMICAL TECHNOLOGY,
UNIVERSITY OF BOMBAY.

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Vegetable oils are used in India in large quantities for edible purposes. The second largest use of the vegetable oils in this country is for the manufacture of soap, as some consider the presence of animal fat in soap as objectionable. Unsaturated oils, especially those like linseed oil, are of great importance in paint and varnish industries. Several other oils of which the most important is castor oil, are used for lubricating purposes either themselves or mixed with mineral oils. Some of the oils are also used for medicinal purposes either internally or externally. Vegetable oils were also used for burning in lamps in former days before the discovery of petroleum and even now they find uses in distant corners of countries like India and China. Apart from the various uses of vegetable oils as mentioned above, they can also be used as fuel in Diesel type internal combustion engines. Recently actual experiments have been undertaken with this object by the Industrial Research Bureau Council (*vide* Reports 1935-36, 1936-37, 1937-38) and it has been found that vegetable oils produce from 10-12% less power in Diesel engine than that produced by mineral oil fuel. The maximum horse power output in the case of groundnut oil at 1200 revolutions per minute was 7·6 as against 7·85 for shell Diesel mineral oil, while both stood on the same footing regarding smoothness and starting facility. One difficulty to be met with in using vegetable oils as such for fuel in internal combustion engines, is the corrosion produced due to the rancidity of the oil. This can, however, be avoided by removing the rancidity of the oil or by finding out an alloy which can resist the corrosion from fatty acids. In Germany also, recently, tests[1] have been completed to compare the performance of vegetable oil fuels with a gas oil fuel in an oil engine. The results obtained are similar to those mentioned above with respect to higher consumption of vegetable oils and their tendency to corrode certain metals. In addition, palm oil and groundnut oil fuels were found to be slightly superior to soyabean and sesame oil fuels. Similar type of work has been carried out by Walton[2].

The use of vegetable oils as liquid fuel cannot be restricted to its use in raw condition as it cannot suit all purposes. Industry requires various types of liquid fuels, *e.g.* motor spirit, aviation spirit, kerosene, Diesel oil etc. All these requirements can be met with the different fractions of crude oil produced from the earth, but they cannot be met with from vegetable oils as such, unless they are suitably processed.

The proportion of natural liquid fuels consumed in comparison with the artificially produced liquid fuels is quite large, but the question arises as to whether the crude oil coming out of the earth is an infinite supply or is going to be exhausted at some time. According to Lt. Col. J. H. M. Greenly[3] the world consumption of petroleum at present is 250 million tons a year and its use has continued to be so rapid as to create a situation quite different from that of the solid fuels. The rate of growth could only be appreciated from the following figures.

Year.	World consumption of petroleum in tons.
1890	10.499,000
1900	20,460,000
1910	44,924,000
1920	93,188,000
1930	196,620,000
1936	248,626,000

Greenly says that the present known resources of petroleum amount to 4066 million tons, which give a life of the world's mineral oil fuels of not more than 18 years. It may, therefore, be taken as more than probable that the world's oil reserves cannot indefinitely withstand the ever increasing demand of natural liquid fuels and that a shortage will make itself felt with measurable time.

In comparison with other countries, India is producing far smaller quantities of mineral oil, which is 0·54% of the total crude oil production of the world. This production is quite small in comparison with its consumption as shown by its import figures having practically no export. The average annual imports of foreign mineral oil in India amounted to 194,518,757 gallons as against an average export of 89,401 gallons during the period 1929 to 1933.

The petroleum supplies of the world though vast, are not evenly distributed among the five continents and many countries occupying important positions in the conduct of the world affairs are without a safe supply of this commodity. It is not surprising, therefore, to find serious efforts being made to eliminate or largely reduce dependence on foreign supplies. Apart from the apprehension that the supply of petroleum would soon be exhausted and the uneven distribution of oil fields on the surface of the earth, the increasing tendency of the nations to be autonomic both in thinking and action has resulted in the feverish search for petroleum substitutes, by the utilisation of their own potential resources such as coal, wood, natural gas, oil shells, cereals, oil seeds, etc. This search is not directed solely towards producing fuels for motor vehicles, but also with a desire to become nationally self-sufficient, to keep people employed and to utilise their own resources. These extreme nationalistic tendencies of today have resulted in encouraging the use of home produced alcohol fuels by many European countries by imposition of heavy taxes upon all imported engine fuels. The cost of producing motor fuels is not specially involved since gasoline produced from crude oil is markedly less in cost than any of the sources enumerated above.

Of the various attempts made to produce liquid fuels as petroleum substitutes, the following deserves special mention here. In the Bergius process, a ton of coal, when hydrogenated at rather low temperatures and high pressure, yields 40 gallons of motor spirit, 50 gallons of Diesel oil and 35 gallons of fuel oil. The Fischer-Tropsch process, which is extensively developed in Germany, consists in hydrogenating carbon monoxide or circulating water gas rigorously freed from sulphur at atmospheric or slightly superatmospheric pressures in the presence of hydrogenating catalysts at temperatures of the order of 250-350°.

In India the production of oil seeds such as linseed, groundnut, cottonseed, castor, sesame, rapeseed and mustard seed, mowrah and niger seed, even at a conservative estimate, exceeds 7,000,000 tons and is worth about Rs. 773,000,000.

In the year 1937, the figures for the production of oil seeds in million of tons are: India 8·0, China 7·0, Nigeria 1·0, U.S.S.R. 1·9, Argentina 2·0, Dutch East Indies 0·6, U.S.A. 4·3.

Thus India tops the list and the quantity, besides satisfying in full the present local requirements of Indian industries and home consumptions, leaves a large surplus for export.

India especially with her vast resources of oil seeds has much to look forward towards the use of vegetable oils as liquid fuel, as she has practically very little mineral resources of her own. According to Hilditch[4] the petroleum reserves, though very great, have a definite limit and in view of the enormous and increasing demand for petroleum fuels for various power purposes, it is unlikely that it will ever prove economical to convert mineral oil on any scale into fatty acids. This argument is reinforced by the consideration that the fat resources of the world are not limited to fixed deposits, but are dependent on recurrent crops, the amount of the latter depending largely on the intensity of cultivation. Indeed, the contrary process of conversion of fats into hydrocarbon oils, is receiving investigation by Mailhe and others, who have tried to effect this by destructive distillation of the fats or fatty acids over catalyst such as nickel at an elevated temperature and it is suggested that even in near future, districts remote from oil wells with abundant fat resources might well obtain motor fuel from fatty material in this way.

The work on cracking of vegetable and animal oils dates back to 1888 when Engler[5] and his collaborators tried to synthesise petroleum from fatty oils in order to establish the organic theory regarding the occurrence of petroleum in nature. They were successful in certain respects to prepare products petroleum-like from fatty oils and from that time most of the other workers have tried to synthesise substances like petroleum from fatty materials. The methods followed till now for the cracking of vegetable oils can be classified into three parts, *viz.*, (1) cracking by passing the oil over a heated catalyst enclosed in a tube or tube cracking, (2) cracking by distillation in presence of metallic salts, and (3) cracking under pressure in an autoclave.

Tube Cracking.

Most of the work on cracking of fatty oils by this method has been carried out by Mailhe [6-11]. He has cracked various oils of the vegetable as well as of animal origin. *e.g.* linseed oil[6], colza oil[7], peanut oil[8], palm oil, rapeseed oil[9], shea butter[10], shark oil[11], etc. The temperature range utilised for cracking was between 550° and 660°. The cracking was carried out by passing the oil as such over the catalyst or in the vapour state. The catalysts used by him were balls of electrolytic copper, magnesium oxide, aluminium oxide, kaolin, a mixture of aluminium and copper oxide, and various other combinations from the above mentioned catalysts. In general, two types of products were obtained, *viz.*, the gaseous and the liquid product. The gaseous product was found to consist mainly of carbon dioxide, carbon monoxide, hydrogen, unsaturated hydrocarbons, methane and hydrocarbons above methane and acrolein. The liquid product was subjected to distillation and the heavy boiling fraction was recracked by passing it over again the hot catalyst whereby further quantities of lighter products were obtained. The liquid portion was then subjected to alkali treatment to remove the fatty acids and the natural oil so obtained was then distilled into different fractions. The fraction boiling between 80° and 90° in almost all the cases was found to contain benzene free from its nitro derivative and the fractions between 110° and 115° and 135° and 140° were found to consist of toluene and xylene respectively. Further quantities of aromatics were obtainable on hydrogenating the residual liquid after the removal of aromatics. The fraction boiling between 150° and 250° was a better substitute for kerosene oil. From the higher fraction above 250°, portions suitable for Diesel engine and lubricating purposes were separated.

The decomposition of castor oil[10] furnished products quite different from other oils. The products of cracking were as usual gas and liquid, but the liquid portion after neutralisation with caustic soda and subsequent distillation furnished heptaldehyde which was not obtainable from any other oil.

The decomposition of various fatty acids like oleic, linoleic, pelargonic and acetic as well as of ketones has been studied by Mailhe[12]. The products obtained from oleic, linoleic and pelargonic acids were more or less those obtained from fatty oils, though the decomposition was more pronounced as the unsaturation went high. Acetic acid when decomposed at 600° over copper and aluminium catalyst yielded unchanged acid, acetone and a gas comprising CO_2, CO, H_2, and CH_4. The decomposition of ketones readily occurs at 600°. The molecule is disrupted at the ketonic group with the formation of CO, and liberation of two residues. The latter react by gain or loss of hydrogen to yield either saturated or an ethylenic hydrocarbon. When the residues are of certain degree of complexity they are decomposed into simpler substances.

