New Catalytic Hydrogenation

A Continuous Process for the Hydrogenation of Oils, Employing Unique Catalyst Preparation and Activation

By E. J. LUSH*

IN A previous article an attempt was made to review the oil hydrogenation industry by considering the numerous patents taken out to improve each step in the process.

The disadvantages inseparable from the use of a powder catalyst may be summarized as follows:—

(1) The preparation of powder catalyst is costly with respect to both the labor involved and the plant required.

(2) Just as the catalyst is warming to its work, the process must be stopped, because the particular charge of oil has been sufficiently hydrogenated.

(3) The kieselguhr or other inert support mixed with the powder catalyst adsorbs water which hydrolyses the oil. The products of hydrolysis poison the catalyst, and necessitate subsequent "soda refining" of the hydrogenated oil if it is required for edible purposes.

(4) Oils, especially semi-drying oils, such as cottonseed, deteriorate in color and flavor by prolonged heating. In a discontinuous process the oil must be heated from one to two hours.

(5) Filtration of the hydrogenated oil from the suspended catalyst in most cases involves removing the catalyst from the hydrogenation vessels.

(6) Heat interchangers which are indispensable for economical production lose efficiency in discontinuous processes.

(7) The recovery of spent catalyst involves several processes, and is costly in plant and labor. Only comparatively large factories can employ labor economically in catalyst recovery, and this gives an advantage to the large manufacturer.

It is apparent therefore that the ideal process of hydrogenation would be continuous, would avoid the use of inert supports, and yet use a rigid catalyst, which would remain in the hydrogenation vessel, and would obviate filtration. A rigid catalyst involves the necessity of opening up the plant for its removal, and if this disadvantage is to be minimized, the catalyst must have very high activity to ensure a long life, and its removal from and return to the hydrogenation vessel must be made quick and easy. Moreover, the reactivation of spent catalyst must be cheap and simple, and the method used must lead to complete recovery of activity whatever the nature of the poison including accidental poisons not common to the process. The process of the Technical Research Works, Limited, lays claim to have approached this ideal.

To avoid the use of inert supports, efforts were concentrated on making nickel its own support by the use of a compact form of nickel. A description of the early work in this direction has been published by Bolton[1] and the writer.[2] A more recent account of large-scale development of this process has been given by Bellwood.[3]

The Catalyst

THE catalyst consists of pure nickel in the form of turnings or wire, the surface of which is first oxidized and then reduced back to nickel by hydrogen. This form of catalyst avoids the use of an inert support. Further, the catalyst is spread over nickel, and not over an inner core of unreduced oxide, such as is formed by the reduction of nickel oxide in powder form. Under these conditions, reduction is thorough, and it can be carried out at low temperatures. Palmer[4] has shown, in a study of the reduction of copper oxide by hydrogen at low temperatures, that reduction takes place at the interface between copper oxide and copper. It is probably for this reason that the surface film of nickel oxide is reduced to nickel by hydrogen at 180°C., or even lower. As Sabatier[5] has pointed out, the surface oxidation of a catalyst is readily removed by hydrogen at 180°C., although higher temperatures are necessary for the reduction of nickel oxide.

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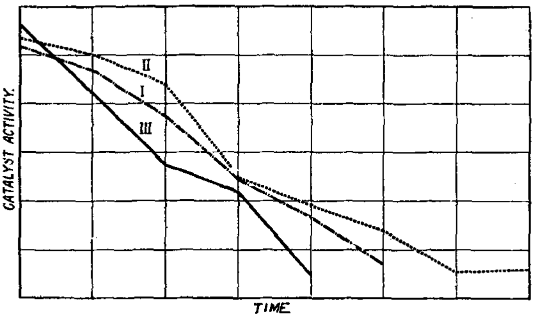


Fig. 1.—Fall in activity of catalyst during hydrogenation.

Probably the reduction at the interface between metal and oxide is bought about by the nascent or atomic hydrogen formed on the surface of the metal from molecular hydrogen.

