HYDROGENATION OF OILS BY THE CONTINUOUS PROCESS.

PART I. HYDROGENATION OF GROUNDNUT OIL BY CATALYSTS OF NICKEL AND ITS ALLOYS.

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INTRODUCTION.

Since the discovery of nickel catalyst by Sabatier many papers have been published dealing both with the theoretical and practical aspects of the problem of hydrogenation of oils. In 1921 Lush and Bolton (*J.S.C.I.*, 1923, **42**, 219 T; 1924, **43**, 53 T) discovered the use of electrolytically oxidised nickel turnings as a catalyst which was superior to that prepared by the precipitation method. This discovery was received in scientific circles with some hesitation; in fact, Hilditch (*J.S.C.I.*, 1923, **42**, 219 T) was surprised to see that 'it would have been made possible to make so novel a development in oil hydrogenation at that late date'. It was incredible to believe that solid metal could give a better catalyst than one supported on porous materials such as kiesulguhr.

Extensive researches by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1921, **99A**, 490) has proved the superiority of the nickel-kiesulguhr catalyst, which was confirmed by researches carried out in our laboratory by Athavale, Sudborough and Watson (This *Journal*, 1922, **5**, 47) and the use of this catalyst in all researches on hydrogenation of soils has now become a standard method.

Most of the researches on the comparative activity of different preparations of nickel catalyst have been made by the batch process which is not an ideal method from the point of view of the surface exposed to the combined action of hydrogen, oil and catalyst. In heterogeneous catalysis where a solid-liquid-gas system is involved, such as in hydrogenation of oils, the most rational method by which a maximum surface can be exposed to the reactants is the 'continuous process', which gives a better opportunity both for the oil and hydrogen to come into contact with the catalyst, and it appeared that the advantages claimed by Lush were due more to the change in the method of operation rather than due to increased activity of the catalyst itself.

The methods followed in actual practice in a batch process are in many ways different from the laboratory experiments and therefore the results obtained in the laboratory are in many cases not exactly applicable on an industrial scale.

In the batch process where the hot mixture of oil and catalys is circulated over baffles as in the Maxted plant, the mode of operatio so far as exposing the surface of the catalyst is concerned, approache that in a continuous method. However, the hot mixture of the oi and the catalyst has to be forced through pumps and there is a possibility of the catalyst being poisoned apart from the mechanical disadvantages of keeping the whole system heated to a high temperature

The activity of a nickel catalyst depends on many conditions such as the method of preparation, the temperature of reduction and purity of oil and varies even in case of catalysts prepared from the same sample under similar conditions. Except for the papers by Lush (*loc. cit.*) and a large number of patents, the literature on the hydrogenation of oils by continuous method is very scanty and no systematic attempt has been made to compare the activity of the different preparations of nickel in this process, which has so fa employed only catalysts like nickel wire or turnings, with the resul that their activity could not be compared with those catalysts which ar worked by the 'powder method'. The object of the present investigation is to compare the activity of the different preparations of the supported and non-supported catalysts in the hydrogenation of oil by the continuous flow method. The powder catalysts were easily converted into a form suitable for continuous operation by the simple process of compressing through a press, the semi-dried mass, in the form of thin rods. The present paper deals with the result obtained by using catalysts made from nickel wire and other alloys o nickel.

EXPERIMENTAL.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1 The oil is contained in a separating funnel which is closed with a cork through which passes a glass tubing reaching nearly the bottom o the funnel. This arrangement together with a double tap system maintains a steady flow of the oil. A nickel plug serves the purpose of a pre-heater. The hot oil subsequently flows over the catalyst held in place by a nickel spiral resting on a constriction in the reaction tube The end of the spiral comes up through the catalyst and terminates in a hook so as to facilitate the removal of the catalyst without disturbing any other arrangement. The catalyst in all the cases occupied a length of seventeen inches in the centre of the furnace. The precipitated catalysts were used in the form of cylindrical rods one eighth inch thick, prepared by pressing the semi-dried mass through an orifice. The oil after passing over the catalyst comes to a bulb which is joined to the reaction tube by a ground joint. The hydrogen escapes through a side tube attached to this bulb while the oil drops