Cracking by Distillation in presence of Metallic Salts.

Kobayashi[13] has distilled a mixture of herring oil (4000 c.c., sp. gr. 0·9214, sap. value 187·7) and finely powdered clay (4000 g.) in an iron retort at ordinary pressure and obtained a crude oil (2000 c.c.) which had a sp. gr. of 0·8160 and sap. value of 15·1. The hydrocarbons in the oil were mainly of naphthene series, together with a considerable quantity of olefines. According to him the formation of hydrocarbons is ascribed to the action of acid clay Al_2O_3, $6SiO_2$, XH_2O on oils, whereby the oils are hydrolysed to fatty acids and the fatty acids are decomposed into hydrocarbons partly with the formation of napthenic acids. Similar experiments were carried out by the same author with shark oil, sardine oil and arctic sperm oil[14]. He concluded that the yield of petroleum depends upon the kind of fish oil, the design of the distilling apparatus, the duration of distillation and the properties of the contact material used.

Cracking of colza oil, rapeseed oil and peanut oil has been carried out by Mailhe[15] by distilling them in presence of anhydrous zinc chloride and magnesium chloride. The products of distillation were acraldehyde, water, gas, and a slightly acid liquid. The liquid portion after washing with alkali consisted of paraffins and olefines boiling from 60°-310°, together with higher boiling substances. The gas was found to consist of CO_2, CO, olefines, hydrogen and saturated hydrocarbons. He found that zinc chloride can be replaced by calcium, barium or sodium chlorides.

Some work has been done by Gallo and Correli[16] for the synthetic production of liquid fuel from vegetable oils. They decomposed vegetable oil by steam in the presence of an alkaline earth and the products were led in the vapour state over pumice stone containing nickel at 200°-250° where hydrogenation took place. The yield of the liquid product was form 60-65%.

Melis[17] has resorted to a method which consisted in saponifying the oil with potassium hydroxide and then decomposing with calcium oxide. The oil or fat was heated with potassium hydroxide, calcium oxide and water in amounts corresponding to the equation,

$$2C_{17}H_{33}COOK + Ca(OH)_2 = K_2CO_3 + CaCO_3 + 2C_{17}H_{34}$$

with a slight excess of potassium hydroxide. After complete saponification the product was distilled and the distillates, except from castor oil, were transparent yellowish brown liquids, soluble in petroleum, benzene, chloroform and ether. From castor oil, the first distillate was almost colourless with a bluish fluorescence, an aromatic odour and a burning taste. It boiled at about 170° and was soluble in ether and alcohol. The conversion of soyabean oil into fuel by dry distillation of the calcium and magnesium soap, forms the subject of recent papers by Sato[18] and by Haga[19].

Chang and Chang[20] have prepared petroleum-like liquid, from crude cotton seed oil. They heated crude cotton seed oil with 14% of calcium hydroxide under pressure for eleven hours and the soap obtained was subjected to destructive distillation giving gaseous and liquid products. The liquid product contained 17% of light oil boiling below 150° and resembling gasoline.

The cracking of peanut oil by Ping[21] in liquid phase with 1% aluminium chloride at 250°—400° in a laboratory catch of 15 gallons produced 27% of refined petrol boiling upto 200°, 31% of refined burning oil boiling from 200°-300° and a gas and coke with a good fuel value.

Cracking under Pressure.

Engler[3] distilled train oil under a pressure of 10 atmospheres which, however, during the operation sank to 4 atmospheres. On the whole 60% of distillate were obtained which had a brownish colour and no disagreeable odour.

Such type of work was undertaken by Faragher, Morrell and Levine[22] who cracked menhaden fish oil under a pressure of 60 lbs. and 100 lbs./sq. inch. The yield of pressure distillate was 76·6% by volume at 60 lbs. pressure and 67·9% at 100 lbs. pressure. The gasoline content of the pressure distillates at 60 lbs. and 100 lbs. were respectively 37·5% and 47·5% of the charge. The gasoline after refining with caustic soda, was found to contain 19% of unsaturated hydrocarbons, 35% aromatics, 8% naphthenes and 38% paraffins.

The same authors[23] cracked two different types of palm oil, Sumatra palm and Niger palm oil under a pressure of 135, 75 and 50 lbs. per square inch. It was found that the yield of pressure distillates decreased as the pressure increased, while the percentage of gasoline fraction increased with increase in pressure. Similar experiments with cotton seed oil was carried out by Egloff and Morrell[24]. The oil was cracked at a temperature of 445°-485° under a pressure of 135 lbs./sq. inch, in an autoclave of eight inches diameter. The yield of pressure distillate was 71·1% of the charge and the percentage of crude motor fuel was 58·7% of the charge. The hydrocarbon analysis of the motor fuel gave the following percentages.

Paraffins,	37·1%	Unsaturated,	27·1%
Naphthenes,	9·9%	Aromatics,	25·9%

The coke produced was of firm honeycomb structure and had a calorific value of 15,6000 B.T.U./ lb.

Recently, the conversion of fatty acids into light oils for motor fuel is also receiving attention in Japan. Shinozaki, Kagawa and Sato[23] state that soyabean oil can be transformed into a low boiling oil (sp. gr. below 0·7) in one hour by contact above 430° and under high pressure of hydrogen with a suitable catalyst (3% of nickel being the most useful). C. Abder Halden[24] suggests that increased yields are obtainable by carbonising oil seeds without previous extraction of the fat, the oily condensate is submitted to catalyst hydrogenation cracking and an yield of 70-75% of the original seeds is obtainable in the form of hydrocarbon boiling below 300°.

It will be seen from the above literature regarding the cracking of fatty oils into petroleum products that much interest is taken by different workers in this subject especially from Japan and China, who have at their disposal large quantities of vegetable and animal oils especially soyabean oil and fish oil. The work of Mailhe, Sato, Egloff and Morrell and others, which is mainly for the purpose of preparing low boiling petroleums, indicate the possibility of preparing gasoline and motor fuel. India having practically very little production of this material in limited areas, can well adopt such procedures for the production of her own motor fuels in these days when every country is trying to become self-sufficient. The cost of production is a factor which need not be neglected, but in times of emergency, *e. g.* in war times, the economy of cost of production cannot be of vital importance. It may, therefore, be that in near future the cracking of vegetable oils may serve the useful purpose for the production of motor fuel in general and synthetic chemicals in particular.

In the present investigation, the cracking of vegetable oils was carried out by three different proceedures *viz.* (*i*) by passing over a catalyst in a tube, (*ii*) by distillation in presence of metallic salts, and (*iii*) by distillation under pressure. The preliminary experiments were carried out by the first method using coconut oil, groundnut oil, sesame oil and mowrah oil, whose crops are quite abundant in India. In the beginning the cracking was studied by passing over the hot surface of a glass tube and also on a heated iron catalyst at different temperatures with varying rates of flow. In the second method the cracking of coconut oil and groundnut oil has been studied by distillation in presence of various percentages of anhydrous metallic chlorides, especially zinc chloride. The effect of time of distillation was also studied. The distillation products (both liquid and gaseous) from coconut oil, groundnut oil, sesame oil and mowrah oil by first distilling in presence of 5% anhydrous zinc chloride and then redistilling the fraction above 210° in presence of the distillation residue, were studied in detail regarding the motor fuel content and the gas composition. Finally the cracking of groundnut oil and mowrah oil has been carried out by distillation under pressures ranging from 45—300 lbs. per square inch to study the effect of pressure on the cracked products, *viz.*, motor fuel, composition of the gas and the calorific value of the gas. The hydrocarbon analysis of motor fuels obtained at different pressures, has also been investigated.

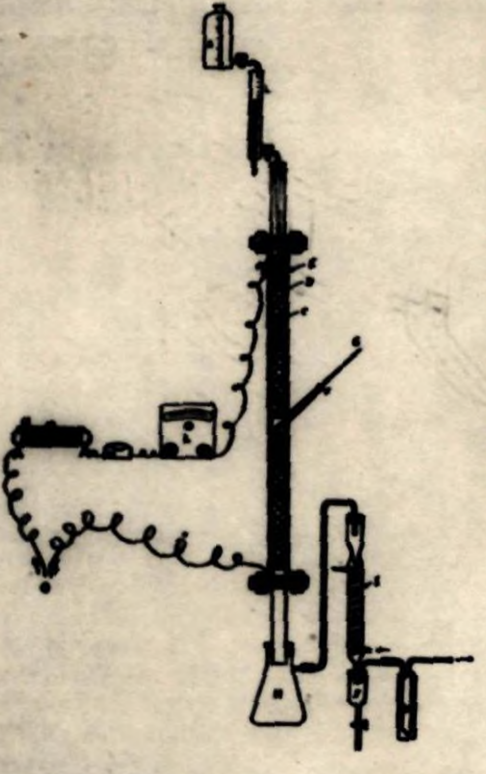
EXPERIMENTAL.

Cracking of Oils in a Tube.

The reaction tube was an ordinary iron tube whose internal and external diameters were 1/2" and 5/8" respectively. Two pieces of 8" length and one piece of 3 ft. length were cut from such a tube. The two short pieces were attached to the longer tube on both the sides by means of flanges after putting a layer of asbestos between the flanges to prevent the short pieces getting heated by conduction of heat from the longer tube which was electrically heated. A hole was drilled in the centre of the long tube to which was welded a 6 inch

FIG. 1.

Cracking tube.



