

PART VI SELECTIVITY OF HYDROGENATION  
CONTINUOUS HYDROGENATION OF OILS

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INTRODUCTION

The edible fat, soft soap and high class lubricant industries demand the use of an oil containing a substantial excess of liquid constituents. The presence of linolein or glycerides more unsaturated than linolein is undesirable in those products, since they are susceptible to oxidation and rancidity. Therefore a process of converting the linolein into olein with the formation of relatively little stearin is of great advantage for the production of oils especially suited for the above mentioned industries. The batch process of hydrogenation answers this purpose on account of its selective character, and has replaced the continuous process which had gained ground during the last decade.

The term selectivity seems to be a comparative one and is defined as the preferential conversion of linoleic acid into oleic acid in mixtures where both of these acids are existing in free or combined state.

The comparison of the batch process and continuous process shows that the latter, though has many advantages over the former from the point of view of working, is not suited for wide industrial application on account of its nonselective character. A considerable amount of work has been done to study the effect of the operating conditions on the degree of selectivity in the batch process. Except some papers by Hilditch no extensive work has been done to study the effect of operating conditions on the selectivity in the continuous process. The present investigation is an attempt to study the influence of various factors in the continuous process in order to find out the optimum conditions under which the continuous process can give selective results.

The possibility of controlling the hydrogenation so as to convert the highly unsaturated linoleic acid into the less unsaturated oleic acid with the formation of relatively little stearic acid was first described in a patent by Burchenal (U S Patent 1135351, 1910). A general survey of the literature reveals that the working conditions during hydrogenation play an important part in the selectivity of hydrogenation. An extensive amount of work has been done to study the influence of catalyst, its concentration, pressure, temperature and agitation on the selectivity of hydrogenation.

*Catalyst.*—Richardson and Snoddy in a comparative study of the hydrogenation of cottonseed oil with nickel and platinum catalysts have concluded that hydrogenation with platinum is by no means so selective as with nickel catalyst (Ind. and Eng. Chem. **18**, 570-1, 1926). Similar conclusions have been drawn by Waterman and Van Vlodiop (Rec Trav Chim **50**, 279-82, 1931) and Ueno, Vikimori and Ueda (J Soc Chem Ind Japan, **34**, Supp B 181-83, 1931). It appears that besides the cost of platinum, its property to give less selective results does not admit its use as a catalyst in industry. Moore and co-workers have found that an increase in the concentration of catalyst decreases the selectivity. They have explained this behaviour in the following manner: An increase in the amount of catalyst diminishes the average distance between a particle of the catalyst and the hydrogen bubble surfaces. This reduction in the distance, which causes a decrease in the lag between the demand for hydrogen at the catalytic surface and the supply which must be kept up by the process of solution and diffusion, increases the concentration of hydrogen at the catalytic surface. The direct formation of steam from linolein caused by an increased concentration of hydrogen explains for the less selective results (Ind. and Eng. Chem., **9**, 451, 1917). Richardson, Knuth and Milligan (Ind. and Eng. Chem., **16**, 519, 1924), Hilditch and co-workers (J S C I **51**, 195-81, 1932) have drawn conclusions contradictory to those drawn by Moore and co-workers. They have observed that an increase in the amount of catalyst increases the selectivity, but have not given any plausible explanation of such behaviour.

*Pressure*—Moore and co-workers have observed from their results that an increase in pressure leads to less selective results (Ind and Eng Chem, **9**, 451, 1917) Moore's observation has been confirmed by Waterman and co-workers (Rec Trav Chim, **52**, 9-17, 1933) The decrease in selectivity on increase in pressure is explained by the increase in the hydrogen concentration caused by the better solution and diffusion of hydrogen Contradictory views have been held by Richardson, Knuth and Milligan (Ind and Eng Chem, **16**, 519-22, 1924)

*Temperature*—There is no controversy regarding the observation that an increase in the temperature within certain range (100° to 200°) increases selectivity This has been proved by the work of Moore and co-workers (Ind and Eng Chem, **9**, 451, 1917), Williams (J Soc Chem Ind, **46**, 448T, 1927) and Hilditch and others (J S C I **51**, 195, 1932)

