HYDROGENATION OF OILS BY THE CONTINUOUS PROCESS.

PART II. HYDROGENATION OF COTTONSEED AND OLIVE OILS BY NICKEL CARBONATE—KIESELGUHR CATALYST.

By V. T. Athavale and S. K. K. Jatkar.

INTRODUCTION.

In Part I (*This Journal,* 1937, **20A**, 95–109) the activities of the various catalysts prepared from nickel and its alloys in a wire form, were studied by the continuous flow method. It was shown that the wire form of the catalyst could be easily prepared, nickel wire yielding the best results. Difficulties were subsequently met with, in anodically oxidising the nickel wire owing to its having become passive, and also in reoxidising the nickel wire catalyst after being used for a long time, due to the formation of the oxide layer on the surface of the wire, which was non-conducting. It was therefore necessary to find out a method of utilising the precipitated catalyst in a form suitable for continuous operation and to compare the activities of the various catalysts in the same apparatus under the same conditions. As already mentioned the precipitated catalysts were used in the form of cylindrical rods about ⅛″ thick, prepared by pressing the semi-dried precipitated catalysts through an orifice under high pressure. The present paper deals with the hydrogenation of cottonseed and olive oils by nickel carbonate—kieselguhr catalyst.

EXPERIMENTAL.

The apparatus used and the method of experimentation were the same as those described in Part I (*loc. cit.*).

Preparation of Catalyst.—The catalyst was prepared by precipitating nickel carbonate by adding sodium carbonate to a solution of nickel nitrate at 60° C. in presence of kieselguhr, sufficient to give the ratio of nickel : kieselguhr in the catalyst as 1 : 4. After washing and partial drying, the precipitate was forced through a small orifice under a pressure of 15 tons/sq. inch, so that the rods had a compact structure. 70 grams of the catalyst were reduced at 400° for 17 hours.

The oils used had the following constants:— (1) *Refined cottonseed oil:* Acid value 0.2; $n_D^{60} = 1.4575$; Iodine value (Hanus) 105.3; Iodine value of the liquid fatty acids 133.8; composition: olein 42.9%, linolein 39.3% and saturated glycerides 17.8%. The composition was calculated from the iodine values of the original oil and of the liquid fatty acids.

(2) *Olive Oil from Palestine*:—Acid value 0.3; n_D^{60} = 1.4545; Iodine value (Hanus) 82.2; Iodine value of the liquid fatty acids 97.0; composition: olein 82.0%, linolein 6.6% and saturated glycerides 11.4%.

The yields were calculated from the measurements of the refractive indices of the hardened oils by using the relation given by Athavale, Sudborough and Watson (*cf.* Part I).

The yields at various temperatures and rates of the flow of oil are shown graphically in Fig. 1.

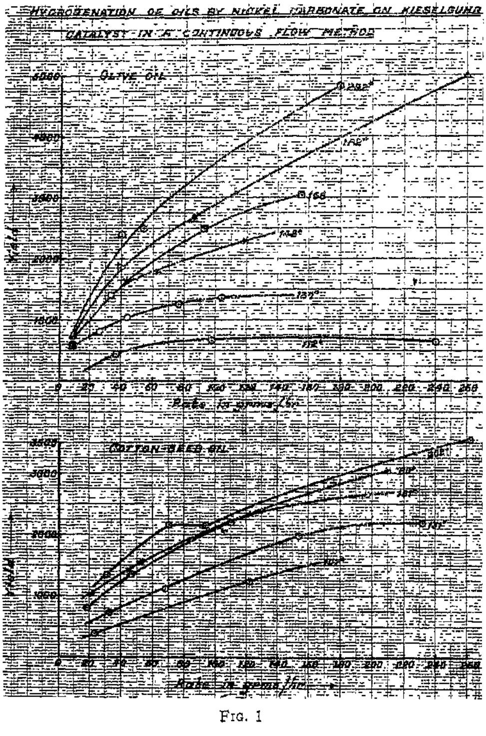

FIG. 1

The velocity coefficients (K) calculated in the same manner as for the different catalysts described in Part I, are shown in Fig. 2, where K is plotted against the rate.