A—Oil reservoir.
B—Const. level oil vessel.
C—Catalyst.
D—Reaction tube.
E—Asbestos lagging.
F—Thermometer pocket.
G—Thermometer.
H—Receiver for cracked oil.
I—Worom condenser.
J—Condensate receiver.
K—Gas washer.
L—Avometer.
M—Fuse.
N—Rheostat.
O—Main.

piece of narrow iron tube at an angle of 45° which served as the thermometer or thermocouple pocket.

The reaction tube proper was wrapped with a flexible mica sheet and over the mica sheet was wound the heating element (nichrome wire No. 5). An avometer, a rheostat and a fuse were the three auxiliaries required in the circuit where the fuse served to protect the meter ; the rheostat to control the heating and the avometer to measure the current. The current was kept constant so that the rate of heating was identical in different experiments (Fig. 1).

With the same arrangements except for the thermometer pocket and the flanges, a glass tube (combustion tube) 85 cm. long and 1·3 cm. internal diameter was used as the reaction chamber, the temperature measurement being carried out by means of a thermocouple introduced from the bottom. The oil was evenly distributed on the sides of the tube by making suitable arrangement when the cracking was done in absence of the catalyst.

The oil was cracked by dropping it into the hot portion of the tube from a constant level head at a constant rate. The cracked oil was collected in a receiver at the bottom which was in turn connected with an upright worm condenser to condense the uncondensed oily vapours escaping from the receiver. A slight vacuum was applied on the condenser side by means of a water-pump to remove the gases formed during cracking in the reaction tube.

The cracking of coconut oil, groundnut oil, mowrah oil and sesame oil was carried out according to the above method and the acid and saponification values of the resulting products were determined. The characteristics of the oils used are shown in Table I.

TABLE I.

Name of oil.	Acid value.	Sap. value.	Ester value.	Iodine value.
Coconut	2·9	258·2	255·3	8·8
Groundnut	1·1	195·2	194·1	93·3
Sesame	1·9	192·3	190·4	111·2
Mowrah	14·2	185·2	171·0	69·7

Expt. 1. *Cracking in Glass tube.*—Cracking of coconut, groundnut, sesame and mowrah oils was carried out over a surface of hard glass tubing at the rate of 2 g. per minute at different temperatures. The analytical constants of the product obtained are given in Table II.

TABLE II.

Coconut oil.

Temp.	Acid value.	Sap. value.	Ester value.	% Ester uncracked.	% Ester cracked.
350°	6·5	258·0	251·5	98·8	1·2
400	20·4	257·6	237·2	93·3	6·7
450	77·6	256·0	178·4	69·9	30·1
500	177·8	251·1	73·3	28·7	71·3

Groundnut oil.

Temp.	Acid value.	Sap. value.	Ester value.	% Ester uncracked.	% Ester cracked.
350°	3·8	193·5	189·7	97·7	2·3
400	35·2	192·3	157·1	82	18·0
450	102·5	168·9	66·4	34·2	65·8
500	105·6	140·6	35·0	18·1	81·9

Sesame oil.

Temp.	Acid value.	Sap. value.	Ester value.	% Ester uncracked.	% Ester cracked.
350°	4·9	189·3	184·4	97·1	2·9
400	67·2	187·6	120·4	68·5	31·5
450	118·5	169·8	51·3	26·9	73·1
500	130·9	167·0	36·1	19	81·0

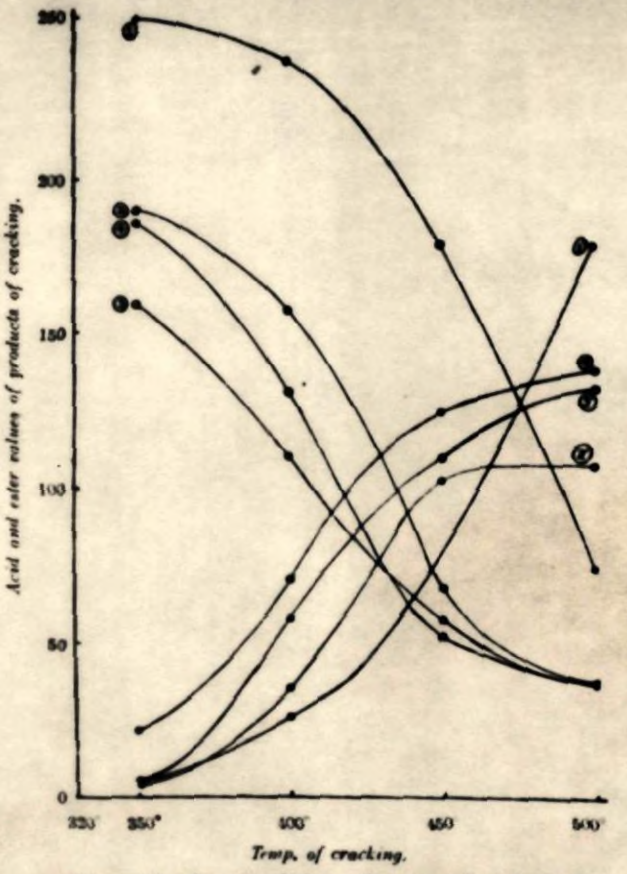
Mowrah oil.

Temp.	Acid value.	Sap. value.	Ester value.	% Ester uncracked.	% Ester cracked.
350°	21·5	180·9	159·4	93·2	6·8
400	70·4	180·5	110·1	64·2	35·8
450	122·7	179·7	57	39·2	60·8
500	136·7	173·0	36·3	22·1	77·9

The percentages of oil cracked increase with rise in temperature at the constant rate of dropping the oil. The acid values rapidly increase in the beginning, but in the case of groundnut, sesame and mowrah oil, the rise is not very marked after 450° in contrast to coconut oil (*vide* Table II and Fig. 2). The saponification values of coconut oil nearly remain constant throughout the rise in temperature, while in the case of other three oils, they go on decreasing with rise in temperatures. This may be due to the comparatively stable nature of the saturated fatty acids derived from coconut oil as against those from the other three oils, the acids of which are further decomposed to neutral products, which would cause decrease in the saponification value.

Expt. 2. *Cracking in Iron tube with Catalyst.*—When the coconut oil was cracked by a passing it at the same rate (2 g. per minute) over 200 g. of iron catalyst, which was prepared from No. 24 iron wire gauze wound in the form of cylinders and enclosed in an iron tube, it gave the results as in Table III. The results indicate that in the absence of catalyst, the glycerides of coconut oil are decomposed into fatty acids while in the presence of catalysts, the fatty acids are further decomposed into neutral products as evident from the drop in saponification values.

FIG. 2.



Curves 1-4 refer respectively to the ester value of oils from coconut, groundnut, sesame, and mowrah and curves 1'-4' refer to acid value of the oils in the same order.

TABLE III.

Temp.	Acid value.	Sap. value.	Ester value.	Percentage of ester uncracked.	cracked.
300°	6·6	253·9	247·3	96·9	3·1
350	19·5	240·3	220·8	86·5	13·5
400	31·0	208·8	177·8	69·7	30·3
450	72·6	173·2	100·6	39·4	60·6

Expt. 3. *Cracking in Glass tube with Catalyst.*—Cracking of oils was carried out with an iron catalyst described in Experiment No. 2, enclosed in the glass tube used in Experiment No. 1 at different temperatures and varying the rate of dropping the oil (Table IV). The results obtained show that the percentage of ester cracked increases with temperature, the rate of dropping the oil remaining constant. On the other hand, cracking is enhanced by decreasing the rate of dropping the oil, but both these observations do not hold good at temperatures higher than 450°, especially when the rate of dropping the oil is less than 2 g per minute. This may be attributed to the catalyst being covered over by the deposition of coke due to the carbonisation of the cracked products at high temperature.

TABLE IV.

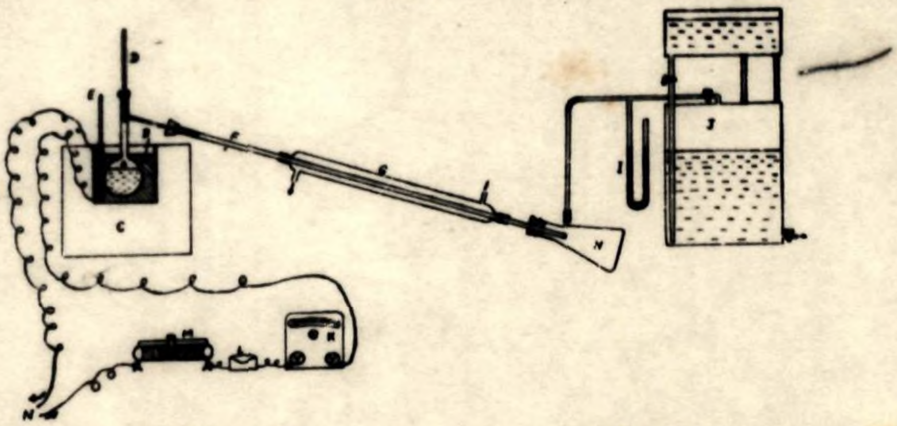
R – Rate of dropping the oil in g./min.