*Agitation*—Moore has observed that an increase in the agitation decreases the selectivity (J Ind and Eng Chem, **9**, 451, 1917) Contradictory views are being held by several workers that decrease in agitation decreases selectivity, considering the fact that low speed increases the time of contact between the oil and catalyst causing complete saturation of linolein

Thus the catalyst, its amount, pressure, temperature and agitation were the factors which were studied as governing the selectivity of hydrogenation In the year 1923, the advent of continuous process by Lush in the field of hydrogenation introduced one more factor namely the difference in the process of hydrogenation Lush himself in his study of the progressive hydrogenation of olive and cottonseed oils by the continuous process noted that the increase of saturated fatty acids begins from the commencement and not as has been found with powder catalysts only after the linoleic acid has been reduced to 10 per cent From these results Lush emphasized that the continuous process, gives less selective results than the batch process, (J S C.I 1924, **43**, 57T, 1925, **44**, 129T). Lush attributes this difference to the different conditions of access of hydrogen

in the two processes. Hilditch and co-workers have reached similar conclusions from their study of the progressive hydrogenation of cottonseed oil (J.S.C.I. 51, 198T, 1932), sesame and groundnut oils (J.S.C.I. 57, 363, 1938). In the case of linseed oil similar results have been observed by Cocehinarias (J.S.C.I. 1932, 51, 403-47).

Recently Athavale and Jafkar who have made a systematic study of the continuous process, have observed 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 the linolein to change straight to stearin increases because the olein formed hydrogenates with equal velocity. They are of the opinion that the selectivity depends not on the process but on the nature of the catalyst (This Journal, Vol. 21A, Part XXIV, pp. 285-289).

It appears, from the study of the literature that very little work has been done to study the influence of relative concentrations of olein and linolein in the oil, the rate of flow of the oil over the catalyst and the temperature, on the selectivity in the continuous process of hydrogenation. In the present work a detailed study of the influence of the various factors on the selectivity is made, in order to find out conditions under which the nature of the product obtained by continuous process will be similar to that of the product obtained by the batch process.

*Method of Investigation*—A general study of the literature reveals that there are three methods of studying the selectivity: (i) By plotting a time-rate curve and noting points of inflection. Armstrong and Hilditch have used this method (Proc. Roy. Soc., 96A, 137, 1919). (ii) By the separation of solid and liquid acids by lead salt-ether method. (iii) By finding out the iodine and thiocyanogen values (Kaufmann Ber. 1927, 60, 50). The method (iii) has been adopted in the present work.

The determination of thiocyanogen value along with iodine value offers the possibility of calculating the percentages of linolein,

olein and saturated glycerides in the oil. The oleic acid isomers formed in hardening behave towards thiocyanogen in the same way as oleic acid. Thus this method obviates the difficulties introduced by formation of solid isomerides of oleic acid.

#### EXPERIMENTAL

*Apparatus*—The apparatus used was the same as described in this Journal (Vol 20 A, Part XII)

*Catalyst*—20 per cent. nickel carbonate kieselguhr was prepared by adding sodium carbonate to nickel nitrate solution in presence of kieselguhr sufficient to give the ratio of nickel kieselguhr in the catalyst as 1:4. The washed precipitate in a semi-dried condition was forced through a small orifice under a pressure of 15 tons per sq. inch. The air-dried catalyst was reduced at 400° for 17 hours. After the reduction the temperature was lowered to 180°, and the oil was allowed to flow over the catalyst.

The oils used had the following constants

Oil	$n_D^{60^\circ}$	Acid Value	Iodine value (Wij's)		SCN value	
			Authors	Holde	Authors	Holde
Cottonseed	1.4573	0.37	101	101-120	64.6	61-65
Sesame	1.4589	0.40	111	103-112	75.4	75-77
Safflower	1.4618	0.30	141	138-150	78.5	.....

