

HYDROGENATION OF OILS BY THE CONTINUOUS PROCESS.

PART IV. KINETICS OF THE HYDROGENATION OF GROUNDNUT OIL BY PRECIPITATED NICKEL CATALYSTS.

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INTRODUCTION.

In Parts I and II (*This Journal*, 1938, 21A, 95-109; 285-293) it was shown that the velocity coefficients (K) at different rates of flow of the oil were concordant in the case of nickel wire catalyst for the hydrogenation of groundnut oil, and in the case of nickel carbonate-kieselguhr catalyst the variation of the velocity coefficients (K) for the hydrogenation of olive oil and cottonseed oil could be expressed by an equation $K = K' (\text{Rate})^{1/3}$ which gave concordant values for K' . The temperature coefficients of the velocity constants indicated the presence of a number of maxima and minima in the case of both the wire catalysts and the precipitated catalysts. Analysis of the hardened cottonseed oil indicated a selective hydrogenation of olein at 150°.

These results could be explained on the basis of the relative velocity of hydrogenation of linolein and olein in the oil. But the absence of similarity in the behaviour of any two catalysts appeared to be due to the difference in the heterogeneity of the catalyst surface as well as to the difference in the composition of the oil. It was, therefore, thought that a study of the hydrogenation of the oils of different compositions with different catalysts would bring out the relative influence of the component glycerides, and might give a clue to understand the nature of the catalyst surface. The present paper deals with the kinetics of hydrogenation of the groundnut oil by nickel carbonate-kieselguhr, unsupported nickel carbonate, nickel hydroxide-silica gel and nickel peroxide-kieselguhr catalysts. The experimental results on the comparative efficiency of the different preparations of the precipitated catalysts for the hydrogenation of oils in the continuous process from the technical point of view, will be published in the near future.

EXPERIMENTAL.

The apparatus used and the procedure followed was the same as that described in Part I.

The groundnut oil used in all the experiments with different catalysts was from the same bulk of the oil as used in Part I.

(1) The nickel carbonate-kieselguhr catalyst was prepared in the same way as described in Part II. 70 grams of the catalyst were reduced at 400° for about 17 hours. The activity of the catalyst was measured by passing the oil at different rates through the catalyst at different temperatures. The percentage conversion was determined from the change in the refractive index of the samples as in Part I. It was found that the activity of this catalyst was as good as that of the nickel wire. The details of these experiments will be published in the near future. In the present paper we will discuss the velocity coefficient of the reaction as calculated from the equation $K = \frac{2.3}{t} \log \frac{a}{(a-x)}$ where x is the percentage conversion at a particular rate and t is the time of contact, which is inversely proportionate to the rate of flow of the oil over the catalyst. It has already been shown in Part II that this velocity coefficient is subject to a further correction for the effect of adsorption which is given by the expression $K = K' (\text{Rate})^{1/n}$ where K' is the corrected velocity coefficient. The results are given in Table I.

TABLE I.
Nickel carbonate-kieselguhr catalyst (thin rods).

Temp. °C.	Rate grams/hr.						Mean K'
	20	40	60	80	100	140	
100 K	3.5	6.0	7.7	8.6	9.7	10.5	0.95
K'	(0.78)	0.95	0.99	0.96	0.97	0.90	
120 K	7.3	11.5	14.3	16.3	17.9	19.2	1.82
K'	(1.66)	1.82	1.86	1.83	1.79	(1.63)	
140 K	9.1	14.8	18.9	21.7	24.1	28.8	2.43
K'	(2.09)	2.34	2.44	2.42	2.41	2.44	
160 K	16.4	18.5	21.1	23.8	26.4	31.4	2.67
K'	(3.67)	2.92	2.72	2.66	2.64	2.66	
180 K	18.3	26.1	29.3	33.9	38.0	44.6	3.79
K'	(4.10)	4.13	3.78	3.79	3.80	3.77	
200 K	18.3	21.7	24.3	25.7	27.2	28.8	8.66
K'	4.10	3.44	3.14	2.88	2.72	2.44	
K''	8.67	8.65	8.77	8.61	8.59	(8.38)	

As in the case of the hydrogenation of the cottonseed oil and olive oil, the velocity coefficient K at any temperature varied with the rates. The values of K' are, however, fairly concordant for temperatures between 100° – 180° when n was equal to 2. At 200° K' decreased with increasing rates when n was equal to 2, and K'' was fairly constant when n was taken as 4.