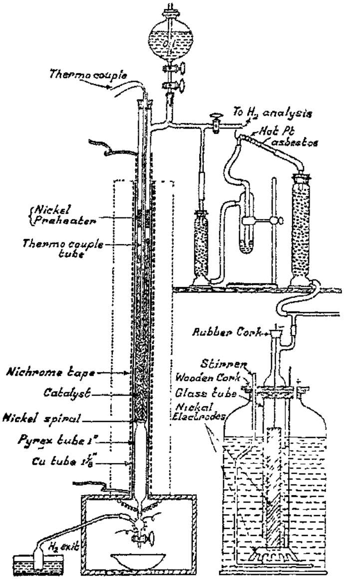

FIG. 1

Apparatus for continuous Hydrogenation of oils

down through a tap in a dish kept below. In order to prevent the hydrogenated oil from solidifying, the bulb and the tap are kept hot by electrical heating. The reaction tube is of pyrex and is heated by a copper tube furnace three feet long and one inch in diameter, heated electrically. A copper constantan thermocouple calibrated against a standard mercury thermometer, was used to measure the temperature in the centre of the catalyst mass.

The Hydrogen.—The hydrogen was prepared by electrolysis of a ten per cent. solution of sodium hydroxide. Three cells similar in design to one shown in the diagram were kept in a tank through which cold water was circulated. Nickel electrodes were used. The anode was made 'passive' by dipping in concentrated nitric acid for half-an-hour.

The hydrogen from the generator is dried over caustic soda flakes and then passed over platinised asbestos heated electrically. It *then passes through a sulphuric* acid bubbler to remove the moisture and then over caustic soda again to remove acid vapours if any.

The Hydrogen Analysis Apparatus.—A simple apparatus for analysis of hydrogen is shown in Fig. 2 and is self-explanatory. The capacities of the bulbs inside the water jacket are 300 c.c. each and that of the combustion bulb is about 800 c.c. The volume of the measuring part of the apparatus is calibrated. As a diminution in volume of 0.1 c.c. can be measured, an oxygen content as low as one part in 20,000 could be detected. For analysis a known volume of the gas is taken into the burette and passed over the hot platinum wire backwards and forwards and the diminution in volume measured. The purity of hydrogen was always more than 99.9%.

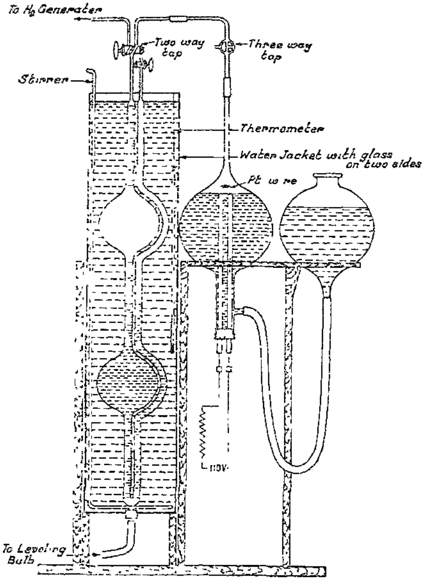

FIG. 2

Hydrogen-Analysis Apparatus

The Oil.—Groundnut oil was used for comparison of the activities of the catalysts. The following are the constants of the refined oil:

Acid value, 0.3; refractive index n_D at 60°, 1.4562; I.V. 88.8 (Hanus); I.V. of the liquid fatty acids 107.1.

The composition of the oil was determined from the iodine value of the original oil and that of the liquid fatty acids by the following formulæ:

% Sat. glycerides = 100 - 104.5 A/B
% Olein = 207.6 A/B - 1.144 B
% Linolein = 100 - (% sat. glycerides + % olein).

where A is the iodine value of the oil and B is the iodine value of the liquid fatty acids. The composition of the oil was found to be saturated glycerides 13.4%, olein 70.6% and linolein 16.0%.