The iodine and thiocyanogen values are of the same order as given by Holde (Kohlenwasserstoffole and Fette Ed. 1933, pp 786-809)

The composition of the oil was calculated from the formula

$$\begin{aligned} \% \text{ L.G.} &= 1.154 (I.V. - T.V.) \\ \% \text{ C.G.} &= 1.162 (2 T.V. - I.V.) \\ \% \text{ S.G.} &= 100 - (\text{L.G.} + \text{C.G.}) \end{aligned}$$

where

I V = Iodine value of the oil,  
 T V = Thiocyanogen value of the oil,  
 L G = Linoleic glycerides,  
 O G = Oleic glycerides,  
 S G = saturated glycerides

*Cottonseed oil* The percentage of linolen in the cottonseed oil was 41.8 and that of olein 33. The amount of saturated glycerides was 25.2 per cent

	I V	Linolen %	Olein '	Satd. glycerides '
Authors	101	41.8	33	25.2
		Linolenic acid %	Oleic acid %	Satd. acids %
Hilditch and co-workers	103.4	15.3	29.6	25.1

The results are found to be very nearly the same as obtained by Hilditch who employed the ester fractionation method of analysis (J S C I 195T, 51, 1932)

*Sesame oil*—The composition of sesame oil used was, linolen 40.6 per cent olein 16.7 per cent and saturated glycerides 12.7 per cent

	I V	Linolen %	Olein %	Satd. glycerides %
Authors	111	40.6	16.7	12.7
		Linolenic acid %	Oleic acid %	Satd. acids %
Jamieson and Boughman		37.7	19.1	12.9
Hilditch and co-workers	109.6	10.4	15.1	14.2

*Safflower oil*—The results given below are different from those of the American safflower oil analysed by Jamieson, on account of the traces of linoleic glycerides in the oil

	I V	Linolein %	Olein %	Satd glycérides %
Authors	111	72.1	18.6	9.3
		Linoleic acid %	Oleic acid %	Satd acids %
Jamieson	.	63	24.6	

*Graphic representation*—The literature on selectivity reveals that there are three different methods of graphic representation for the study of the selectivity in the hydrogenation of oils

(i) Roozebooms triangular diagram This method was first followed by Moore and co-workers (*Ind and Eng Chem*, **9**, 451, 1917)

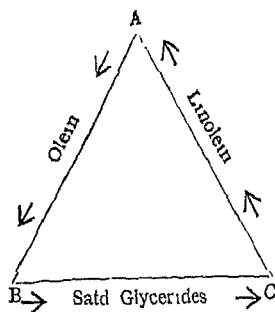
(ii) Plotting a time-rate curve and noting points of inflection Armstrong and Hilditch had based their study of the selectivity on this method (*Proc Roy Soc* **96A**, 137-46, 1919)

(iii) Plotting the iodine values of mixed fatty acids against the percentages of saturated acids This method was suggested by Williams (*J S C.I.*, 447T, **46**, 1927)

The method employed by Armstrong and Hilditch gives only qualitative results The method suggested by Williams necessitates the separation of fatty acids in oil which requires a long time In the present work on account of the great number of samples, the application of the method of Williams was not feasible Moore's method of triangular representation is followed in this work

Oil being a three component system, counting the saturated glycerides as one component, it is possible to represent the percentages through the use of Roozeboom's triangular diagram

In an equilateral triangle ABC, each side is divided into 100 parts. It is customary to represent BC as saturated glycerides, CA as linoleic glycerides and AB as oleic glycerides. Moore has also made use of a remarkable property of the triangular diagram, that lines of equal iodine value are found to be parallel, all making an angle of  $90^{\circ} 11'$  (on the lower side) with the right hand side of the triangle. The concavity of the curves towards the right hand side of the triangle indicates selectivity and that towards the left hand side indicates nonselectivity.



### RESULTS

*Cottonseed oil*—The oil was hydrogenated by 20 per cent nickel carbonate kieselguhr catalyst at  $180^{\circ}$ ,  $160^{\circ}$  and  $140^{\circ}$  at different rates. The composition of the hardened samples was determined by the thiocyanogen iodine value method. The results are recorded in Table I and are plotted in Fig. 1.

*Sesame Oil*—Hydrogenation of sesame oil was carried out at  $100^{\circ}$ ,  $120^{\circ}$ ,  $140^{\circ}$ ,  $160^{\circ}$  and  $180^{\circ}$  at different rates. The percentages of glycerides were calculated from the thiocyanogen and iodine values. The results are given in Table II and are represented graphically in Fig. II.