Oxidizing the Catalyst

REFERENCE was made in the previous article to the advantage of producing nickel oxide at low temperatures. For this reason, air oxidation, which requires high temperatures, does not lead to the production of an active catalyst. The method used by Technical Research Works, Limited, is that of anodic oxidation.[6]

If a nickel surface is made the anode in an electrolytic bath, using as electrolyte a solution of a salt such as sodium carbonate, which will not allow nickel to pass into solution, a film of nickel peroxide is formed over the surface. Such a thin film is easily reduced, and the resulting catalyst is extraordinary active. The method has the merits of simplicity and cheapness without sacrificing the important factor of control, since by means of an ammeter and a voltmeter, the conditions of oxidation can be readily standardized, and the production of a catalyst of uniform activity can be depended upon.

Recovering Spent Catalyst

WHILE anodic oxidation is the method employed to oxidize the nickel turnings to produce a catalyst in the first instance, it also serves another and more important purpose. When the catalyst has been poisoned it is only necessary to extract the oil, and anodic oxidation will remove the poisons so that on reduction a catalyst is formed having its original activity fully restored.

Fig. 1 shows graphically (curve I) the fall in activity of a catalyst used in the hydrogenation of whale oil, and the same catalyst restored (curves II and III) to its original activity by anodic oxidation. In one factory, the same catalyst has been in constant use for four years without loss in either weight or activity, involving nearly a hundred reactivations of anodic oxidation.

Anodic oxidation being the method employed for activating nickel and reactivating spent catalyst, the turnings or wire must be used in a form suitable for treatment in an electrolytic bath. The turnings are therefore packed into cylinders of metal gauze with a centre rod of nickel which supports two circular flanges at its extremities. The metal gauze is fastened to the top and bottom flanges. Such a cylinder is called a *cage*.

The cages are slipped into asbestos covers, and placed upright centrally in nickel or nickel-plated vessels giving a 2-in. clearance between the cage and nickel vessel. The vessel is filled with a solution of sodium carbonate and a current passed through the electrolytic cell, the cage being made the anode and the vessel the cathode. Earthenware pots may be used with nickel sheet cathodes fitted inside.

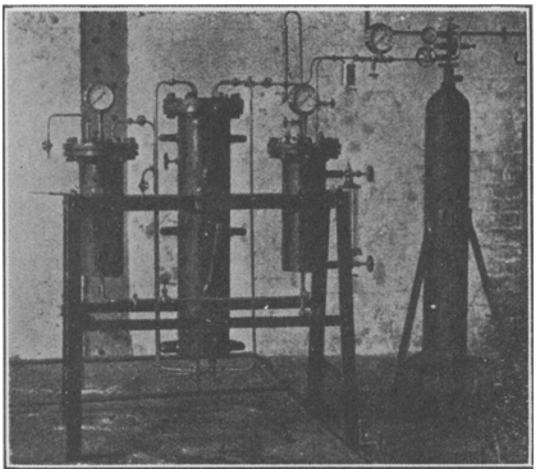


Fig. 2.—One Inch Model Hydrogenation Plant.

The strength of the current will vary with the size of the cage. For example, a cage 12 in. diam. and 3 ft. long, holding 100 lb. of nickel turnings, will require a current of 180 amperes and 7 volts for 8 hours in an electrolyte consisting of a 5 pen cent. solution of sodium carbonate.

After anodic oxidation, the cages are washed in water, which is frequently changed. The water may be changed automatically by syphon action. In this process as in the old powder process, the importance of washing thoroughly cannot be exaggerated.

The Hydrogenation Plant

THE smallest plant in which the catalyst can conveniently be packed into cages, consists of four tubes 3 in. long, containing cages 1 in. diam. Such a model has been supplied to the Battersea Polytechnic, and is shown in Fig. 2 by kind permission of the Principal, Dr. Pickard. Compressed hydrogen from a cylinder supplies hydrogen to the plant and also forces oil from the feed vessel through a drip feed in a sight glass on to the catalyst in the first tube.

The oil flows down the catalyst by gravity and is brought to the top of the next tube by the flow of hydrogen. After passing down the four tubes the oil is collected in the receiver from which it can be drawn off quite free from suspended nickel. Each cage holds 1 lb. of nickel turnings, and the plant will deliver from 10 to 15 lbs. of oil per hour, of, for example, cotton-seed oil hydrogenated to an iodine value of 50. Much information has been gained from the working of such a model, ([7])([8]).