The course of hydrogenation was followed by the change in the refractive index of the hardened oil and using the data on the relation between the iodine value and refractive index given by Athavale and co-workers (This *Journal, loc. cit.*). The refractive indices of the original and completely hardened oils agreed with the values given by these authors for groundnut oil. The yield is calculated by multiplying the rate of flow of oil in grams per hour by the percentage conversion as determined from the change in the refractive index of the sample. This yield is directly proportional to the total hydrogen absorbed by the oil and is a measure of the activity of the catalyst.

Catalysts.—1. *Nickel Wire:* The laboratory model of the Bolton–Lush plant is supplied with nickel turnings contained in a nickel cage, which sometimes gives considerable difficulty in revivifying. The commercial units employ nickel wire wound on a thicker core of the same material which helps the electrolytic reoxidation of the wire by offering a conducting path for the whole length of the thin wire. The thick wire is then wound in a flat spiral and several such spirals being placed one over the other on a central rod with some clearance. We prepared the wire catalyst in the following way: A No. 36 nickel wire was closely wound on a No. 16 nickel wire six feet long. Three such thick wires were wound in the form of helical spirals concentrically packed. This was anodically oxidised in a 5% solution of sodium carbonate for eight hours, washed with water, dried and reduced in a current of hydrogen at 350° for seventeen hours in the reaction tube.

After reduction the temperature was lowered down and the activity of the catalyst was measured at various temperatures. The results are given in Table I and shown graphically in Fig. 3 where yield is plotted against the rate at which the oil flows over the catalyst.

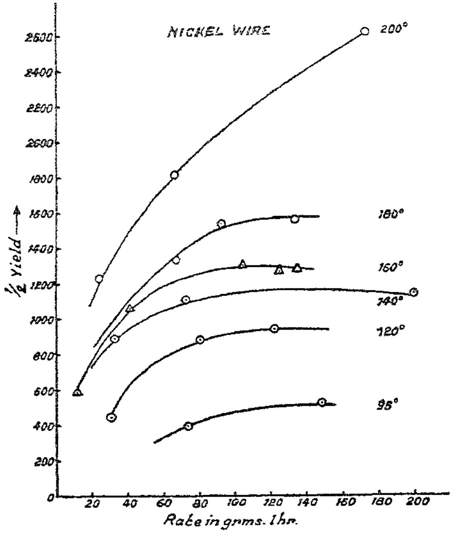

FIG. 3

TABLE I.

Catalyst: Nickel wire.

Temp. C.°	Rate grms./hr.	$n_D^{60°}$	% conversion	Yield
95	72·6	1·4550	10·7	776
,,	147·8	1·4554	7·1	1048
120	30·4	1·4531	29·2	884
,,	79·2	1·4538	39·6	1774
,,	121·2	1·4545	15·6	1890
140	32·6	1·4507	54·5	1776
,,	73·0	1·4530	30·2	2204
,,	252·0	1·4552	8·9	2242
160	12·0	1·4470	97·7	1172
,,	41·6	1·4510	51·0	2120
,,	103·	1·4535	25·0	2610
,,	123·6	1·4540	20·5	2534
,,	133·0	1·4541	19·0	2528
180	66·2	1·4520	40·4	2666
,,	92·0	1·4527	33·3	3060
,,	133·0	1·4537	23·4	3104
200	25·0	1·4470	97·7	2442
,,	65·4	1·4506	55·7	3622
,,	172·2	1·4530	30·2	5200

Life test of the catalyst.—Hydrogenation was carried out continuously at 180° and the activity measured from time to time. The results are given in Table II and shown graphically in Fig. 4 where the fall in the activity with time is plotted against the weight of the oil hydrogenated, the maximum initial activity being taken as 100%.