*Safflower Oil*—Hydrogenation of safflower oil was carried out at  $100^{\circ}$ ,  $120^{\circ}$ ,  $140^{\circ}$ ,  $160^{\circ}$  and  $180^{\circ}$ . The iodine and thiocyanogen values and the composition of the hardened samples are given in Table III. The results are plotted in Fig. III.

*Cottonseed Oil*—Temperature  $140^{\circ}$ —The curve at  $140^{\circ}$  in Fig. I indicates that at higher rates of the flow of the oil the olein percentage remains constant (at about 34%) while there is an increase in the saturated glycerides proportional to the decrease in linolein. At slower rates a decrease in the olein takes place indicating the olein  $\rightarrow$  stearin reaction.

Athavale and Jatkar (loc. cit.) have observed in the case of



TABLE I  
*Hydrogenation of Cottonseed oil*

		I V (W <sub>175</sub> )	SCN No	% Olein	% Linolein	% Saturated glycer- ides
Original Oil		101	64.6	33	41.8	25.2
Temp.	Rate gms /hour					
140°	45.6	61	38.6	18.8	25.8	55.4
"	70.6	78.7	52.1	29.6	30.7	39.7
"	222	87.8	58.6	34.2	33.1	32.1
160°	39.2	55	39.7	28.4	17.6	54
"	92.4	72.6	49	29.5	27.2	43.3
"	190.3	79.3	52.5	29.9	30.9	39.2
180°	35.8	34.8	28.7	26.3	7	66.7
"	55.2	50.6	35.7	24.2	17.2	58.6
"	102.6	66.3	47.3	32.9	21.9	45.2

cottonseed oil that at 130° the reaction is exclusively the hydrogenation of linolein to olein

Hilditch and co-workers have studied the hydrogenation of cottonseed oil by the continuous process at 130°, 170° and 200° (J S C. I 51, 198T, 1932) Hilditch has not given the rates of the flow of the oil, so for comparison, it can be assumed that for a particular temperature the rate increases with increasing iodine value. The results of Hilditch are graphically represented in Fig 1A.

At 130°, the percentage of olein continuously increases with the decreasing iodine value from 25 to 35 per cent and then it

TABLE II

*Hydrogenation of sesame oil*

		I V (Wij's)	SCN No	% Olem	Laurem	% Satt. glycer- ides
Original oil		111	75 1	16.7	40.6	12.7
Temp	Rate gms./hour					
100°	29.2	81.2	58.6	11.8	26.1	32.1
"	57	92.6	64.8	13.1	32.1	21.8
"	174	99.7	66.9	39.7	37.9	22.1
120°	13.2	63.2	16.8	35.1	19	15.6
"	65.2	73.5	52.4	36.3	21.1	39.3
"	100.8	87.9	61.6	41.1	30.3	28.6
140°	21.6	56.2	15.2	39.8	12.7	17.5
"	46.8 <sup>r</sup>	65.7	49.2	38.1	19	12.9
"	101	78.3	54.7	36.3	26.6	37.1
160°	38.8	70.2	54.3	44.6	18.3	37.1
"	63	79.4	58.1	42.8	21.5	32.7
"	145.6	87.6	63	38.4	28.1	33.2
180°	22.8	42.8	33.8	28.8	10.1	60.8
"	57.2	65.1	50.5	41.7	16.8	41.5
"	130.8	86.0	63.7	18	25.8	26.2
"	184.8	86.7	62.1	14.2	26.8	29.0