It has been found that above a certain minimum rate of flow of oil—in this model 5 lb. per hour—the hydrogen absorbed per hour is independent of the flow of the oil, or, in other words, the degree of hydrogenation of the oil as measured by the drop in iodine value is proportional to the speed of the oil passing through the plant.

As coconut oil can be hydrogenated to an iodine value of 0.1 per cent. by a single passage through the plant, it has been calculated that all the oil comes into molecular contact with the catalyst. It is interesting in this connection to note that the hydrogen absorption per hour remains the same whether the final iodine value of cottonseed oil is 70, in which case mostly linolic acid has been hydrogenated, or whether the iodine value is 40, when an equal proportion of linolic and oleic acid has been hydrogenated. This is taken as evidence that the limiting factor in the rate of hydrogenation is the activation of the hydrogen by the nickel.

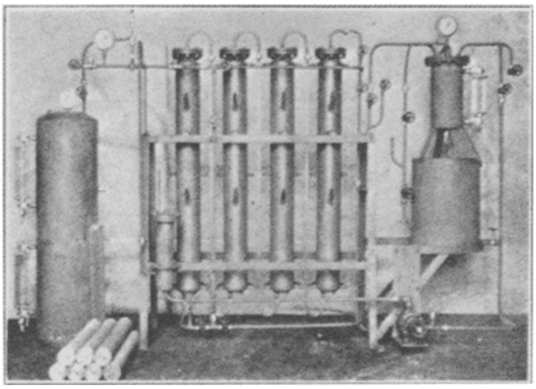


Fig. 3.—Four-Inch Model Hydrogenation Plant. Capacity: 5 tons per week.

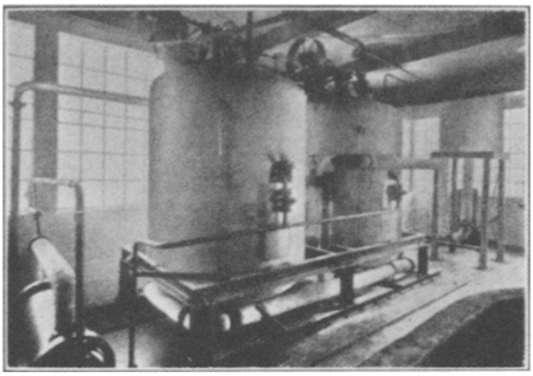


Fig. 4—Preheaters for Vacuum Drying of Oil in Hydrogenating Plant for Cottonseed Oil, &c. View shows Top Floor.

The effect of the pressure of the hydrogen on the rate of hydrogenation is interesting. It has been found that the hydrogen absorption is proportional to the square root of the pressure, from which the writer believes the nickel atomizes the hydrogen which is then added as such directly to the double bond of the unsaturated oil. Table I confirms the results previously published[8], but with a pressure variation of 100 lb. instead of 10 lb. These results are useful in adjusting the working conditions of a large plant. If the flow of oil is too slow the catalyst is not all covered, and the hydrogen absorbed per hour will increase with increased flow of the oil. If, on the other hand, the flow of oil is too fast, in order to reach the nickel the hydrogen must pass through a thick film of oil, and this will determine the amount reaching the catalyst in a given time. Since the solubility of hydrogen in oil is proportional to the pressure, when the flow of oil is too fast, the rate of hydrogenation will be proportional to the hydrogen pressure and not its square root. These considerations enable a plant to be designed with the correct ration of length to diameter of the catalyst cages. They further allow the chemist in charge of the plant to check from time to time the efficiency with which it is working.

The 4-in. Model

A LARGER model plant is shown in Fig. 3, the cages of which are 4 in. diam. and 2 ft. 6 in. long, and there are two cages per

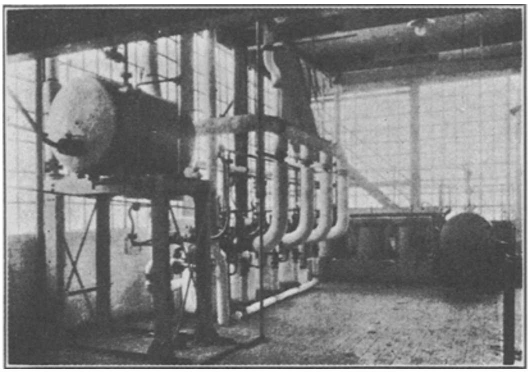


Fig. 5.—Middle Floor of Hydrogenating Plant.

tube. This plant has a capacity of 5 tons per week of cottonseed oil, hydrogenated to an iodine value of 50. Each cage holds 12 lb. of nickel turnings, from which it can be calculated that the turnings occupy 10 per cent. of the total space in the cage.