The values for the velocity coefficient K , when the same catalyst was used in the form of thicker rods which had a more porous structure, are given in Table II. The amount of the catalyst used to fill up a length of 17 inches of the reaction tube was 43 grams.

TABLE II.
Nickel carbonate-kieselguhr catalyst (thick rods).

Rate grams/hr	K at temperatures $^{\circ}$ C.					
	95	120	140	160	180	200
20	4.4	6.0	8.6	10.9	16.4	18.3
40	3.8	7.0	10.4	12.3	18.4	24.6
60	3.1	5.0	8.1	12.8	19.9	24.9
80	1.6	3.5	5.1	13.2	21.8	20.6
100	1.3	3.2	4.0	12.9	21.6	18.1
140	1.0	2.5	4.0	12.7	23.0	18.0

The results for the velocity coefficients show that the velocity decreases with increasing rate between 95° – 140° and remains fairly constant between 160 – 200° .

(2) Nickel carbonate catalyst was prepared by precipitation, adding sodium carbonate to nickel nitrate solution. The precipitate was washed and drawn in the form of rods, which showed considerable shrinkage on drying and reduction at 400° . 150 grams of the air-dried catalyst were used in the reaction tube and occupied a length of 6 inches of the tube on reduction. Oil was passed over the catalyst at different rates and the velocity coefficients were calculated from the percentage conversion. The results for K calculated for the full length (17") of the tube are given in Table III, from which it will be seen that the values of K increase with rates at temperatures above 160° , while at lower temperatures the velocity coefficient rises to maximum and then falls.

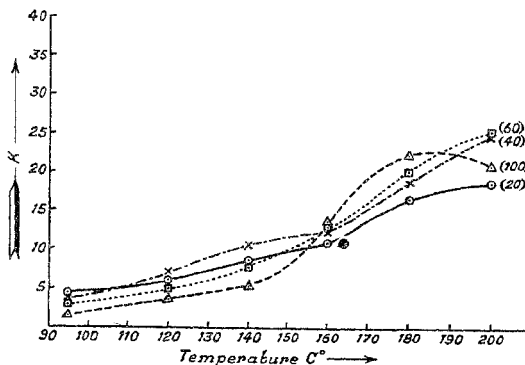
TABLE III.
Unsupported nickel carbonate catalyst.

Temp. °C.	K		Temp °C.	K	
	30 grams/hr.	100 grams/hr.		30 grams/hr.	100 grams/hr.
96	33.0	34.2	159	84.4	100.8
104	33.0	34.2	170	100.6	120.4
114	34.2	34.2	184	120.6	160.0
124	40.4	34.2	200	132.6	186.0
135	47.7	34.2	208	159.0	164.0
149	68.2	62.6			

THE TEMPERATURE COEFFICIENT OF THE REACTION.

The rate at which the velocity of reaction changes with temperature is shown diagrammatically in Figs. 1 and 2 where K at different rates is plotted against the temperature.

VELOCITY OF HYDROGENATION OF GROUND NUT OIL AT DIFFERENT TEMPERATURES WITH NICKEL CARBONATE ON KIESELGUHR CATALYST.
(Figures in brackets indicate rate of the oil)



40 grams of thick rods. 20% Ni

○—○ 20 Rate

×—× 40 "

□—□ 60 "

△—△ 100 "

FIG. 1.

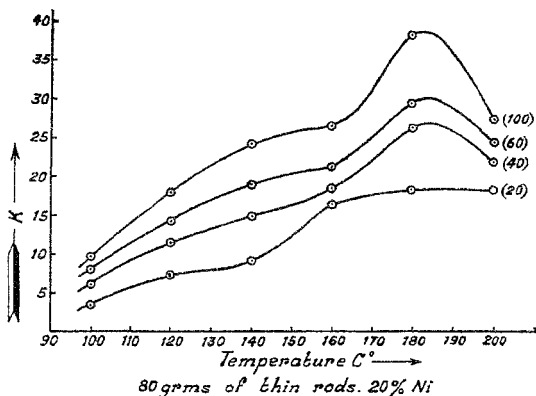


FIG. 2.