TABLE III

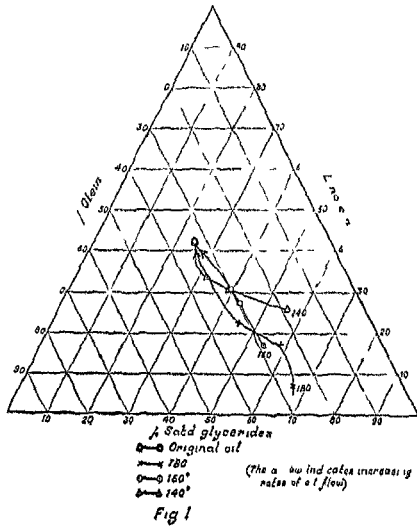
*Hydrogenation of safflower oil*

		I V (Wij's)	SCN No	% Olein	% Linolein	% Satd glycer- ides
Original oil		141	78.5	18.6	72.1	9.3
Temp	Rate gms /hour					
100°	27.1	110.9	70.5	35	46.6	18.4
"	176	128.8	78.3	32.2	58.3	9.5
120°	28.1	103.8	67.3	35.6	42.1	22.3
"	52.8	112.8	74.3	11.6	44.4	14
140°	26	96.6	65.4	39.7	36	24.3
"	71.6	107.8	70.6	38.9	42.9	18.2
"	114	118.8	74.6	35.2	51.1	13.7
160°	16.8	51.1	10.8	32	15.4	52.6
"	126	118.8	68.5	20	58	22
180°	22.8	74.7	19.8	29.4	28.7	41.9
"	37	85.9	60.3	40.4	29.6	30

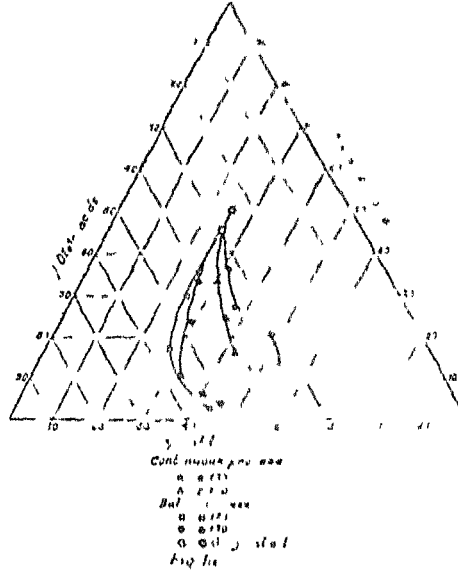
decreases with decreasing iodine value. This indicates that olein  $\rightarrow$  stearin reaction proceeds when the time of contact is long. Even with shorter time of contact, the saturated acids increase appreciably. The results of the present research are in confirmation of those obtained by Hilditch.

*Temperature 160°*—Fig. 1 indicates that at 160°, the olein does not change at all during hydrogenation. There is an increase

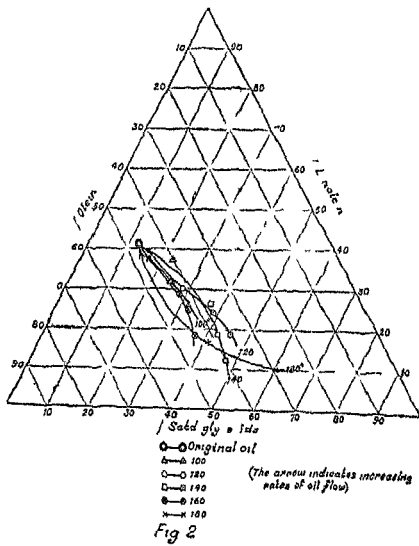
HYDROGENATION OF COTTONSEED OIL



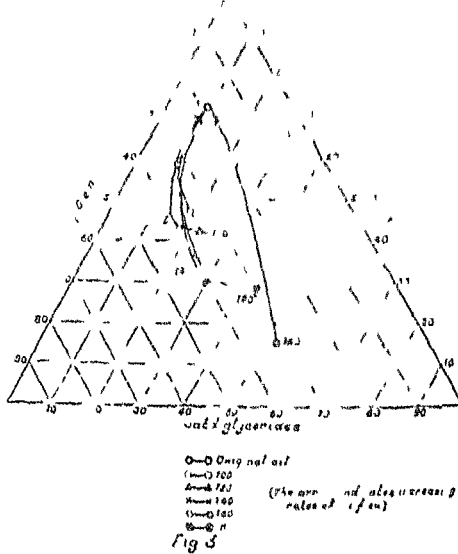
HYDROGENATION OF COTTONSEED OIL



HYDROGENATION OF SESAME OIL



HYDROGENATION OF SESAME OIL



in the saturated glycerides proportional to the decrease in linolein. At 160° it appears that the main reaction is linolein  $\rightarrow$  stearin at all the rates of the flow of the oil. Athavale and Jatkar (loc cit) have shown that at 154° with faster rates the linolein changes to olein without much rise in saturated glycerides but at low rates the selectivity disappears.