As nickel is ten times heavier than oil, the weight of oil in lbs. equivalent to the cubic capacity of the cage is equal to the weight of turnings used to fill it. For estimating the output from a plant of given size one can therefore use the cubic capacity of the plant expressed in lbs. of oil or the weight of turnings. Experience has shown that a plant will deliver cottonseed oil hydrogenated to an iodine value of 50 at an average hourly rate expressed in lbs. per hour equal to its own cubic capacity or the weight of the catalyst contained in it. For example, the plant shown in Fig. 3 requires 100 lbs. of oil to fill it; the weight of nickel turnings contained in the eight cages is also 100 lbs., and it will deliver 100 lbs. per hour of cottonseed oil (average iodine value of 50).

TABLE I.

Effect of Hydrogen Pressure on the Rate of Hydrogenation

P Hydrogen Pressure lb. per sq. in.	Iodine Values Original Oil 106.2 Final Product	Difference	Time in Minutes	C.C. of Oil	Hydrogen absorbed P	Hydrogen absorbed $\sqrt{P}$
0	95.6	10.6	5	200	708	272
100	66.2	40.0	5	200	347	372
200	51.1	55.1	5	200	256	377
300	40.8	65.4	5	200	207	370
200	48.2	58.0	5	200	270	396
100	60.3	45.9	5	200	393	425
0	91.2	15.0	5	200	1000	384

12-in. Factory Model

FOR the hydrogenation of oils in the factory, standard cages each 12 in. diameter and 3 ft. long have been found most convenient. Each tube contains three cages. The first plant was erected in 1922 at the works of Loders & Nucoline Limited, Silvertown, London, E.

In this plant the oil is circulated *in parallel* through five tubes, while the sixth is being reactivated. By stopping a tube for reactivation every second day, a uniform output of hydrogenated oil can be maintained continuously with a variation in iodine value not exceeding 1 per cent. The oil from the five tubes flows by gravity down the catalyst in the cages, and collects in a receiver situated below the tubes. It is taken by an oil pump from the receiver and pumped into the tops of the tubes by a suitable manifold connection. The continuous flow of oil is maintained by adjusting on outlet valve from the receiver to deliver the same volume of hydrogenated oil as is supplied to the manifold by a pump connected to the storage tanks of untreated oil.

A strictly continuous process, such as is used in the 4-in. model plant, is preferable for the hydrogenation of cottonseed, soya bean, whale oil, and other oils having high iodine values.

By the courtesy of Mr. Pearson, Chairman of the British Oil & Cake Mills Limited, the following photographs of a plant operating in this latter way are reproduced. The plant is arranged on three floors. On the top floor, Fig. 4, the two preheaters can be seen arranged for vacuum drying of the oil to be hydrogenated. These have now been substituted by a continuous tubular preheater, and are used as storage tanks.

On the middle floor, Fig. 5, the four tubes are shown with the various connections for supplying the plant with oil and hydrogen. The solvents store tank for use in connection with the extraction *in situ* of spent cages is shown, as also the three earthenware activating vessels and high pressure hydrogen storage vessel.

Fig. 6 shows the bottom of the four tubes, the solvent recovery still, and the hydrogenated oil receiver. The oil is carried from the bottom