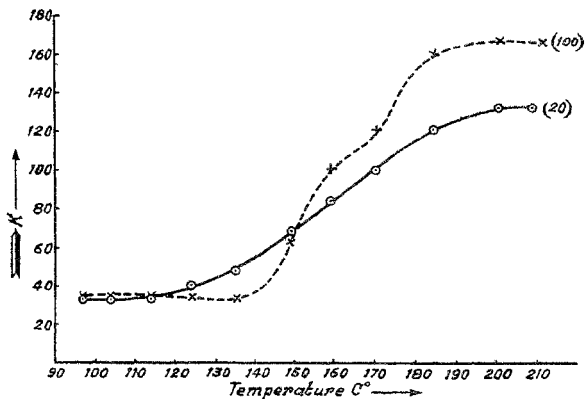
Figs. 1 and 2 refer to the results with two catalysts both prepared from nickel carbonate supported on kieselguhr and containing 20% nickel, the only difference in the two being in the porosity and thickness of the rods so that different quantities of the catalyst were required for same length of the reaction tube. The curve with the thin rods of the catalyst shows the presence of two maxima at about 140° and 180°, which become more and more pronounced as the rates of the oil are increased. The velocities with the catalyst when the rods were more porous are low at all temperatures because of the lesser amount of active nickel in the reaction tube. Simultaneously the maximum at 140° is much less pronounced and the one at 180° disappears at the rates of 20, 40 and 60, while at the rate of 100 grams of oil per hour, the curve shows only one peak at 180°.

It is thus clear that the various peaks in the K-temperature curves, are brought out at a higher rate of flow of the oil over the catalyst, *i.e.*, when the time of contact of the catalyst and the oil is less. In the hydrogenation of groundnut oil, the velocity of hydrogenation of linolein will be much faster than that of the olein (*cf.* Part II). Consequently, when the time of contact is small the major portion of the absorption observed will be due to the hydrogenation of linolein, and the temperature at which there is a peak in the curve will be the temperature at which linolein reacts at the greatest velocity.

It appears from the results shown in Fig. 2 that the maxima at 140° and 180° are due to a higher velocity of hydrogenation of linolein at these temperatures.

At slow rates of oil of the order of 20 grams per hour, most of the linolein will be hydrogenated and the effect of temperature on the reaction observed will be due to the hydrogenation of olein. The curve in the present case shows that the velocity rises continuously up to 160° after which it remains steady up to 200° , showing a maximum conversion of olein at about 160° C.

The results obtained with an unsupported nickel carbonate catalyst are in many ways different from those with the kieselguhr supported catalyst. Fig. 3, where these results are given graphically,



VELOCITY OF HYDROGENATION OF GROUND NUT OIL AT DIFFERENT TEMPERATURES WITH UNSUPPORTED NICKEL CARBONATE CATALYST

○—○ 20 Rate ×--× 100 Rate

FIG. 3.

indicates that at the rate of 100, the velocity does not rise within the ranges of temperatures from 95° to 140° and from 188° to 200° . Between 140° and 180° the velocity rises sharply, a deviation in the curve being shown at about 160° . The velocity at the rate 30 increases continuously up to 200° after which it remains constant up to 208° . The absence of kieselguhr as the support has not impaired the activity of the catalyst as can be judged from Table IV,

giving the relative velocities of hydrogenation of the supported and unsupported catalyst at different temperatures and rates. Nickel carbonate on kieselguhr (thin rods) has been taken for comparison.

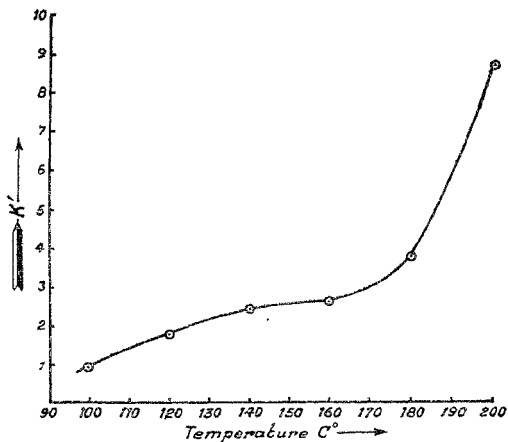
TABLE IV.