Temperature 180°—The curve of 180° in Fig. 1 appears to be composed of two parts. The part representing higher rates is concave to the right hand side of the triangle while the part indicating slower rates is convex. In the concave part the olein percentage slightly increases from 33 to 31 and then in the convex part it appreciably decreases and the olein to stearin reaction becomes perceptible. The general nature of the curve however, shows that an increase in the saturated glycerides takes place at the cost of linolein. Hilditch has observed similar results at 170°. The olein increases from 25 to 35 per cent and then practically remains constant. The main change proceeding is an increase in the saturated glycerides and a decrease in the linolein.

Athavale and Jatkar have observed that at 182° with faster rates the linolein changes to olein without appreciable change in saturated glycerides. As the rates decrease the main change observed is the disappearance of linolein and an increase in the saturated glycerides the percentage of olein remaining constant. Their results point that with faster rates the hydrogenation at 180° is selective and the selectivity disappears with slower rates.

Athavale and Jatkar (loc cit) showed that the selectivity of hydrogenation of cottonseed oil by the continuous process using nickel kieselguli catalyst was similar to that observed in batch process in which the same catalyst was used. They ascribed selectivity to the nature of the catalyst. As the sample of oil used by these workers was dark and far from pure, as shown by the iodine and thiocyanogen value, it was necessary to check their results using reliable sample. The present results indicate that selectivity of hydrogenation is more dependent on the method and not on the catalyst. The oil used by Athavale might have contained some impurities.

The results with the cottonseed oil indicate that at 140°, 160° and 180°, the linolein  $\rightarrow$  stearin reaction predominates and no selectivity is observed. This observation is in confirmation with all the previous results by the continuous process. It is also found that with slower rates the olein  $\rightarrow$  stearin reaction occurs, its velocity at 140° being highest and at 160° being lowest. It is interesting to note that neither in the present work nor in Hilditch's results the percentage of olein rises beyond 40 per cent. The Fig. 1A shows that in the batch process the olein content rises continuously to 60 per cent.

*Sesame Oil*—Temperature 100° and 120°—From the Fig 2 it appears that at 100° the percentage of olein practically remains constant and the main reaction proceeding is linolein  $\rightarrow$  stearin. With faster rates at 120° the olein does not change but an increase in the saturated glycerides seems to occur at the cost of linolein. With slower rates however, the olein  $\rightarrow$  stearin reaction is perceptible.

Temperature 140° and 160°—At 140° the decrease in olein is observed even with faster rates. The saturated glycerides appear at the commencement as at 100° and 120°. The linolein  $\rightarrow$  stearin reaction takes place exclusively at 160°.

Temperature 180°—At 180° the olein nearly remains constant with faster rates and the main reaction occurring is linolein  $\rightarrow$  stearin and with slower rates the olein  $\rightarrow$  stearin reaction is perceptible.

Thus the study of the hydrogenation of sesame oil at various temperatures points out that the main reaction occurring is linolein  $\rightarrow$  stearin and only at slower rates the olein  $\rightarrow$  stearin reaction predominates, its velocity at 140° being highest as observed in the cottonseed oil. The increase in the saturated glycerides is marked from the beginning which is in confirmation with the cottonseed oil results in the present work and all other previous work.

*Safflower Oil*—The concavity of the curves at 100°, 120°, 140° and 180° towards the right hand side of the triangle indicates that with faster rates there is no considerable increase in the saturated glycerides but the olein increases appreciably, not increasing beyond 40

per cent at any temperature. With slower rates, however, as in the previous two oils, the olein steam reaction takes place.

The Fig. 3 indicates that at 160° the steam increases continuously and there is also slight increase in olein.

The hydrogenation of safflower oil, which is selective at faster rates, appears to differ from that of the cottonseed and sesame oils on account of its high content of linolein.

#### DISCUSSION

The results indicate that during the hydrogenation of cottonseed and sesame oils in which the linolein and olein are in the ratio of nearly 1:1 the formation of steam occurs at the cost of linolein quantitatively, indicating the simultaneous saturation of both the double bonds in linolein. In safflower oil however, with faster rates the main reaction appears to be linolein  $\rightarrow$  olein. Thus the course of the reaction of linolein hydrogenation appears to be a function of the relative concentrations of linolein and olein in the oil and the rate of the flow of the oil over the catalyst.

The presence of two or more double bonds in the unsaturated glycerides gives rise to variety of reactions during hydrogenation. Linolein may give rise to a direct formation of steam, olein or its isomers as intermediate products. Thomas (loc. cit.) was of the opinion that a compound containing two double bonds may follow one or all the possible courses of reaction, depending upon the nature of the catalyst and temperature. He also states that in normal practice all the three reactions linolein  $\rightarrow$  steam, linolein  $\rightarrow$  olein  $\rightarrow$  steam and linolein  $\rightarrow$  iso-olein  $\rightarrow$  steam occur simultaneously (J. S. C. I. **39**, 10T, 1920).

I. Ubbelohde and T. Svane concluded from their study of the course of hydrogenation of whale oil that clupanodonic acid absorbed four mols of hydrogen and was converted into linoleic acid without forming linolenic acid as an intermediate product (Z. angew. Chem., 1919, **32**, 257-262). The formation of no intermediate product indicates that the hydrogenation of an unsaturated acid containing two or more double bonds may not be strictly stepwise.

Waterman and co-workers during their investigation of the

course of hydrogenation of methyl linolate have realized the possibility of the direct formation of stearic acid from linoleic acid under certain conditions namely, high pressure with platinum on active carbon as a catalyst at 65°C, stearic acid is found to be formed practically without formation of oleic acid. Thus besides, two possible courses of reaction [linoleic acid  $\rightarrow$  oleic acid (or) isomeric acids, and oleic acids and (or) isomeric acids  $\rightarrow$  stearic acid] they have claimed to have suggested a third possibility namely the direct formation of stearic acid from linoleic acid.

In the present work also it appears that in the case of oil containing equal percentages of olein and linolein the course of the reaction which predominates is that of linolein to stearin. If the hydrogenation of linolein is assumed to be stepwise then the present results indicate that the reactions linolein  $\rightarrow$  olein and olein  $\rightarrow$  stearin proceed with equal velocities.

Armstrong and Hilditch have supposed that the specific attractive influence of the nickel for the unsaturated organic compound diminishes as the unsaturation is lowered (Proc. Roy. Soc. 96A, 1919). Thus the attraction of the catalyst for the unsaturated compound is directly proportional to the degree of unsaturation. Since the first step in hydrogenation is the attraction between the unsaturated compound and the catalyst, it is not probable that in a mixture containing equal quantities of linolein and olein the hydrogenation of both the glycerides proceed with equal speeds.

In the batch process the hydrogenation of olein to stearin does not occur till linolein concentration drops below 10 per cent which shows that the more unsaturated linolein is hydrogenated in preference to less unsaturated olein. The specific attractive influence of the catalyst seems to be responsible for such preferential action. Regarding the attractive influence there appears to be no difference in the two processes. In the continuous process also the linolein must be selectively hydrogenated, but the course of the reaction may differ from that in the batch process on account of the difference in the operating conditions.



There is unanimity among several workers that increasing pressure decreases the selection in the batch process. Moore has pointed out that the increase in pressure facilitating the solution and diffusion of hydrogen causes direct formation of stearic acid from linoleic acid on account of the increase in the concentration of hydrogen at the catalytic surface.

The continuous process which gives nonselective results can be compared with the batch process working at high pressure. Lush has shown that in the continuous process diffusion is better than in the batch process. He imagines the picture of the experimental conditions in both the processes in the following manner:

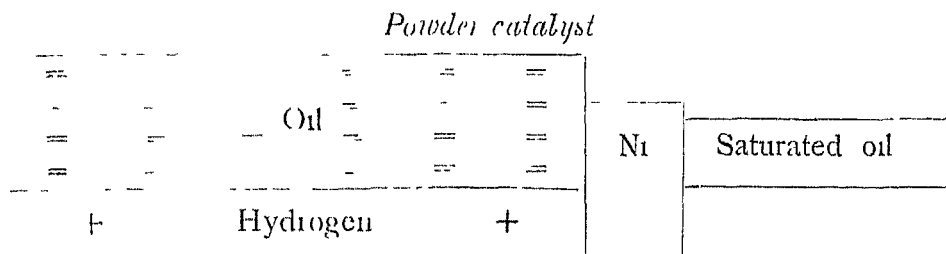


FIG. 1

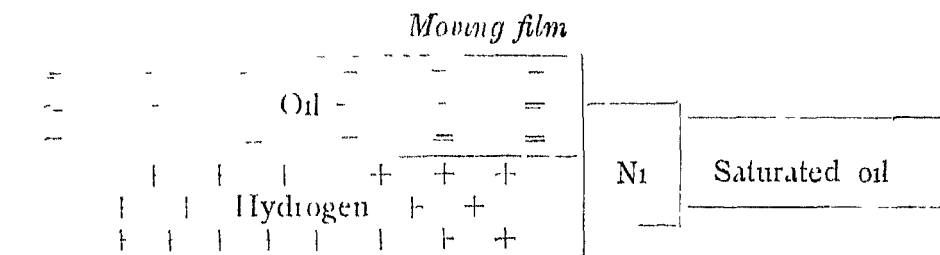


FIG. 2

The centre portion represents a constant mass of catalyst. In the Fig. 1, the hydrogen only reaches the catalyst in limited amount while the oil is present in excess. But in Fig. 2, the hydrogen is in excess and the oil is in limited amount. The formation of saturated oil appears to be more in Fig. 2 than in Fig. 1 (J. S. C. I., 1925, 44, 129T). Thus the two processes differ regarding the availability of hydrogen. In the continuous process where the diffusion is better, the hydrogen available at the catalytic surface is more and the direct formation of stearic acid from linoleic acid takes place.

The hydrogenation of the component glycerides of safflower oil has not been previously studied either in a batch process or in a continuous process. The results obtained in the present investigation throw light on the influence of the relative proportion of linolein to olein on the selectivity of hydrogenation.

In the hydrogenation of safflower oil, it is observed that with faster rates the linolein  $\rightarrow$  stearin reaction takes place. This result is different from that obtained for cottonseed and sesame oils. It appears that this change in the course of reaction of linolein occurs on account of the excess linolein as compared with olein.

It is well known that unsaturated acids like linolenic or oleic are more easily digested than saturated acids having the same number of carbon atoms (Spieckermann *Zt. Nalu II GmV* 27, 83, 1914) (Rudolf *Zt. Physiol Chem* 101, 99, 1918). From this point of view, a semi-solid fat should contain a considerable amount of unsaturated acids. The presence of olein is preferred to linolein, as it is susceptible to oxidation and rancidity.

The serious difficulty of several factories using the continuous method in producing hydrogenated fats with good keeping quality is now well understood in light of the fact that hydrogenation by this process is nonselective. The present results have indicated that with fast rate of flow of the oil over the catalyst the linolein  $\rightarrow$  olein reaction proceeds and olein  $\rightarrow$  stearin reaction does not occur considerably. Thus to improve the keeping qualities, and to produce a sample most suitable for edible purposes by continuous process, it is advisable to recirculate the oil over the catalyst with faster rates in order to obtain the desired degree of hardness. It is also essential to choose an oil containing less of linolein as a starting material.

#### SUMMARY

A brief survey of the literature on the selectivity of hydrogenation is given.

The selectivity in the hydrogenation of cottonseed, sesame and safflower oils at various temperatures by the continuous process is studied by the use of Roozeboom's triangular diagram.

In the case of cottonseed and sesame oils, the hydrogenation is found to be non-selective, which is in confirmation with previous results

Selectivity is observed during the hydrogenation of safflower oil with faster rates of the flow of the oil

The results also indicate that the course of the reaction of linolein depends upon the relative concentrations of linolein and olein in the oil. The linolein  $\rightarrow$  stearin reaction predominates when linolein and olein are in the ratio of nearly 1 : 1. On the other hand the linolein  $\rightarrow$  olein reaction takes place when they are in the ratio of 1 : 0.25

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