Temp.	R.	Acid value.	Sap. value.	Ester value.	Percentage of ester uncracked.	cracked.
			Coconut oil.			
375	1·8	33·6	256	222·4	87·1	12·9
	1·4	48·9	221·5	172·6	67·6	32·4
	1·0	51·6	203·4	151·8	59·5	40·5
	0·6	83·6	122·7	39·1	15·3	84·7
425	3·6	64·3	227·7	163·4	64	36
	2·1	102·1	199·5	97·4	38·2	61·8
	1·4	105·5	161·4	55·9	21·9	78·1
	0·8	96·7	120·3	23·6	9·2	90·8
475	3·8	77·2	239·5	162·3	63·6	36·4
	2·0	101·3	206·8	105·5	41·3	58·7
	1·3	94·6	192·5	97·9	38·3	61·7
			Groundnut oil.			
375	4	11·7	190·78	178·9	92·2	7·8
	2·2	28·3	190·8	162·5	83·7	16·3
	1·1	85·3	189·8	104·1	53·6	46·4
425	3·3	58·7	183·9	125·2	64·5	35·5
	2·1	96·6	168·7	72·1	37·1	62·9
	1·2	116·8	157·9	41·1	21·2	78·8
475	3·5	108·1	159·0	50·9	26·2	73·8
	2·0	105·8	156·6	50·8	26·2	73·8
	1·3	98·8	162·5	63·7	32·8	67·2
			Sesame oil.			
375	5·0	7·1	191·1	184·0	96·6	3·4
	2·6	13·6	190·6	177	92·9	7·1
	1·5	28·2	185·8	157·6	82·8	17·2
425	3·7	46·1	180·5	134·4	65·3	34·7
	2·5	107·3	177·8	70·5	36·9	63·1
	1·3	118·8	174·8	56	29·4	70·6
475	3·8	100·3	140·4	40·1	21·1	78·9
	2·4	111·0	156·4	45·4	23·8	76·2
	1·3	113·3	173·5	60·2	31·6	68·4

Cracking of Oils by Distillation in presence of Metallic Salts.

The distillation was carried out in a round bottom distilling flask (250 c.c.) and the heating of the flask was carried out by means of a molten alloy placed in an enamel pot. The enamel pot was heated by nichrome wire which was wound round it. Electrical heating had certain advantages over flame heating, as it avoided local heating of certain parts and the whole apparatus was uniformly heated throughout. The quantity of the alloy was just sufficient to cover the bulb of the distilling flask when it was perfectly immersed in it.

FIG. 3.



A—Distilling flask.
B—Molten alloy.
C—Asbestos.
D—Thermometer.
E— Do.
F—Air condenser.
G—Water condenser.

H—Receiver.
I—Hg-manometer.
J—Gas holder.
K—Avometer.
L—Fuse.
M—Rheostat.
N—Main.

The delivery tube of the flask was connected with a condenser which served partly as air-cooled condenser and partly as water-cooled condenser. The condensed liquid was received in a filter flask attached to the outlet of the condenser and the uncondensible gas was collected over water in a gas holder. A mercury manometer was placed between the receiver and the gas holder which served to check the pressure of the gas. The top of the distilling flask was closed by a cork through which a thermometer was fixed. The general arrangement of the apparatus is shown in Fig. 3.

When the alloy melted and the thermometer placed in the alloy showed a temperature of 220°, the flask was immersed into the molten alloy and rigidly clamped. Other connections were then made as is shown in Fig. 3. The rate of heating in all distillations was maintained constant by passing a known amount of current and the heating was discontinued when no further distillate was obtained.

Expt. 1-5. *Distillation of Coconut Oil.*—The distillation was carried out (1) in absence of catalyst, (2) with 10% calcium chloride, (3) with 10% calcium chloride, but with prolonged time of distillation, (4) with 10% calcium chloride, but the oil was distilled after refluxing with calcium chloride for 1¼ hours and (5) with 10% calcuim chloride-zinc chloride. The distillates obtained in all the cases had an acrid smell and were bright yellow in colour which darkened on standing. They were composed of two layers (*i*) an aqueous layer and (*ii*) the oily layer. A black solid residue was left in the flask after the distillation was over. The distillates were washed with water and analysed for their chemical components (Table V).

TABLE V.

Experiment No. ...	1	2	3	4	5
Quantity of oil (g.) ...	100	100	100	100	100
Salt used	Nil	*$CaCl_2$	*$CaCl_2$	*$CaCl_2$	*$ZnCl_2$
% of salt	Nil	10	10	10	10
Method of cracking	Direct distillation.	Direct distillation.	Direct distillation.	Refluxing and distilling.	Direct distillation.
Distilled for (hr.) ...	1	1	2	¼ hr. for refluxing 1 hr. for distilling.	1
Distillate.					
Sp. gravity	0·872	0·862	0·835	0·867	0·859
Weight (g.)	82·9	84·0	79·4	81·1	68·8
Volume (c. c.)	95·0	97·5	95·1	93·5	80·1
Acid value	184·8	159·7	113·1	167·6	222·9
Sap. value	223·2	195·7	135·1	202·7	223·8
Ester value	38·4	36·0	22·0	35·1	0·9
Ester uncracked (%)	14·8	13·9	8·5	13·6	0·3
Ester cracked (%)	85·1	86·1	91·5	86·4	99·7
Aqueous layer (c. c.)	1·0	1·5	2·0	1·5	4·6
Residue (g.)	9·1	15·0	18·0	17·2	24·8

*Anhydrous.

On comparing the acid values, the saponification values and the specific gravity of the products obtained by distilling coconut oil with and without $CaCl_2$, it is found that cracking is increased in presence of $CaCl_2$ (Experiments 1 and 2). That the time of distillation is an important factor in cracking is shown by the results of Experiments 2 and 3. The results of Experiments 3 and 4 show that so far as the ester value is concerned, the direct distillation and distillation after refluxing practically make no difference. The results of Experiments

3 and 5, however, show that by using $ZnCl_2$ in place of $CaCl_2$, the ester is completely decomposed which is not the case in $CaCl_2$ cracking. Even though the acid value is high in case of $ZnCl_2$ cracking, the percentage of moisture, the specific gravity of the cracked oil and the residue left in the flask, show that greater amount of cracking is effected by $ZnCl_2$ than by $CaCl_2$.

Expt. 6—8. *Distillation of Coconut Oil in presence of Varying Percentages of* $ZnCl_2$.—Coconut oil was distilled in presence of 1%, 2·5%, and 5% $ZnCl_2$ within a period of about an hour. The distillates obtained had an acrid smell and were composed of two layers (*i*) an aqueous layer and (*ii*) an oily layer. The chemical and physical constants of the oily layer were determined after washing the distillates with water till free from mineral acid (Table VI).

TABLE VI.

Experiment No.	1	6	7	8	5
Quantity of oil (g.)	100	100	100	100	100
% of salt	Nil	1	2·5	5	10
Temp. range of distillation ...	...	235°-303°	225°-295°	200°-292°	202°-285°
Distillate.					
Sp gravity	0·872	0·866	0·870	0·866	0·859
Weight (g.)	82·9	81·3	79·7	76·8	68·8
Volume (c.c.)	95·0	94·0	91·5	88·9	80·1
Acid value	184·8	225·0	222·7	222·3	222·9
Sap. value	223·2	237·3	233·0	230·6	223·8
Ester value	38·4	12·3	10·3	8·3	0·9
Ester uncracked (%) . . .	14·9	4·8	4·0	3·2	0·3
Ester cracked (%) . . .	85·1	92·5	96·0	96·8	99·7
Aqueous layer (c.c.) . . .	1·0	2·0	3·2	3·8	4·6
Residue (g.)	9·1	11·6	13·0	15·6	24·8

As the percentage of the catalyst increases the ester value of the cracked products decreases. The amount of distillate obtained decreases, while the amount of residue and aqueous layer increases with an increase in the amount of catalyst used. It is to be noted that the acid values remain nearly same, even when different amounts of catalyst are used.

Expt. 9-13. *Distillation of Groundnut Oil in presence of Varying Percentages of* $ZnCl_2$.—Groundnut oil was cracked by distillation in presence of 1, 2·5, 5 and 10% $ZnCl_2$. It was also distilled in absence of the metallic salt (Table VII).

TABLE VII.

Experiment No. ...	9	10	11	12	13
Quantity of oil (g.)	100	100	100	100	100
% of salt	Nil	1	2·5	5	10
Temp. range of distillation	140°-324°	130°-311°	120°-314°	120°-312°	120°-302°
Distillate.					
Sp. gravity	0·870	0·859	0·862	0·858	0·854
Weight (g.)	84·2	78·3	75·7	73·1	66·3
Volume (c.c.)	96·8	91·5	87·9	85·2	77·7
Acid value	121·6	103·6	81·6	63·4	38·2
Sap. value	130·9	112·2	90·1	71·1	42·0
Ester value	9·3	8·6	8·5	7·7	3·8
Ester uncracked (%)	4·8	4·4	4·3	3·9	2·0
Ester cracked (%)	95·2	95·6	95·7	96·1	98·0
Aqueous layer (c.c.)	1·2	2·5	3·4	4·3	5·3
Residue (g.)	4·1	12·1	15·0	18·1	29·6

FIG. 4.

Curves 1-2 refer respectively to groundnut and mowrah oils.

With increase in the percentage of $ZnCl_2$ used as a catalyst, the weights and volumes of the cracked products decrease with a simultaneous decrease in specific gravity. The ester value decreases from 9·3 to 3·8 and the amount of residue left in the flask and the aqueous layer obtained during distillation, increase with an increase in the percentage of the catalyst. The behaviour of $ZnCl_2$ towards groundnut oil, is different from that towards coconut oil so far as the acid values and saponification values are concerned. It was observed in the case of coconut oil that these values nearly remain the same throughout, indicating thereby that the cracking does not proceed beyond the formation of acids, while in the case of groundnut oil, the amount of neutral products formed goes on increasing as shown by the decrease in saponification values.

Expt. 14. *Recracking of Oils.*—The distillate from the cracking of groundnut oil with 2·5% $ZnCl_2$ (Experiment 11) was recracked by distilling in presence of 2·5% $ZnCl_2$. The distillate obtained was washed with water to free it from mineral acid and analysed for its chemical constants (Table VIII).

TABLE VIII.

Chemical constants.		At the end of first cracking.	At the end of second cracking.
Acid value	...	81·6	22·5
Sap value	...	90·1	26·2
Ester value	...	8·5	3·7
Ester cracked (%)	...	95·6	96·1

The analytical results show that further cracking is effected when the first distillate is redistilled in presence of a fresh catalyst. The acid value is appreciably lowered down.

Expt. 15—18. *Cracking of Oil by Double distillation in presence of* $ZnCl_2$.—The oil was distilled with 5% $ZnCl_2$ as in previous experiments and after washing an aliquot portion of the distillate, its chemical constants were determined. The distillate was then separated into two fractions (*i*) distilling up to 210° and (*ii*) the higher fraction above 210°. The higher fraction was returned to the distilling flask containing the solid residue and distilled. The higher fatty acids which generally do not distil below 210° under ordinary conditions, are automatically submitted for recracking by this separation. The fraction below 210° at the end of the first distillation and the distillate at the end of second distillation, were mixed together, washed with water and analysed for its chemical constants. The washed distillate was then distilled and the fraction up to 210° was separated. This was washed with caustic soda solution to remove the fatty matter and finally with water till free from alkali. The resulting product is expressed as gasoline fraction in Table IX.

TABLE IX.

Experiment No	...	15	16	17	18
Name of oil	...	Coconut.	Mowrah.	Groundnut.	Sesame
Quantity of oil (g.)	...	100	100	100	100
Weight of distillate after double distillation (g.)	...	71·8	55·5	53·5	49·5
Aq. layer after double distillation (c.c.)	...	5·2	6·4	7·5	9.0
Residue (g.)	...	14·2	23.2	25·6	24·9
Volume of gas (litres)	...	6·1	10·9	11·2	14·5
Gasoline fraction G (g)	...	8·5	10·5	9·0	12·1
Distilling range of G	...	75°-210°	70°-210°	55°-210°	55°-210°

		Chemical const. at the end of 1st cracking.				Chemical const. at the end of 2nd cracking.			
		Coconut.	Mowrah.	Groundnut.	Sesame.	Coconut.	Mowrah.	Groundnut.	Sesame.
Acid value	...	222·3	52·8	63·4	46·3	20·2	29·7	19·0	14·8
Sap. value	...	230·6	66·5	71·1	49·6	27·6	39·0	21·0	17·0
Ester value	...	8·3	13·7	7·7	3·3	7·4	9·3	2·0	2·2
Ester uncracked (%)		3·2	7·8	3·9	1·9	2·9	5·4	1·0	1·1
Ester cracked (%)		96·8	92·2	96·1	98·3	97·1	94·6	99·0	98·9

TABLE IX (*continued*).

Analysis of the gas.

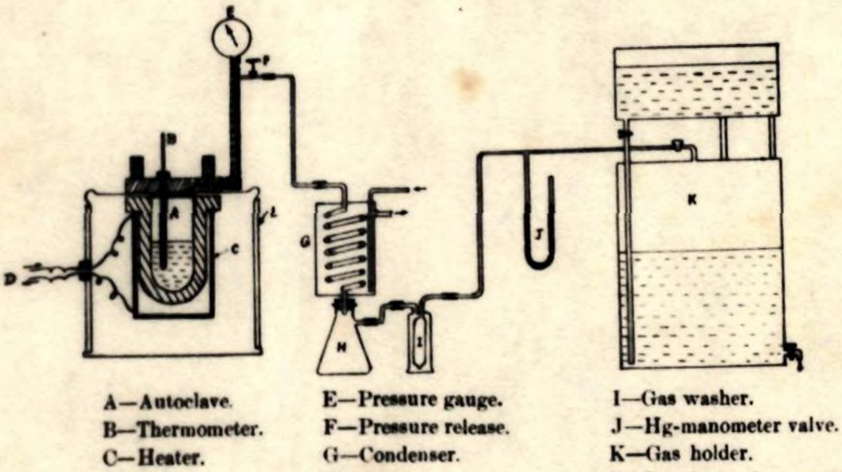
	Coconut.	Mowrah.	Groundnut.	Sesame.
CO_2 (%)	7·8	4·2	3·8	3·2
Olefines (%)	4·0	6·7	5·4	6·0
CO (%)	10·1	4·8	4·3	4·7
H_2 (%)	56·5	59·6	59·0	56·5
Saturated hydrocarbons (%)	21·6	24·7	27·5	29·6

The experimental results indicate that the cracking is a function which is directly related to the unsaturation in the oil, *i.e.* the iodine value of the oil. The oils, if arranged in the increasing order of their iodine values, stand as indicated in Table XVI, *i.e.*, (*i*) coconut oil, (*ii*) mowrah oil, (*iii*) groundnut oil and (*iv*) sesame oil. As the iodine value increases, the amount of distillate obtained decreases, while the volume of gas and the residue in the flask increase. In the gas analysis, the percentages of CO_2 and CO decrease while the percentages of olefines and saturated compounds increase, with increase in the iodine value.

Cracking of Oils by Distillation under Pressure.

The oil was cracked by the non-residium method of distillation as followed by Egloff and Morrell[24]. The apparatus employed was an electrically heated autoclave of stainless steel with an internal diameter of 8·1 cm. (3·2 in.) and 22·4 cm. (8·81 in.) deep, thus having an approximate capacity of 1100 c.c. The autoclave was fitted with a pressure regulating valve and a thermometer pocket. To the pressure regulating valve was attached a vapour line which in turn was connected with a water-cooled condenser. To the outlet

FIG. 5.



A—Autoclave.
B—Thermometer.
C—Heater.
D—Main.
E—Pressure gauge.
F—Pressure release.
G—Condenser.
H—Receiver.
I—Gas washer.
J—Hg-manometer valve.
K—Gas holder.
L—Lagging (asbestos rope).

of the condenser a filter flask was attached whose side-tube was connected to a mercury manometer and then to the gas holder as shown in Fig. 5. The gas was collected over water by displacement method.

The autoclave was charged with 550 c.c. of the oil to be cracked (nearly half the capacity of the autoclave). It was then heated till a required pressure was reached. The pressure release valve was then opened on to the receiver and the distillation was carried out maintaining the required pressure in the autoclave throughout the experiment. The heating was discontinued when a temperature of 485° was reached at which no distillate came out. The products of cracking were coke, pressure distillate, water and gas (Tables XII and XX).

FIG. 6.

Pressure (lb./sq. in.).

Products of cracking of groundnut oil as a function of pressure.

FIG. 7.

Pressure (lb./sq. in.).

Products of cracking of mowrah oil as a function of pressure.

After finishing the distillation the volume of the pressure distillate and the water that had collected during cracking were measured. The specific gravity of the pressure distillate was also determined. The pressure distillate was then analysed for its chemical constants such as acid value and saponification value (Tables XIII and XXI). It was then washed with water till free from soluble acids and dried over anhydrous sodium sulphate. The chemical constants of the washed distillate were again determined and its A.S.T.M. distillation was carried out. The washed pressure distillate was then fractionated under a fractionating column fitted with glass beads up to a height of 3 inch into (*i*) fraction boiling up to 225°, called crude motor fuel, and (*ii*) the higher fraction above 225°, called crude Diesel oil. The crude motor fuel was then analysed for its chemical constants (Tables XIV and XXII). It was then washed with caustic soda solution to remove the fatty acids as soap and then with water till free from alkali. The refined motor fuel and the crude Diesel oil were then subjected to A. S. T. M. distillations (Tables XVI, XVII, XXIV and XXV). The refined motor fuel was analysed for its unsaturated and aromatic contents by the method of (*i*) Egloff and Morrell[27] with a modification of Faragher, Morrell and Levine[28] and (*ii*) Morrel and Levine[29] (Tables XVIII and XXVI).

The volume of the gas collected during cracking was measured and its analysis was carried out both for its composition and calorific value after washing the gas with water and then storing the gas over water for complete removal of acraldehyde. As the gas was considerably rich in calorific power, it was diluted with a known volume of air before determining the calorific value (Tables XIX and XXVII).

TABLE X.

Expt. 1—5. *Cracking of groundnut oil by distillation under a pressure of* 45, 90, 135, 180 *and* 300 *lbs. per sq. in.*

Characteristic of the groundnut oil: acid value, 1·1; sap. value, 195·2; ester value, 194·1; iodine value, 93·3.

100 c.c. distillation of groundnut oil.

% Distilled over.	Temp.	% Distilled over.	Temp.
10	310·0°	60	324·0°
20	318·0	70	332·0
30	322·5	80	331·0
40	323·2	90	319·0
50	323·2	95	222·0

The specific gravity of the distillate was 0·867. A black tarry residue was left in the flask.

TABLE XI.

Expts. 6—10. *Cracking of mowrah oil by distillation under a pressure of* 45, 90, 135, 180 *and* 300 *lbs. per sq. in.*

Characteristics of mowrah oil: acid value, 14·2; sap. value, 185·2; ester value, 171·0; iodine value, 67·9.

100 c. c. distillation of mowrah oil.

% Distilled over	Temp.	% Distilled over	Temp.
10	311·0°	60	327·0°
20	315·0	70	329·0
30	316·0	80	324·0
40	320·5	90	312·0
50	321·0	94	247·0

The specific gravity of distillate was 0·862. A black tarry residue was left in the flask.