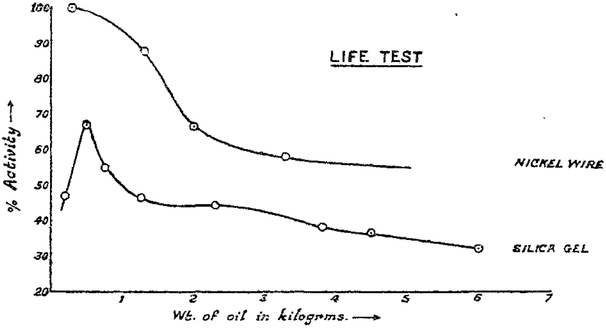

FIG. 4

TABLE II.

Life Test of Nickel Wire at 180°.

Nickel wire catalyst	
Wt. of oil hydrogenated	% of original activity from yield at Rate 60 grms./hr.
250	100
1300	88
2000	67
3200	58

2. *Monel Wire*: It has been reported by Sei ichi Uno and Zensaku Okamura (*J. Soc. Chem. ind. Japan*, 1931, 349–51) that a coprecipitated catalyst with metals in the proportion of Ni : Cu = 75 : 25 with traces of manganese is reduced at a very low temperature and gives a highly active catalyst. The composition of the alloy 'Monel' is identical with the one given above. It was therefore of interest to try this alloy under the same conditions as nickel wire and to compare its activity with that of the latter.

Preparation.—Spirals similar to one of nickel wire were prepared by winding monel wire No. 30 on No. 16 nickel wire. The spirals were anodically oxidised in a 5% solution of sodium carbonate for 12 hours. Even then the oxide film formed on the outer spiral was very thin and the inner one was not at all oxidised.

After washing, drying and reduction at 220° for 17 hours the activity was measured at 180°. The results are given in Table III and shown graphically in Fig. 5. The activity was considerably less when compared with that of nickel wire at the same temperature.

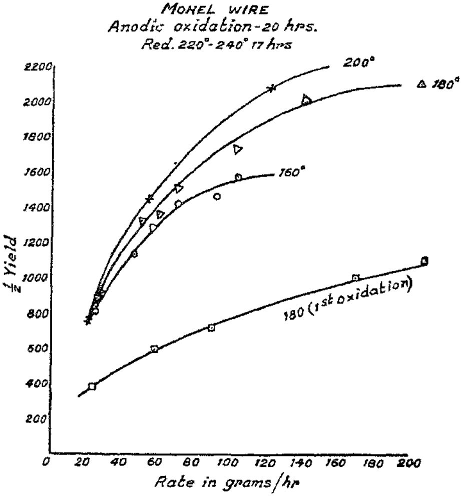

FIG. 5

TABLE III.

Catalyst: Monel Wire (Ni : Cu :: 75 : 25 *with traces of Mn*).

(Anodic oxidation for 12 hrs. Red. Temp. 220° for 18 hrs.)

Temp. C.°	Rate grms./hr.	$n_D^{60^\circ}$	% conversion	Yield
180	22·4	1·4527	33·5	750
,,	55·6	1·4539	21·4	1188
,,	90·0	1·4545	15·6	1404
,,	169·2	1·4549	11·7	1980
,,	182·0	1·4550	10·7	1946
,,	208·0	1·4550	10·7	2200

Reoxidation.—After extracting the oil from the spiral it was reoxidised for 20 hours when a comparatively thicker oxide film was formed. After reduction at 220°–250° for 17 hours the activity was measured in the usual manner. The results are given in Table IV and shown graphically in Fig. 5.

TABLE IV.

Catalyst: *Monel Wire.*

(Anodic reoxidation for 20 hrs. Red. Tem. 225° for 17 hrs.)

Temp. C.°	Rate grms./hr.	$n_{D}^{60^\circ}$	% conversion	Yield
160	24·0	1·4496	67·4	1616
,,	45·0	1·4510	49·9	2244
,,	70·2	1·4520	40·3	2830
,,	92·4	1·4529	31·3	2890
,,	103·2	1·4530	30·2	3120
180	23·6	1·4494	69·7	1644
,,	24·8	1·4492	72·0	1786
,,	27·0	1·4496	67·4	1820
,,	50·8	1·4509	52·2	2652
,,	56·4	1·4515	45·5	2566
,,	60·0	1·4515	45·5	2730
,,	69·6	1·4517	43·5	3028
,,	103·0	1·4527	33·3	3428
,,	141·4	1·4532	28·3	4002
,,	205·2	1·4540	20·4	4186
200	20·4	1·4492	72·9	1486
,,	55·2	1·4509	52·2	2880
,,	121·6	1·4526	34·0	4134

For a short time in the beginning the hydrogenated oil carried the finely divided catalyst. Subsequent reoxidation of the catalyst offered some difficulties. Carbon tetrachloride and light petrol were the solvents used for extracting the oil. These are not satisfactory solvents for stearin. The small amounts of undissolved stearin on the surface prevents the reoxidation. It was thought that electrolytic reduction of the spiral might possibly remove the surface layer and the subsequent oxidation would be easy. But even after 24 hours there was no appreciable oxidation. The activity of the catalyst was very much less than that after first reoxidation.

3. *'Ferry' Wire* (Ni : Cu :: 54 : 46).—Spirals were prepared using a thin 'Ferry' wire. It was oxidised anodically for ten hours and reduced at 230° for 18 hours.

The catalyst showed a very long induction period. The activity at 180° was increasing for two days. The results given in Table V (Fig. 6) were those obtained on the third day when a steady state was reached.

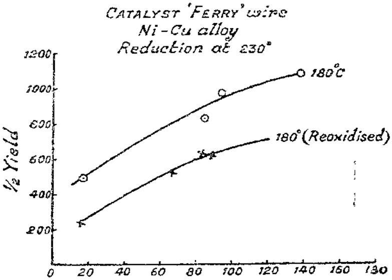

FIG. 6

Reoxidation for 8 hours after the extraction of the fat showed only a poor activity probably for reasons discussed already.

TABLE V.

Catalyst: *Ferry Wire* (Ni : Cu : : 54 46).

(Anodic oxidation for 10 hrs. Red. Tem. 230° for 18 hrs.)

Temp. C.°	Rate grms./hr.	$n_D^{60^\circ}$	% conversion	Yield
180	18·4	1·4508	53·4	982
,,	85·6	1·4541	19·5	1669
,,	96·0	1·4540	20·5	1968
,,	140·2	1·4545	15·6	2190

4. *Raney's Catalyst* (Alloy Ni : Al : : 27 : 73): It was reported by Bag and co-workers (*Russ. Pat.*, 23523, Oct. 31, 1931) that a highly active catalyst suitable for use in a batch process can be prepared by alloying nickel with aluminium preferably in the ratio of Ni : Al = 27 : 73 and dissolving the aluminium by sodium hydroxide. R. Henblyum in a paper recently published (*Mat. grasseo*, 1935, 27.10, 589–90; 10, 618–19) has drawn attention to Bag's highly active Ni-Al catalyst and to its advantages, the most important of which is the possibility of working continuously instead of in batches.

Preparation.—An alloy of nickel and aluminium in the ratio of 27 : 73 was prepared by fusing the metals together. The reaction tube was filled with the granules of the alloy and a 5% solution of caustic soda was passed over the alloy in the atmosphere of hydrogen until one-third of the aluminium was dissolved. The catalyst was washed *in situ* first with distilled water and then with alcohol.

The yield of the catalyst was measured at 180° with five different rates while at other temperatures with only two rates, one slow and another fast were tried, and the general nature of the yield-rate curve being known the values at other rates could be easily computed. The results are given in Table VI (Fig. 7).

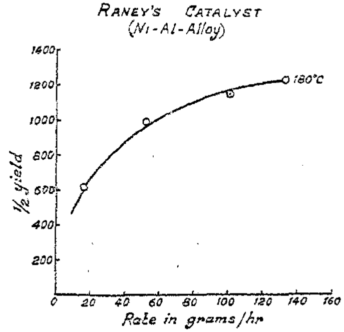

Fig. 7

TABLE VI.

Raney's Catalyst (Ni : Al : 27 : 73).

Temp. C.°	Rate grms./hr.	$n_D^{60°}$	Yield	Temp. C.°	Rate grms./hr.	$n_D^{60°}$	Yield
96	42·0	1·4550	450	162	46·6	1·4535	1180
95	112·8	1·4556	600	172	45·0	1·4529	1404
104	110·0	1·4556	584	174	97·6	1·4544	1066
108	46·8	1·4549	548	*180	18·2	1·4491	1232
116	105·0	1·4555	652	*180	54·6	1·4524	1982
118	51·4	1·4549	566	*180	103·6	1·4538	1320
125	129·6	1·4550	1388	*180	134·0	1·4542	2480
125	44·6	1·4545	696	184	43·0	1·4520	1734
135	40·8	1·4540	832	186	124·8	1·4548	1578
137	94·0	1·4550	1006	*200	53·6	1·4523	2000
147	55·2	1·4543	966	*200	232·0	1·4550	2484
151	87·0	1·4549	1018	204	113·4	1·4540	2314
160	147·6	1·4550	1580	206	40·2	1·4513	1890

DISCUSSION OF RESULTS.

Of all the metal catalysts the nickel wire catalyst is the most active and is the easiest to be prepared. The activity of the metal catalysts decreases in the order: Nickel wire > "Monel" wire > Raney's catalyst > Ferry wire.

The life test of the nickel wire catalyst shows a marked fall in activity in the beginning which afterwards remains constant at about 60% of its initial value indicating the step-wise nature of the poisoning of the catalyst.

The 'Monel' wire gives a catalyst which is as active as the nickel wire with the further advantage that it can be reduced at a lower temperature. This result is in agreement with the observations of Sie ichi Uno and co-workers (*loc. cit.*) who found that a co-precipitated catalyst having nickel, copper and manganese in the same proportion in which these metals are present in "Monel" wire, is reduced at a low temperature and is also very active. The promoting action of copper in nickel catalyst is thus confirmed in contradiction to the findings of Patel (This *Journal,* 1924, 7, 197). This alloy has, however, one disadvantage that it requires a long time for anodic oxidation.

The "Ferry" wire, the composition of which is (Ni:Cu::54:46), is considerably less active than nickel wire, which is obviously due to the fact that copper in such large quantities does not act as a promoter.

In a batch process Raney's catalyst is said to be very active especially at low temperatures. This was not found to be the case in our experiments and the catalyst showed no particular advantage.

VELOCITY COEFFICIENT OF THE REACTION.

The activity of the catalysts has been given hitherto in terms of the space-time-yield, which is proportional to the amount of hydrogen absorbed by the oil at any particular rate.

The activity of a catalyst is, however, more accurately determined by calculating the velocity coefficient. It can be shown that in a continuous flow method of hydrogenation, the velocity of the reaction, *i.e.,* the reaction in unit space in unit time could be calculated from an equation similar to the one for reactions of the first order, *viz.*:—

$$K = \frac{2 \cdot 3}{t} \log \frac{a}{a-x}$$

The initial concentration a may be taken as 100 and x as the percentage conversion after a time of contact t.

The percentage conversions for different fixed rates at regular intervals of temperature have been calculated from the yield-rates curves already given. The velocity coefficients calculated from the above equation for monel wire, nickel wire and Raney's catalyst are given in Tables VII and VIII.

TABLE VII.

Rate grms./hr.	K at Temperatures C.°					
	95°	120°	140°	160°	180°	200°
20	2·6	7·7	25·5	28·6	34·3	..
40	4·7	14·9	25·4	28·3	33·8	52·4
60	7·0	18·1	25·4	30·0	34·0	52·9
80	8·6	19·9	25·9	29·9	35·1	53·9
100	9·7	20·3	25·9	29·6	36·3	55·9
140	10·8	20·5	25·4	28·0	35·9	59·0

TABLE VIII.

Monel Wire Catalyst				Raney's Catalyst			
Rate grms./hr.	160°	180°	200°	Temp. C.°	K at Rate 40	Temp. C.°	K at Rate 100
20	24·1	25·5	26·9	96	4·3	95	6·0
40	28·9	32·8	37·7	108	5·3	104	6·0
60	32·7	37·7	42·8	118	5·3	116	6·6
80	32·1	40·4	46·1	125	7·2	125	13·7
100	36·8	43·7	48·5	135	9·2	137	11·0
140	37·9	46·2	52·0	147	9·4	151	11·0
				162	12·9	160	15·1
				172	16·3	174	14·0
				184	21·4	186	16·9
				206	25·5	204	25·3

In the case of nickel wire catalyst the velocity coefficients for different times of contact above 140° are approximately the same, thus justifying the equation given above. Below 140° there is a considerable difference in the values of K. With monel wire, however, the calculated velocity coefficients show considerable variation with different rates. The velocity at higher rates at 160° and 180° is much higher with this catalyst than with nickel wire, though at 200° reverse is the case. Raney's catalyst shows a considerable irregularity in the values of K with the time of contact.

The change of the velocity coefficients with temperature for the nickel wire, monel wire and Raney's catalyst, is shown in Fig. 8, where

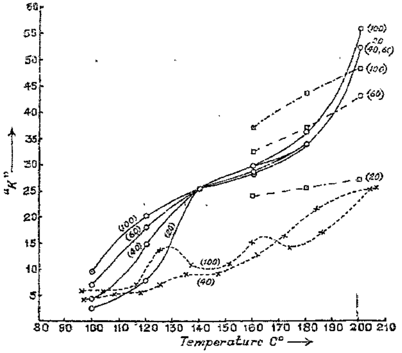

FIG. 8

Velocity of the hydrogenation of Groundnut oil at different temperatures with metal catalysts. (Figures in brackets indicate the rate of oil)

○—○ Nickel wire.
□--□ Monel wire.
×--× Raney's Catalyst.

the velocity coefficients at different rates of oil are plotted against the temperature. In the case of nickel wire catalyst, the velocity rises continuously from 100° to 140° but the difference in the velocities at these two temperatures becomes less as the rate of oil is increased. There is a break in the curve at 150° above which the velocity rises continuously with temperature. The temperature coefficient of the velocity constant in the case of monel wire is comparatively small. The lower temperature coefficient and the greater activity at high rates of oil may be due to the promoting action of the copper in this alloy. With Raney's catalyst a maximum is shown in the curve at 140°, after which the velocity rises continuously up to 200 °, when the rate is 40 grams per hour. At the rate of 100 grams per hour, the velocity coefficients show three maxima at 130°, 165° and 200°.

In view of a number of maxima in the velocity-temperature curve and variations in the values of K with rates at different temperatures, the temperature coefficient of the reaction and the heat of activation could not be calculated. The anomalous nature of the results obtained with the various catalysts will be discussed in a subsequent communication.

SUMMARY.

The hydrogenation of groundnut oil by various catalysts prepared from nickel wire and its alloys has been studied by the continuous flow method.

It has been shown that the nickel wire catalyst is the easiest to be prepared in a high state of activity. Life tests of this catalyst showed a sudden fall in the activity to 60% of its original value after five days continuous run.

The activity of monel wire is equal to that of nickel, but the former is difficult to reactivate. Ferry wire showed considerably lower activity. Raney's catalyst did not give promising results.

Velocity coefficients of the hydrogenation reaction for the different catalysts were calculated on the basis of a unimolecular formula. Concordant results for different times of contact were obtained only in the case of nickel wire.

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