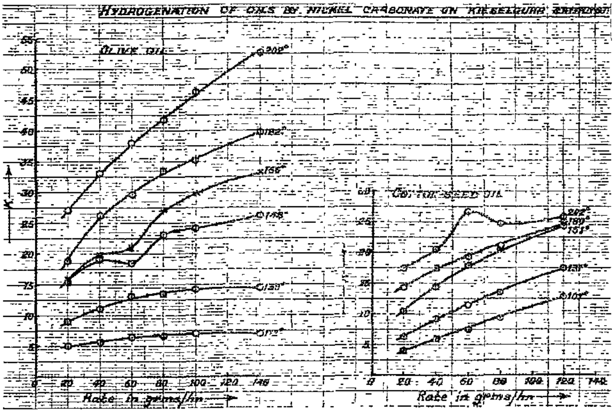

FIG. 2.

With cottonseed oil, the velocity increases practically linearly with rate at 107° and 131° but as the temperature is raised the curves deviate from linearity. At 200° a definite maximum in the curve is obtained at a rate of 60 grams of oil per hour. With olive oil on the other hand, the curve is practically linear at 200°, while at 150° and 170° the curves are irregular.

TEMPERATURE COEFFICIENT.

The change in the velocity coefficient with temperature for the oils hydrogenated by the same catalyst is shown in Fig. 3. The results for groundnut oil shown in the figure will be published in the near future.

Two curves for each oil with the rates of 40 and 100 grams of oil per hour respectively, have been given. With olive oil the curve is composed of two parts; the velocity rising continuously from 100° to 150° where a break is shown in the curve especially with a rate of 40 grams/hr., after which the velocity rises continuously up to 200°. With cottonseed oil at the rate of 100 grams of the oil per hour, the velocity rises continuously up to 150° but no further rise is observed even after raising the temperature to 200°.

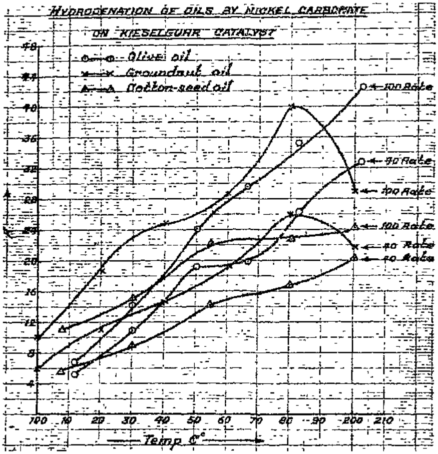

FIG. 3.

It appears therefore that the change in the composition of the oil has a considerable effect on the velocity with which hydrogen is absorbed at any temperature and also on the temperature coefficient of the reaction.

In order to investigate whether any glyceride is selectively hydrogenated at a particular temperature, the composition of the samples of hardened cottonseed oil were determined. The method was based upon the determination of the thiocyanogen and the iodine numbers of the hardened oil and calculating the composition from these values. Although necessary precautions were taken to prepare the thiocyanogen reagent, it was found that the analysis so obtained was too far out from the actual composition. As however, all the determinations of the thiocyanogen numbers of the hardened and original oils were done simultaneously with the same stock of reagent, the error in the calculated percentages of the glycerides will be systematic. The results based upon these values, though they are only of a qualitative nature have confirmed some of the conclusions arrived at by other investigators. The velocity coefficients for the linolein to olein and olein to stearin reactions were calculated separately, based upon the above analysis. For the linolein to olein reaction,

a in the equation $K = \frac{2 \cdot 3}{t} \log \frac{a}{a - x}$, is the percentage of linolein in original oil and $(a - x)$ is the percentage of the same in the hardened oil. For the olein to stearin reaction a is the initial percentage of olein in the oil *plus* the logarithmic mean of the linolein changed to olein at a particular time of contact and $(a - x)$ is the percentage of olein in the hardened product. Fig. 4 shows the relation between the temperature and the velocity coefficients, K_1 and K_2 calculated in the above manner for the two reactions.

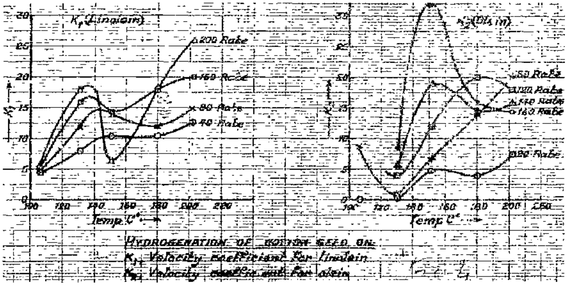

Fig. 4.