TABLE XII.

Pressure cracking of groundnut oil.

Experiment No.	1	2	3	4	5
Pressure of cracking (lbs./sq. in.) ...	45	90	135	180	300
Temp. of cracking ...	365-485°	365-485°	365-485°	365-485°	365-485
Pressure distillate (% of charge) ...	84·2	80·6	75·2	69·5	60·0
Sp. gr. of pressure distillate ...	0·843	0·820	0·805	0·795	0·780
Water (% of charge) ...	1·9%	2·5%	2·9%	3·1%	3·6%
Coke, gas and loss (% of charge) ...	13·9%	16·9%	21·9%	27·4%	36·4%
Coke (g./liter of oil) ...	40·3g.	57·7g.	72·2g.	75·8g.	89·1g.
Gas (litres/litre of oil) ...	93·3	127·6	152·4	161·8	196·7
Motor fuel (% of charge) ...	22·7%	35·0%	42·8%	43·8%	47·4%
Sp. gr. of motor fuel	0·773	0·762	0·765	0·768	0·762
Diesel oil (% of charge)	61·5%	45·6%	32·4%	25·7%	12·6%
Sp. gr. of Diesel oil	0·869	0·869	0·868	0·868	0·870

TABLE XIII.

Chemical constants of pressure distillate.

b=before washing. a=after washing.

Experiment No. ...	1		2		3		4		5	
	b	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*
Acid value ...	102·8	89·1	77·9	59·4	63·1	42·7	60·0	41·3	50·1	36·4
Sap. value ...	116·4	102·0	83·7	64·3	69·3	79·0	78·3	69·7	69·1	57·6
Ester value ...	13·6	12·9	5·8	4·9	6·2	6·3	18·3	19·4	19·0	21·2
Ester (%) ...	7·0	6·6	2·9	2·5	3·2	3·2	9·3	9·9	9·7	10·8

TABLE XIV.

Analysis of crude motor fuel.

Experiment No.	1	2	3	4	5
Acid value	66·3	42·6	36·3	28·2	25·5
Sap. value	70·9	45·0	39·3	31·6	28·4
Ester value	4·6	2·4	3·0	3·4	2·9
Ester (%)	2·4	1·2	1·5	1·7	1·5

TABLE XV.

A.S.T.M. distillations of washed pressure distillate.

Experiment No. ...	1	2	3	4	5
% Distilled over.	Temp.	Temp.	Temp.	Temp.	Temp.
10	141°	120°	111°	98°	88°
20	194	155	134	120	106
30	235	189	160	145	123
40	260	218	185	170	140
50	280	239	207	198	158
60	299	258	233	220	181
70	331	278	253	240	201
80	(76%) 339	303	275	260	226
90	(78%) 326	(86%) 320	317	294	263
		(88%) 318	(91%) 314	(95%) 320	(94%) 283
				(96%) 317	(96%) 279

TABLE XVI.

A.S.T.M. distillations of refined motor fuel.

	Experiment No.				
	1	2	3	4	5
% Distilled over.	Temp.	Temp.	Temp.	Temp.	Temp.
10	92°	100°	98°	96°	91°
20	105	114	111	108	103
30	115	125	121	118	113
40	124	135	131	129	124
50	136	145	142	140	135
60	148	158	152	151	146
70	161	172	166	165	160
80	177	189	180	179	174
90	199	202	202	200	194
95	221	224	219	217	209

TABLE XVII.

A.S.T.M. distillations of crude Diesel oil.

	Experiment No.				
	1	2	3	4	5
% Distilled over.	Temp.	Temp.	Temp.	Temp.	Temp.
10	242°	234°	236°	237°	233°
20	263	241	242	245	242
30	277	252	252	250	248
40	292	263	258	259	255
50	308	273	265	268	262
60	325	290	274	277	271
70	339	308	290	287	281
80	347	328	308	303	296
90	(84%) 346	337	328	330	330
		(94%) 349	(91%) 331	(94%) 342	(95%) 340
		(95%) 345	(92%) 324	(95%) 333	(96%) 336

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TABLE XVIII.

Hydrocarbon analysis of refined motor fuel.

The figures in the column (*i*) are according to the method of Egloff and Morrell with a modification of Faragher, Morrell and Levine and those in column (*ii*) are according to the method of Morrell and Levine.

Experiment No. ...	1		2		3		4		5	
	i	*ii*	*i*	*ii*	*i*	*ii*	*i*	*ii*	*i*	*ii*
Unsaturated (%) ...	11·0	41·6	30·0	40·1	12·0	45·7	16·6	39·2	18·0	37·3
Aromatics (%) ...	45·7	15·6	46·9	13·7	44·9	12·0	34·7	12·5	30·5	11·6
Naphthenes and paraffins(%)	43·3	39·8	40·1	46·2	43·1	42·3	48·7	48·3	51·5	51·1

TABLE XIX.

Analysis of the gas.

Expt. No.	1	2	3	4	5
CO_2 (%)	7·1	6·9	7·1	7·9	5·7
Olefines (%)	14·3	14·4	14·5	14·2	15·2
CO (%)	29·2	28·2	28·5	25·6	25·7
H_2 (%)	13·7	13·1	14·9	13·2	13·2
Sat. hydrocarbons ...	35·7	37·4	35·0	39·1	40·2
Calorific value B.T.U./Cu. ft. ...	778·8	953·1	975·9	1028·7	1135·5

TABLE XX.

Pressure cracking of mowrah oil.

Experiment No. ...	6	7	8	9	10
Pressure of cracking (lbs./sq. in.) ...	45	90	135	180	300
Temp. of cracking ...	358-485°	360-485°	365-485°	373-485	390-485°
Pressure distillate (% of charge)	87%	79·8%	74·1%	69·1%	59·6%
Sp. gr. of pressure distillate	0·840	0·809	0·796	0·784	0·776
Water (% of charge) ...	2·1%	2·9%	3·4%	3·5%	3·6%
Coke, gas and loss (% of charge)	10·8%	17·3%	22·5%	27·4%	36·8%
Coke (g./liter of oil) ...	39·1 g.	59·2 g.	63·8 g.	73·6 g.	79·3 g.
Gas (litres/litre of oil) ...	89·5	129·5	148·6	167·6	205·7
Motor fuel (% of charge)...	20·9%	33·9%	39·3%	44·5%	45·9%
Sp. gr. of mortor fuel ...	0·769	0·766	0·766	0·761	0·758
Diesel oil (% charge) ...	66·2%	45·9%	34·8%	24·9%	13·7%
Sp. gr. of Diesel oil ...	0·863	0·841	0·835	0·833	0·851

TABLE XXI.

Chemical constants of pressure distillate.

b = before washing. a = after washing.

Experiment No.	6		7		8		9		10	
	b	a	b	a	b	a	b	a	b	a
Acid value	101·2	89·0	72·1	62·3	61·5	48·9	52·2	39·5	50·1	38·2
Sap value	114·1	101·5	76·3	67·3	69·4	55·1	54·7	43·2	52·9	39·5
Ester value	12·9	12·5	4·2	5·0	7·9	6·2	2·5	3·7	2·8	1·3
Ester (%)	7·5	7·3	2·4	2·9	4·6	3·6	1·5	2·2	1·6	0·7

TABLE XXII.

Chemical analysis of crude motor fuel.

Experiment No. ...	6	7	8	9	10
Acid value	59·3	56·4	49·6	38·6	35·1
Sap. value	61·9	59·3	53·2	42·4	37·2
Ester value	2·6	2·9	3·6	3·8	2·1
Ester (%)	1·5	1·7	2·1	2·2	1·2

TABLE XXIII.

A.S.T.M. distillations of washed pressure distillate.

	Experiment No.				
	6	7	8	9	10
% Distilled over.	Temp.	Temp.	Temp.	Temp.	Temp.
10	158°	119°	116°	109°	98°
20	210	167	148	133	117
30	244	192	175	155	133
40	268	220	199	177	150
50	291	242	220	198	167
60	312	262	241	218	186
70	338	280	262	243	205
80	350	304	280	260	232
90	(88%) 365	328	317	290	264
		(94%) 336	(94%) 331	(95%) 327	(96%) 302

TABLE XXIV.

A. S. T. M. distillation of refined motor fuel.

	Experiment No.				
	6	7	8	9	10
% Distilled over.	Temp.	Temp.	Temp.	Temp.	Temp.
10	101°	98°	100°	97°	96°
20	116	110	113	108	108
30	126	121	124	121	119
40	137	132	135	134	130
50	149	142	146	144	140
60	160	159	157	154	152
70	171	166	167	165	164
80	183	179	180	176	177
90	197	197	195	193	199
95	218	218	(97%) 217	(97%) 217	(97%) 216

TABLE XXV.

A. S. T. M. distillation of crude Diesel oil.

	Experiment No				
	6	7	8	9	10
% Distilled over.	Temp.	Temp.	Temp.	Temp.	Temp.
10	246°	245°	239°	231°	229°
20	266	254	247	239	239
30	279	260	254	247	245
40	292	269	261	255	250
50	309	281	268	262	257
60	326	293	276	269	266
70	334	306	287	278	276
80	(78%) 329	324	301	289	292
		(87%) 337	(89%) 323	(90%) 307	(90%) 312
			(90%) 321	(95%) 332	(94%) 318

TABLE XXVI.

Hydrocarbon analysis of refined motor fuel.

The figures in column (*i*) are according to the method of Egloff and Morrell and in column (*ii*) are according to the method of Morrell and Levine.

Expt. No. ...	6		7		8		9		10	
	i	*ii*	*i*	*ii*	*i*	*ii*	*i*	*ii*	*i*	*ii*
Unsaturated (%) ...	—	42·4	—	40·6	20·4	37·9	17·6	38·1	19	34·2
Aromatics (%) ...	—	17·2	—	18·6	39·4	20·5	35·3	15·7	30·3	13·6
Naphthenes and paraffins (%)	—	40·4	—	40·8	40·2	41·6	47·1	46·2	50·7	52·2

TABLE XXVII.

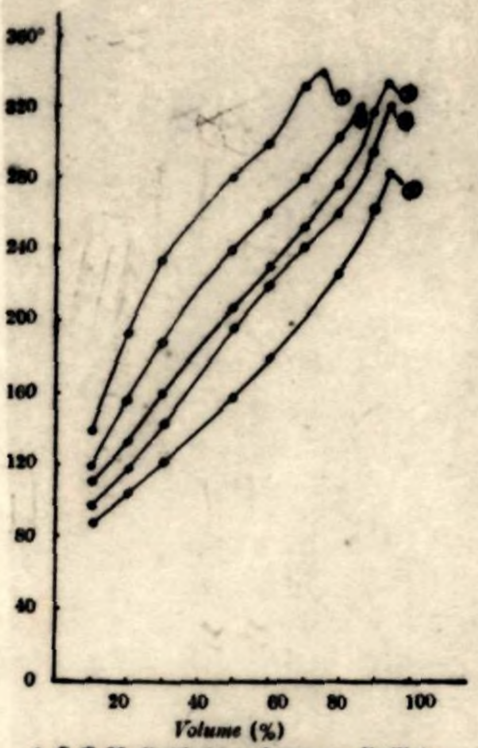
Analysis of the gas.

Experiment No. ...	6	7	8	9	10
CO_2	7·7%	8·3%	6·8%	5·9%	5·4%
Olefines	13·3	13·5	14·1	14·4	15·6
CO	31·6	33·4	29·5	26·7	22·5
H_2	15·7	16·1	15·6	13·6	11·0
Saturated hydrocarbon ...	31·7	28·7	34	39·4	45·5
Calorific value (B.T. U./cu. ft.).	816·6	888·8	984·8	1022·9	1168·6

DISCUSSION.

The cracking of mineral oils consists of a complex series of chemical reactions involving both decomposition and polymerisation, the nature of the ultimate products and the degree of cracking being determined mainly by the character of the charging stock, the temperature and pressure of cracking, the time of

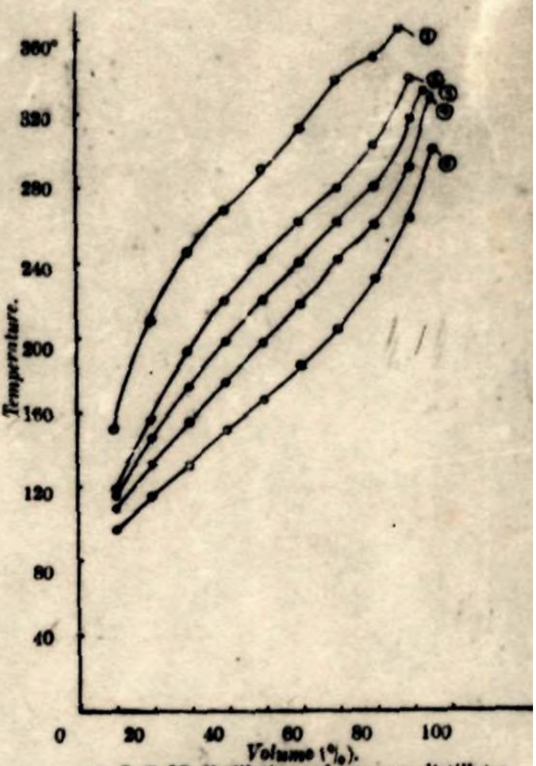
FIG. 8.



A. S. T. M. distillations of pressure distillates from groundnut oil.

Curves 1—5 refer respectively to 45, 90 135, 180 and 200 lbs. pressure/sq. in.

FIG. 9.



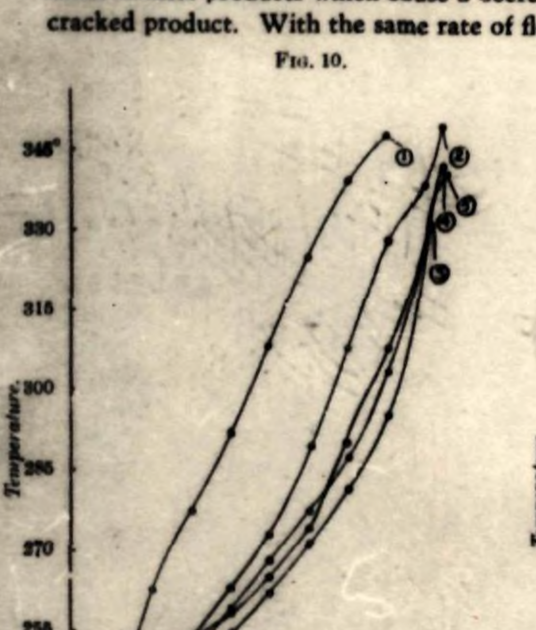
A. S. T. M. distillations of pressure distillates from mowrah oil.

Curves 1—5 refer to the same amounts of pressure as in Fig. 8.

exposure to the cracking conditions, the catalyst used and on the conversion per pass, where recycling is employed. From the results of the various experiments carried out to crack the vegetable oils by three different methods, it can be seen that all the above facts play an equally important role in the cracking of vegetable oils.

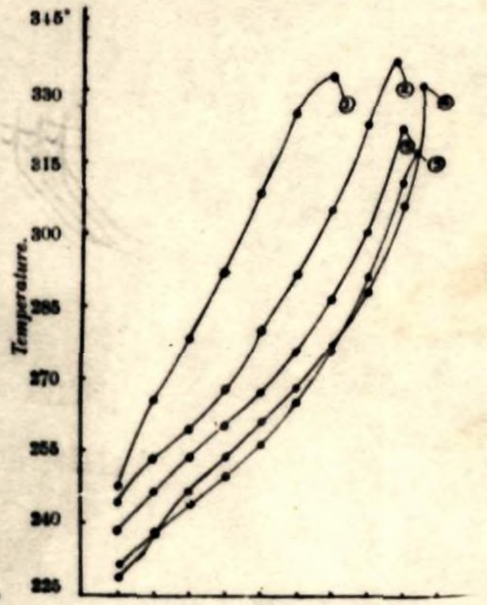
Temperature.—The experiments on tube cracking clearly bring out the fact that the degree of cracking is closely related to the temperature at which the cracking is carried out. It has been found that with the rise in temperature, the amount of decomposition increases as indicated by the percentage of the ester decomposed and decrease in saponification value. The glycerides are first broken up to a large extent into fatty acids and acraldehyde between temperatures of 400° and 450°. The fatty acids are then further decomposed to hydrocarbons or other neutral products which cause a decrease in the saponification value of the cracked product. With the same rate of flow, the degree of cracking is enhanced with the rise in temperature of cracking. But temperatures higher than 450 seem to be unfavourable especially when cracking takes place in presence of

FIG. 10.



A.S.T.M. distillations of crude Diesel oil from groundnut oil.
Curves 1-5 refer to the same amounts of pressure as in Fig. 8.

FIG. 11.



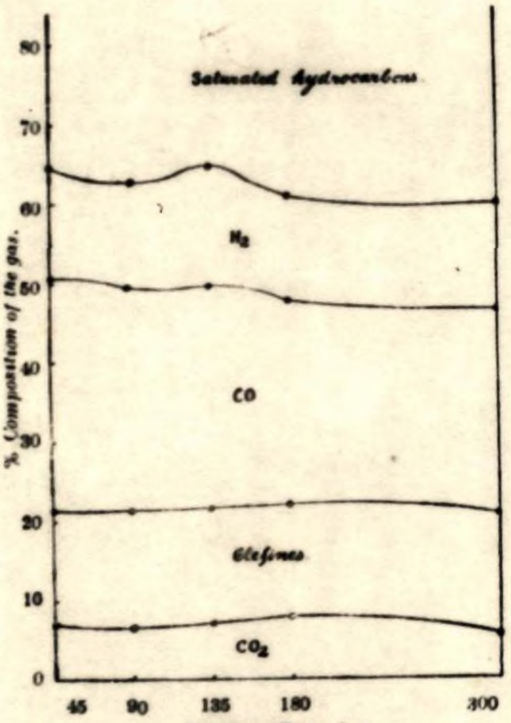
A. S. T. M. distillations of crude Diesel oils from mowrah oil.
Curves 1-5 refer to the same amounts of pressure as in Fig. 8

metallic surfaces, since the products undergo carbonisation to some extent resulting in deposition of carbon on the metallic surface exposed, with a consequent decrease in the efficiency of the catalyst.

Time.—The time for which the oil is exposed to the conditions of cracking also affects the degree and the nature of the cracked products. Thus in the experiments on cracking in a tube at a constant temperature, decomposition increases with a decrease in the rate of flow of oil. Here also this observation does not hold good above 450° due to carbonisation effect. When the cracking is carried out by distillation in presence of metallic salts as catalysts, more cracking is effected by prolonging the time required for distillation.

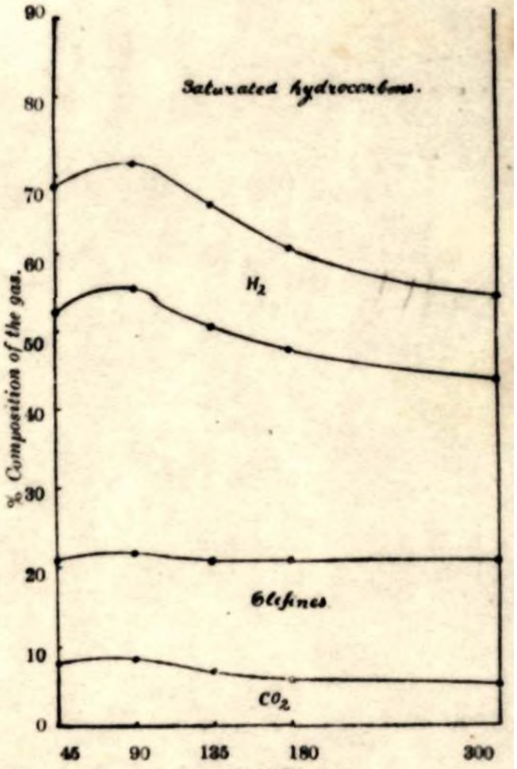
Character of the Oil.—Comparison of the results of various experiments on the cracking of different oils under the same conditions indicates that the nature of the cracked products and the extent of decomposition depend to a great extent on the nature of the oil used. Thus, when the cracking of oils is carried out in a hot glass tube, it is observed that in the case of coconut oil, which contains a very small percentage of unsaturated acids, decomposition does not proceed

FIG. 12.



Ground-nut oil

FIG. 13.



Mowrah oil.

further than the formation of fatty acids; while in the case of other three oils, *viz.*, groundnut, mowrah and sesame oils containing large percentages of unsaturated acids, the acid and the saponification values go on decreasing continuously with the increase in temperature indicating clearly a further decomposition of the fatty acids into neutral products. The same thing is observed when cracking of oils is carried out by distillation in presence of various percentages of metallic salts as catalysts. In the case of coconut oil the acid and the saponification values remain nearly constant, whereas in the case of groundnut oil these values decrease with the increase in the amount of catalyst used. The analysis of the gas obtained during these cracking experiments also indicates that with the increase of the percentage of unsaturated acids in the oil, the percentages of carbon dioxide and carbon monoxide decrease, while those of saturated hydrocarbons and olefines increase. The volume of the gas obtained, the aqueous layer in the distillate and the amount of residue together with the gasoline fraction and its distilling range increase with the increase in the unsaturation of the oil for the same amount of catalyst used.

Catalyst.—The presence of substances like anhydrous calcium chloride and zinc chloride also affects the decomposition taking place to a considerable extent. The action of zinc chloride is found to be slightly different and more vigorous than that of calcium chloride. It is also found that increase in the amount of catalyst used results in the decrease in the amount of cracked oil and an increase in the amount of residue and aqueous layer. The distilling range of the oil is also reduced with a simultaneous decrease in its specific gravity. The formation of neutral products increases with the increase in the amount of catalyst in the case of groundnut oil.

Recycling or Recracking.—The cracking of oils is considerably affected by redistilling the cracked distillate in presence of either solid distillation residue or a fresh catalyst. This is clearly indicated by a comparison between the chemical constants of the first and second distillates. There is a considerable reduction in the values of the chemical constants. On the other hand, if the oil is simply heated in presence of a catalyst under a reflux condenser, thus bringing the cracked products into reaction zone again and again, the degree of cracking is not enhanced as the temperature of reaction goes on decreasing to a considerable extent due to the accumulation of low boiling cracked products.

Pressure.—The experiments of cracking these oils under pressure readily indicate that pressure influences the nature of cracked products and the degree of cracking to a considerable extent. In general, when the results obtained by cracking oil under pressure are compared with those of the other two methods, it appears that in the case of cracking under pressure the gasoline fraction is very high, while the amount of solid residue comparatively low. The amount of pressure distillate decreases while the gasoline fraction in the preassure distillate increases with increase in pressure. The increase in the amount of gasoline is not directly proportional to pressure, since above 135 lbs. pressure the gasoline fraction obtained does not so rapidly increase as it does at lower pressures. On the other hand, the amount of Diesel oil decreases with the increase in pressure. A comparison of the acid values and saponification values of pressure distillate shows that they also decrease with increase of pressure.

The results of gas analysis still bring out another fact, *viz.* that the percentages of carbon dioxide, carbon monoxide and hydrogen go on decreasing as the pressure increases, while the percentage of the saturated hydrocarbons increases. In this connection it might be mentioned that Ipatieff[30] has already observed in his work on the decomposition of organic substancs that the percentages of carbon monoxide and hydrogen decrease with increase in pressure due to their combination to form methane and other hydrocarbons, an observation which was used by him to support the organic hypothesis of the formation of petroleum. The calorific value of the gas obtained during cracking also increases with the increase in pressure.

Utilisation of the Products of Cracking.—It would be clear that the cracking of vegetable oils under pressure yields different products like gasoline, Diesel oil and gas having a high thermal value with the simplest possible equipment. The nature of the cracked products can be well regulated by proper adjustment of pressure. The products of cracking, *viz.*, gas, liquid distillate and coke, can very well be used for various purposes other than fuel. The analysis of motor fuel indicates considerable proportions of unsaturated with 15—20% of aromatics. These can be separated and utilised for the the production of synthetic chemicals of the type of alcohol solvents, rubber-like substances and resinons products. The aromatics may be utilised as basic material for various industrial preparations. The gas produced can also serve a duplicate purpose as it can be utilised both for heating purposes as well as for the production of synthetic chemicals from its olefinic contents. The calorific value of the gas is nearly 2-2·5 times the calorific value of ordinary city gas.

CONCLUSION.

With the increase in pressure, the initial temperature at which the distillation starts, rises from 365° to 395° in the case of groundnut oil and from 358° to 390° in the case of mowrah oil. The amount of pressure distillate and its specific gravity decrease with increase in pressure. The amount of water, coke and gas produced during cracking, increase with increase in pressure (Figs. 6 and 7).

The percentage of motor fuel and in the pressure distillate increase while the percentage of Diesel oil falls with the increase in pressure (Figs. 6 and 7). The acid value of the washed pressure distillate decreases with increase in pressure (Fig. 4). The higher acid values of pressure distillates before washing (Tables XIII and XXI) show that soluble fatty acids are formed during cracking. The acid value of crude motor fuel goes on decreasing with increase in pressure (Tables XIV and XXII).

The A. S. T. M distillations of washed pressure distillates and of the crude Diesel oils, obtained from these, show that comparatively low boiling distillates are obtained with increase in pressure (Fig. 8-11), while the refined motor fuels have nearly the same boiling range on A. S. T. M. distillation. The calorific value of the gas increases with increase in pressure.

The percentages of saturated hydrocarbons and olefines in the gas increase while the percentages of CO. H_2 and CO_2 decrease with increase in pressure.

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REFERENCES.

1. *Oil Col. Trades J.*, 1938, **23**, 1249.
2. Walton, *Gas Oil Power*, 1938, **33**, 167.
3. Greenly, *J. Inst. Fuel*, 1938, **12**, 1.
4. Hilditch, "Fats and Waxes", 1927, pp. 147-48.
5. Engler, *Ber.*, 1888, **22**, 1816.
6. *Compt. rend.*, 1921, **173**, 358,
7. *Ibid.*, 1921, **173**, 658.
8. *Bull. Soc. chim.*, 1922, **31**, 567.
9. *Ann. chim.*, 1922, 17, 304.
10. *J. Usines Gaz.*, 1923, **47**, 65.
11. *Bull. Soc. chim.*, 1922, **31**, 249.
12. Mailhe, *Compt. rend.*, 1922, **174**, 873 ; *Bull. Soc. chim.*, 1922, **31**, 863.
13. Kobayashi. *J. Soc. Chem. Ind. Japan*, 1921, **24**, 1.
14. *Ibid.*, 1921, **24**, 1399.
15. Mailhe. *Compt. rend.*, 1923, **177**, 202, 329.
16. Gallo & Correli. *Atti Congresso. Naz. Chim. Pura Application*, 1923, p. 257.
17. Melis, *ibid.*, 1924 p. 238.
18. Sato, *J. Soc. Chem. Ind. Japan*, 1926, **29**, 109 ; 1927, **30**, 242.
19. Haga, *ibid*, 1927, **30**, 618.

20. Chang & Chang. *J. Chinese Chem. Soc.*, 1934, **2**, 211 ; *J. Chem. Eng. China*, 1935, **2**, 32.

21. Ping. *J. Chinese Chem. Soc.*, 1935, **3**, 95.

22. Faragher, Morrell & Levine, *Ind. Eng. Chem.*, 1932, **24**, 440.

23. *J. Soc. Chem. Ind.*, 1932, **51**, 133 T.

24. Egloff & Morrell. *Ind. Eng. Chem.*, 1932, **24**, 1426.

25. Shinozaki, Kagwa & Sato, *J. Soc. Chem Ind. Japan*, 1936, **39**, 22B.

26. Abder Halden. *Mat Grasses*, 1938, **29**, 194.

27. Egloff & Morrell, *Ind. Eng. Chem.* 1926, **18**, 354.

28. Faragher, Morrell & Levine *Ind. Eng. Chem. Anal. Ed.*, 1930, **2**, 18, 321.

29. Morrell & Levine, *ibid.*, 1932, **4**, 321.

30. Ipatieff, *J. pr. Chem.*, 1911, **84**, 800.