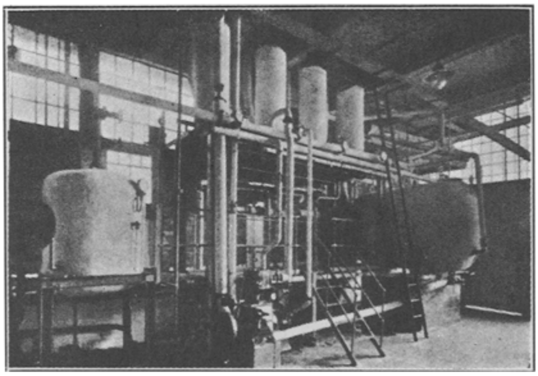


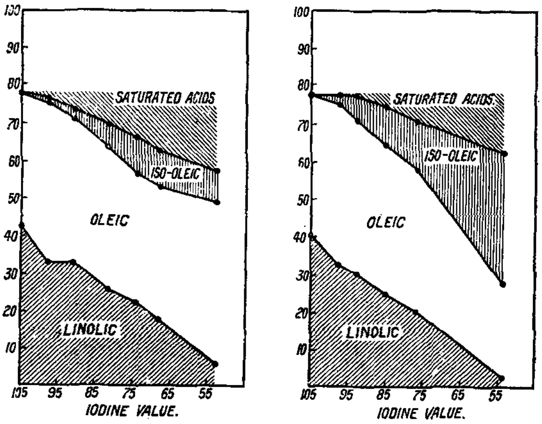
Fig. 6.—Lower Floor, showing Bottom of Tubes, Recovery Still, &c.

of one tube to the top of the next by means of the hydrogen, which is circulated round the tubes. This procedure avoids the use of oil pumps between the vessels, and incidentally by watching the pressure gauges on the tubes one can see at a glance whether there is a free passage throughout the system. The time taken from the moment the oil enters the preheater or heat interchanger until it reaches the hydrogenated oil receiver is about 10 minutes. From here it is forced by the hydrogen pressure in the system—60 lb. per square inch—through the heat interchanger to preheat the incoming oil.

The fact that the catalyst is free from unreduced nickel oxide or kieselguhr explains why the free fatty acids are not increased by this process. The average free fatty acids of cottonseed oil with an iodine value of 50-55 made in this plant is 0.08 per cent. In the powder process they frequently rise to 0.5 per cent., or even 1 per cent., with inferior oils where fresh catalyst has to be added to complete hydrogenation. In this plant oil is hydrogenated continuously for three weeks, and the plant is then shut down for two days for reactivation of catalyst. After cooling down, the cages are extracted *in situ,* the solvent removed, and the cages taken out and reactivated by anodic oxidation for eight hours in the electrolytic bath. They are then washed, returned to the plant and reduced in hydrogen at 180° C and hydrogenation recommenced.

The length of time a set of cages will remain active depends upon the nature of the oil and the care taken in refining it, particularly in the removal of soap. In the laboratory common edible cottonseed oil can be hydrogenated continuously for a month by the use of an electrically heated tube provided with a sufficiently large store tank placed above it for supplying the oil by gravity. The apparatus can be left unattended even over the week-ends. Care must be taken by electrically heating the hard oil receiver to prevent the formation of stalagmites of hydrogenated oil which will otherwise rise even over a foot in height and choke the tube.

It is interesting to note the capacity of the activating baths for supplying cages. A set of three earthenware vessels to take the three cages used in each tube will reactivate the cages in eight hours, and since the cages remain active in use from 200 to 400 hours, three vessels will supply cages for 25 to 50 tubes where their cages are reactivated in rotation.



The Hydrogenated Oil

Reference has already been made in a previous article to the importance of encouraging selective hydrogenation and repressing the formation of iso-oleic acid. The writer considers the effect of the hydrogen pressure on the rate of hydrogenation, is evidence of the direct addition of single atoms of hydrogen to the double bond of the unsaturated oil (see Table I). On this view iso-oleic acid is formed by the single atom being ejected before another atom arrives to stabilize the semi-saturated double bond. If this be so then conditions which facilitate the arrival of more atoms, should decrease iso-oleic acid formation. Experimental evidence proves that the continuous hydrogenation process described above keeps the catalyst working at its maximum efficiency in supplying atoms of hydrogen Therefore this process should produce the minimum amount of iso-oleic acid at any given temperature. That this is true experimentally has already been published, and Fig. 7 is reproduced as suport to the theory and evidence of the importance of the process to the oil hydrogenation industry.

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[1] *J.S.C.I.,* 41, 384 R, 1922.

[2] *J.S.C.I.,* 42, 219 T, 1923.

[3] *Chem. Trade Jour.,* Mar. 6, 1925.

[4] *Proc. Roy. Soc.,* A. 103, 1923.

[5] *Journ. Ind. and Eng. Chem.,* Oct., 1926.

[6] U.K. Pat. 203,218.

[7] *J.S.C.I.,* 43, 53 T.

[8] *J.S.C.I.,* 44, 129 T.