The curves for linolein to olein reaction show maxima at about 125°. The difference in the velocities at 180° and 200° is not very great except at the rate of 200 grams of oil per hour. The curves for the olein to stearin reaction are the reverse of those in the former case. The velocity at 125° is minimum but rises to a high value at 150°, the velocity at 200° being slightly higher than that at 180°. It appears from these results that there is a preferential hydrogenation of linolein at 125° and of olein at 150°, above which the velocity of hydrogenation of both the olein and the linolein increases continuously.

The course of hydrogen of the glycerides in cottonseed oil can be followed from the triangular diagram (Fig. 5). The figure indicates that at 107° and 130° the reaction is exclusively the hydrogenation of linolein to olein. At 154°, with faster rate the linolein changes to olein without much rise in saturated glycerides but at low rates the selectivity disappears. At 182° with faster rates the linolein changes to olein without appreciable change in saturated glycerides. As the rates decrease the main change observed

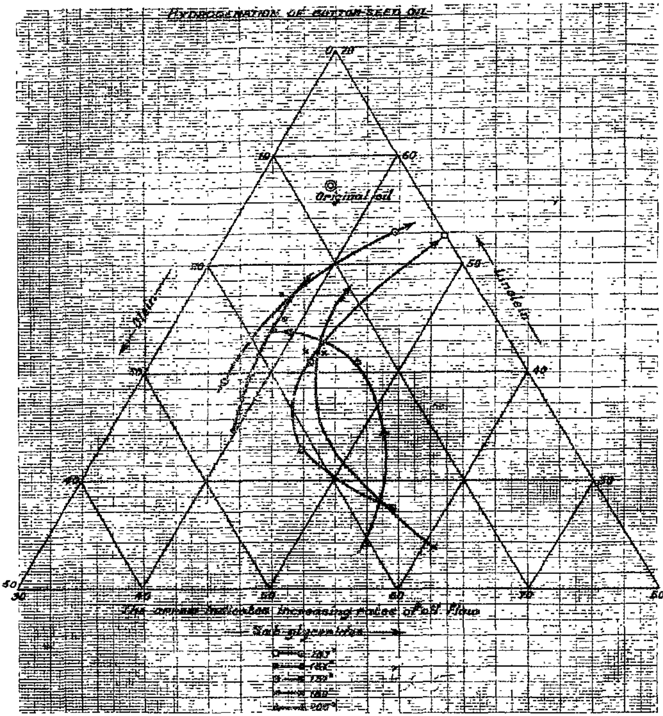

Fig. 5.

is the disappearance of linolein and an increase in the saturated glyceride, the percentage of olein remaining practically constant. At 200°, with comparatively faster rate, both linolein and olein hydrogenate to stearin and at slow rates the percentage of olein remains sensibly the same, the apparent reaction being the hydrogenation of linolein straight to stearin. Thus although the reaction is selective at 125° and 150°, at higher temperatures there is no appreciable difference in the velocities of the two reactions.

In this connection, a fundamental difference between the hydrogenation by the batch process and by the continuous process may be pointed out. It has been shown by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, **96A**, 137), and many others, that in the hydrogenation of oils containing linolein and less saturated glycerides by the batch process, the linolein is hydrogenated almost entirely to glycerides of oleic acid or its isomer before glycerides of saturated acids begin to form. The effect is, in general, incomplete since small amounts of saturated glycerides are formed as soon as the proportion of glycerides of linoleic acid has dropped to less than 10% of the oil. Lush (*J.S.C.I.*, 1923, **42**, 2147; 1924, **43**, 53 T; 1924, **44**, 129 T) on the other hand in his experiment on hydrogenation of cottonseed and olive oils in presence of activated nickel turnings, and Cocchinaras (*J.S.C.I.*, 1932, **51**, 403–4 T) during his investigation on the hydrogenation of linseed oil, found that the increase in saturated glycerides begins right from the commencement. Thus in the continuous process of Lush, the hydrogenation of linolein and olein proceed simultaneously. As the selectivity persists in our experiments also, the nature of the catalyst, and not the process, seems to be the deciding factor in the selective hydrogenation.