Temp. °C.	Relative velocity of the supported : unsupported catalyst	
	Rate 30	Rate 100
100	1 : 6.7	1 : 3.4
120	1 : 4.5	1 : 1.6
140	1 : 4.7	1 : 1.4
160	1 : 4.9	1 : 3.9
180	1 : 5.2	1 : 4.1
200	1 : 6.6	1 : 6.1

It has been mentioned previously that at a slow rate of the oil over the catalyst the velocity of the reaction will be due mostly to the hydrogenation of olein. Table IV shows that the ratio of the velocities at the rate of 30 grams of oil per hour is nearly 1:5 at all temperatures indicating that the absence of kieselguhr does not materially affect the hydrogenation of olein. However a low ratio of the velocities at the rate of 100 grams of oil per hour at 100°, 120° and 140°, indicates that the hydrogenation of linolein is less favoured by the unsupported catalyst.

The plot of K against temperature shows a maximum reaction at about 180°. If, however, the values of K', the corrected velocity coefficients for nickel carbonate on kieselguhr (thin rods) are plotted against temperature (Fig. 4) the maxima in the curve at 180° disappears. The curve shows a break at 150° after which the velocity rises continuously up to 200°.

(3) *Nickel Hydroxide on Silica Gel Catalyst.*—This catalyst was prepared by adding a 10% solution of water glass to nickel nitrate solution at 60°. The mixed precipitate of silica gel and nickel hydroxide was washed and after partial drying, the paste was extruded into rods of about one-eighth inch thickness. These were dried and broken up into pieces of suitable lengths. The catalyst contains 20% nickel. The rods were put into the reaction tube so as to fill seventeen inches of its length, the weight of the catalyst being 78 grams. Reduction was carried out at 350° for 17 hours



NICKEL CARBONATE ON KIESELGUHR CATALYST
 $n=2$ From 100°-180°; $n=4$ at 200°; $K=K'(Rate)^{1/n}$

FIG. 4.

though it was practically complete after nine hours only, as judged from the amount of water formed during the reaction.

After lowering the temperature to 180°, the oil was passed over the catalyst and the velocity of the reaction measured in the usual way. The results are given in Table V.

TABLE V.
Nickel hydroxide-silica gel catalyst.

Rate grams/hr.	K at temperature °C.						
	100	120	140	160	180	200	230
20	(1.0)	(3.7)	(4.5)	(7.0)	(11.2)	(18.1)	(32.2)
40	2.1	5.8	7.2	9.3	11.5	16.6	23.9
60	2.4	6.3	8.6	10.0	12.3	16.5	24.0
80	2.6	6.7	9.5	10.2	13.0	16.9	24.6
100	2.4	6.2	9.9	9.9	13.7	16.9	26.7
140	2.1	6.2	10.0	(7.2)	14.6	17.1	28.7
Average ..	2.3	6.2	9.0	9.8	13.4	16.8	25.6

(4) *Nickel Peroxide-Kieselguhr Catalyst*.—This catalyst was prepared by precipitation of nickel peroxide with sodium hypochlorite. A solution of sodium hypochlorite was added to an ice-cold solution of 500 grams of nickel nitrate in three litres of water. The catalyst was washed, drawn in the form of rods in the usual way and dried in air to avoid as far as possible the decomposition of peroxide. The catalyst contained 20% nickel. It was reduced at 400° and the experiments on hydrogenation were carried out in the usual way at different rates and temperatures.

The velocity coefficients (K) calculated in the same way as before are given in Table VI.

TABLE VI.
Nickel peroxide-Kieselguhr catalyst.

Temp. °C.	Rate grams/hr.						Mean K'	
	20	40	60	80	100	140		
95	K	4.5	7.9	9.1	9.8	9.7	9.3	2.17
	K'	(1.64)	2.32	2.31	2.27	2.08	(1.78)	
120	K	11.2	15.4	17.3	17.9	18.6	16.2	4.25
	K'	4.14	4.50	4.41	4.14	4.01	(3.66)	
140	K	8.9	14.2	17.8	19.9	20.3	20.6	4.41
	K'	(3.29)	4.17	4.55	4.63	4.38	(3.96)	
160	K	18.3	23.2	26.8	29.1	31.8	33.7	6.73
	K'	6.75	6.77	6.84	6.75	6.84	6.49	
180	K	23.4	31.0	36.6	40.4	43.4	46.8	9.34
	K'	(8.63)	9.32	9.33	9.37	9.34	(9.01)	
200	K	28.6	33.2	36.6	38.9	39.5	39.0	12.88
	K	10.52	9.72	9.34	(9.02)	8.50	7.49	
	K'	(13.50)	12.91	13.13	13.01	12.48	(11.33)	

In the case of nickel peroxide-kieselguhr catalyst the velocity coefficient K increases with an increase in the rate of flow of the oil at all temperatures. On the other hand, nickel-silica gel catalyst gives fairly constant values for K at 100°, 120°, 160° and 200°. The behaviour of the nickel peroxide-kieselguhr catalyst is exactly similar to that of the nickel carbonate-kieselguhr catalyst. The change of K with rates can be expressed by the equation $K = K'(\text{Rate})^{1/n}$, where K' is the corrected velocity coefficient and n is a positive constant. The values of K' for nickel peroxide-kieselguhr catalyst when n = 3, are fairly constant at all temperatures from 100° to 180°. At 200° concordant values for the velocity coefficients K'' are obtained when n = 4.

TEMPERATURE COEFFICIENT.

The rate of change of the apparent velocity coefficients (K) with temperature in the case of the two catalysts, nickel peroxide-kieselguhr and nickel hydroxide-silica gel, is shown in Figs. 5 and 6.

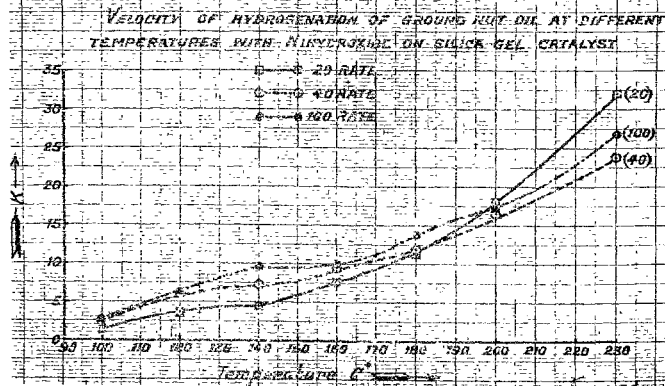
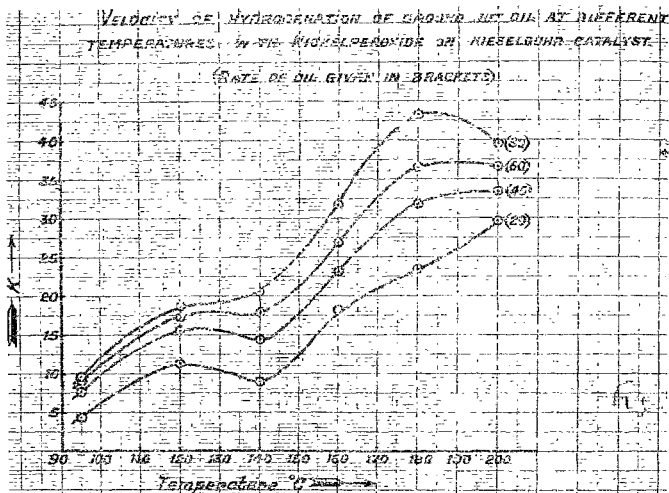


Fig. 5, which represents the results with nickel peroxide-kieselguhr catalyst, shows distinctly two maxima in the curve at 125° and 180°. The one at 125° is more pronounced at a slower rate of the flow of oil, while the other becomes prominent at a higher rate. It is found that the maxima at 180° disappears when the catalyst is poisoned.

Nickel hydroxide-silica gel catalyst (Fig. 6) shows a continuous rise in the velocity upto 230°.

If, instead of the velocity coefficient (K) for the peroxide-kieselguhr catalyst, the mean value of the corrected temperature coefficient (K') is plotted against temperature, the curve so obtained (Fig. 7)

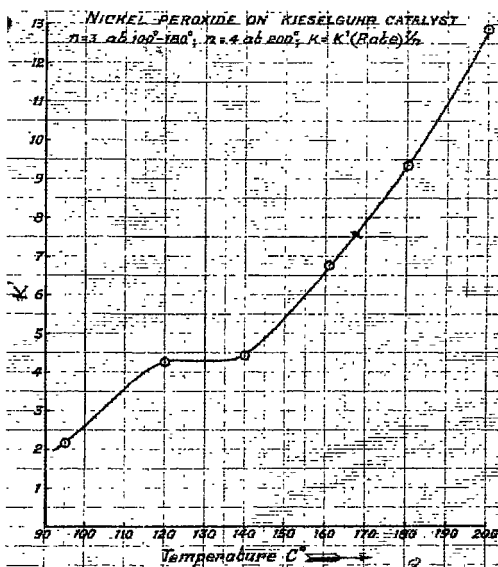


FIG. 7.

shows a break between 120°-140° after which the values rise continuously upto 200°.

The mean values for K' for the hydrogenation of groundnut oil along with the corresponding values of n for nickel carbonate-kieselguhr and nickel peroxide-kieselguhr catalysts are shown in

Fig. 8, where similar curves for the hydrogenation of cottonseed oil and olive oil by nickel carbonate-kieselguhr catalyst have been shown for comparison. The number against each point indicates the value of n from which K' is calculated. The curve for olive oil is flat between 150° and 180° , after which it shows a rapid rise. Groundnut oil hydrogenated with the same catalyst gives a similar curve but

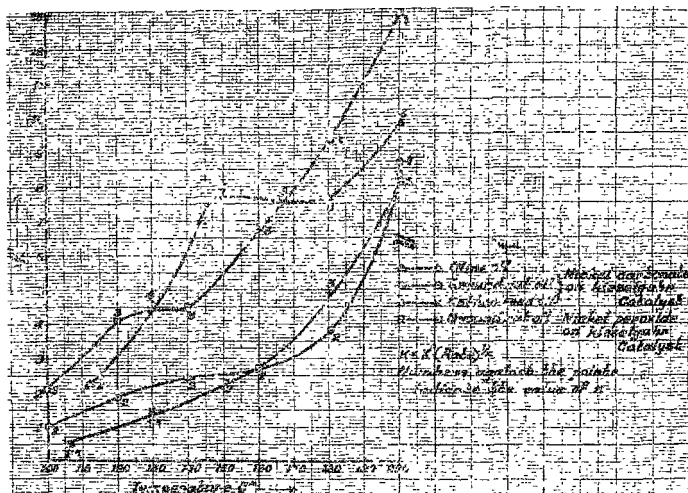


FIG. 8.

the maximum is less pronounced than in the case of olive oil. Cottonseed oil shows a continuous variation of K' with temperature. The maximum at 150° appears to depend upon the percentage of olein in the oil, due to its selective hydrogenation at that temperature.

SUMMARY.

The velocity coefficients for the hydrogenation of groundnut oil by nickel carbonate-kieselguhr, unsupported nickel carbonate, nickel-silica gel and nickel peroxide-kieselguhr catalysts have been studied, and the results have been compared with the velocity coefficients of the hydrogenation of the same oil over nickel wire catalyst. The apparent velocity coefficients of the reaction were calculated by the

formula $K = \frac{2.3}{t} \log \frac{a}{(a-x)}$ which gave concordant values for K in the case of nickel-silica gel catalyst at 100° , 160° and 200° , as in the case of nickel wire catalyst. In the case of other catalysts and other oils, the values differed with rates of flow over the catalyst, the variation being expressed by an equation $K = K' (\text{Rate})^{1/2}$ which gave concordant results for K' at all temperatures. The temperature coefficient of the corrected velocity K' showed that the rate of reaction was high at two temperatures 150° and above 200° , the high reaction velocity at the former temperature being selective towards the hydrogenation of olein, in agreement with the results of experiments on the hydrogenation of olive oil, cottonseed oil and ethyl oleate (*cf.* Parts II and III of this series).

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