It has been shown in Part I, that for the nickel wire catalyst, the velocity coefficients at different rates were fairly constant. From Fig. 2 given above, it will be noticed that the velocity coefficients at any temperature change with rates, and if the two are plotted, curves are obtained, which are similar to the yield-rate curves given previously. Thus the variation of K with rates shows that the velocity is influenced by factors other than the mere time of contact. Similarly, the nature of the curves at different temperatures is not the same. The change of K with rate can be expressed in terms of an equation similar to the one given by Freundlich for adsorption process in solution, *viz.*, $\mu = ax^{1/n}$, where μ is the amount adsorbed and x the concentration in solution, a and n being positive constants.

The velocity coefficient K as calculated above is the amount of reaction in unit space and may be substituted in place of μ in the above equation, as the catalytic activity is due to the association between the unsaturated glyceride and the nickel. The formation of the complexes between the unsaturated compound and nickel, will depend on the amount of oil coming into contact with the catalyst in unit time, and therefore, K will be a function of the rates with which the oil is flowing over the catalyst. The equation thus becomes $K = K'(\text{Rate})^{1/n}$ where K' and n are positive constants.

The variation of the velocity coefficients (K) with rates could be expressed by the above equation. Tables I and II give values for K′

for cottonseed oil and olive oil for different temperatures. The values of n varied with temperature and the nature of the oil.

TABLE I.

Cottonseed oil.

Rate grams/hr.	K′ at temperatures °C.				
	107	130	151	180	200
	$n = 1·5$	$n = 1·7$	$n = 2·0$	$n = 3·0$	$n = 4·0$
20	(·54)	1·03	(2·05)	(5·28)	8·20
40 .. .	·48	1·05	2·26	4·97	8·12
60 . .	·48	1·03	2·29	4·88	9·53
80	·49	1·00	2·29	4·85	8·22
120	·52	1·02	2·22	5·05	7·70
Mean K′ ..	0·49	1·03	2·26	4·92	8·20

TABLE II.

Olive oil.

Rate grams/hr.	K′ at temperatures °C.						
	112	130	148	166		182	200
	$n = 4$	$n = 4$	$n = 4$	$n = 4$	$n = 3$	$n = 3$	$n = 3$
20	2·37	(4·26)	(7·25)	7·64	5·91	(6·93)	9·96
40	2·19	4·38	7·60	7·85	5·76	7·66	9·62
60	2·26	4·64	7·69	7·48	5·31	7·57	9·59
80	2·24	4·51	7·69	8·90	6·21	7·68	9·65
100	2·15	4·58	7·60	9 37	6·37	7·56	9·96
140	(1·91)	(4·16)	7·61	9 53	6·32	7·65	10·17
Mean K′ ..	2·24	4·54	7·54	8·46	5·98	7·62	9·82

It can be seen from the tables that the values of K′ at the various temperatures are in fair agreement for different rates,

SUMMARY.

(1) The nature of the yield-rate curves with different oils hydrogenated with the same catalyst depends on the composition of the oil. (2) Calculations of the velocity coefficients (K) by the unimolecular formula do not give concordant results. (3) The velocity coefficients (K) when plotted against temperatures show irregularity in the curves at 125°, 150°, 180° and above 200°, depending on the composition of the oil. Thus maximum activity is observed at 150° and above 200° with olive oil, and at 150° for cottonseed oil. (4) The analysis of the samples of hardened cottonseed oil shows that the velocity of hydrogenation of olein is maximum at 150° while that of the hydrogenation of linolein is maximum at 125°, due to the selective hydrogenation. At temperatures above 160° the tendency of linolein to change straight to stearin increases, because the olein formed hydrogenates with equal velocity. (5) The variation in the velocity coefficients with rates can be expressed by the formula $K = K' (\text{Rate})^{1/n}$ in the case of all the oils, concordant results for K′ being obtained. The value of n varies with the oils, and the temperature of hydrogenation. (6) The corrected velocity coefficients when plotted against temperatures show maxima at 150° and above 200°. The high velocity coefficients above 200° are common to all the oils but the value at 150° depends on the composition of the oil being more pronounced with higher percentage of olein in the oil.

Department of General Chemistry,
Indian Institute of Science,
Bangalore (India).

[Received, 26–9–1938.]

1624-38—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent