

vertor as was done at the start of the operation. With electrolytic hydrogen, dried by compressing to 300 pounds per square inch pressure in storage tanks, this venting during the run is usually unnecessary.

The presence of gases other than hydrogen in the upper convertor space is undesirable primarily because they retard the absorption of hydrogen and, if present in sufficient quantity, prevent the further flow of hydrogen to the convertor. But there are also other objections: oxygen oxidizes the oil and catalyst, carbon monoxide poisons the catalyst, and steam reacts with the oil.



HYDROGENATION PLANT SHOWING REDUCER, MIXING TANK, FILTER PRESS, AND CONVERTOR

Separation of Catalyst from Hardened Fat

When the tests show that the desired hardness has been reached, the hydrogen supply is shut off and the hard fat charge is cooled preliminary to filtration. Water is turned into the internal cooling coil or to the external heat exchanger, and the oil is cooled to such a temperature that on filtration it will leave the filter press at a temperature low enough not to darken; this temperature is 120° to 160° F. (49° to 71° C.), depending on the oil.

The clear oil is run to the finished oil-receiving tank. The filter press cake is dropped into the catalyst mixing tank and

held there for mixing with the next batch of oil. The catalyst is used over and over, either alone or with slight addition of fresh catalyst, until it is no longer sufficiently active to harden a charge of oil within the normal hardening period.

The handling of the hardened fat depends upon the oil and the use for which it is intended. Completely hardened oils are usually employed for technical purposes without deodorizing. Such oils may be pumped directly to tank cars, or flaked or molded into cakes for packing in bags.

Partially hardened oil for edible purposes is deodorized and is then further processed to shortening or other products.

CATALYSTS FROM ALLOYS

Nickel Catalysts

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A LARGE portion of the literature relating to hydrogenations is devoted to the preparation of catalysts. Because nickel is so generally adaptable, there is more reference to the preparation and use of nickel catalysts than to all others combined. Fraser published a comprehensive abstract of the literature relating to the subject (6).

Any critical discussion of the many proposed and practiced methods for producing nickel catalyst should be approached with tolerance. Consideration of these methods does lead to the conviction that nickel is not only a versatile catalyst, but that its catalytic properties may be developed in many ways. Whether this means that nickel may be prepared in the same form by many different methods or that it is a good catalyst in many different forms is probably not known at present.

Comparison of Catalysts

There are recognizable differences in good nickel catalysts prepared by different methods for the same reaction, but these

differences do not fix the value of the catalysts. While the catalytic property may be associated with one or more of them, it is not determined by specific gravity, state of division, magnetic or pyrophoric properties, or any other measurable characteristic of the metal. The probability that nickel or any other substance will catalyze a given reaction is based on the great amount of work that has been done in many fields, rather than on any correlated, calculable properties of either the catalyzing substance or the reacting elements or compounds. The catalytic value of a substance is determined by trial; if it does its work, it is good. The statement that nickel, cobalt, chromium, iron, copper, and other metals are catalysts is true or false, depending entirely on the form in which the metals are used. Because nickel prepared in a certain way may not be a satisfactory catalyst for a given reaction does not show that nickel is not a catalyst for the reaction. Such a conclusion should be modified by a description of the method used in preparing the catalyst and, as has been said (1), of the operator's state of mind.

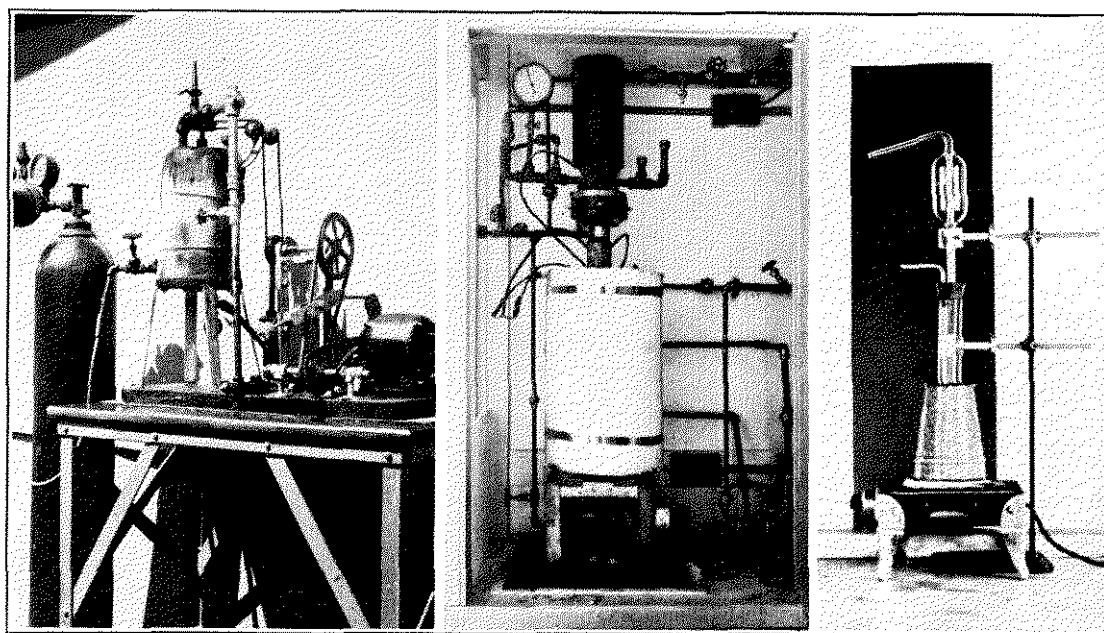


FIGURE 1. THREE TYPES OF LABORATORY HYDROGENATING EQUIPMENT FOR EDIBLE AND OTHER FATTY OILS

The types of hydrogenating equipment and methods of operating are also of great importance. Work done in the same laboratory is seldom subject to variation in these factors, but many conflicting results in different laboratories, with the same catalyst, may be accounted for by them.

Experimental Equipment

Figure 1 shows three types of convenient laboratory hydrogenating equipment for use with edible and other fatty oils:

A is a one-liter vessel arranged with a mechanical agitator and a pump for continuous circulation of the oil from the bottom of the vessel back into the top where it is discharged through the gas space in a coarse spray. A gas burner under the vessel is the heat source.

B is a tube-type converter arranged for circulation of both oil and gas. The oil pump draws the oil from the bottom of the tube and discharges it back into the top. The gas pump draws the hydrogen from the separator at the top of the tube and discharges it through the oil by means of a distributing spider in the bottom of the tube. This arrangement gives extremely good agitation and gas contact. The tube is immersed in an oil bath heated by electricity.

C is a test tube converter for quick work with 75 cc. or less of oil. Agitation is obtained by introducing the gas into the bottom of the test tube with a pointed glass tube. It bubbles up through the oil and thus gives good agitation and contact. By using the connecting bulb shown, the gas may be circulated. Heating is by means of an oil bath.

A and *B* are suitable for pressures up to 100 pounds per square inch. *C* is intended for use at atmospheric pressure or a few inches of water pressure.

Catalyst Alloys

It is in the preparation of catalysts that the chemist is most likely to revert to type and to employ alchemical methods. From all the evidence, it seems the work should be approached with humility and supplication, and the production of a good catalyst received with rejoicing and thanksgiving. The discussion which follows covers a convenient method for preparing catalysts.

Good catalysts, particularly nickel, can be prepared from alloys of metals (9). The simplest form of alloy consists of two components. One is the catalytic material, and the other is a substance that may be dissolved by a solvent which will

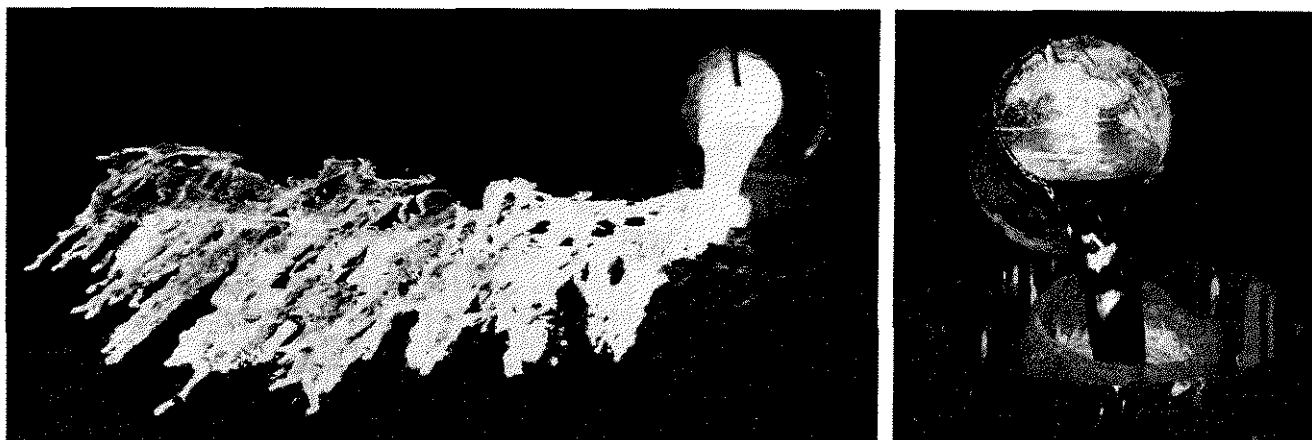


FIGURE 2. APPEARANCE OF MOLTEN NICKEL-ALUMINUM CATALYST ALLOY (left) AND OF MOLTEN ALUMINUM

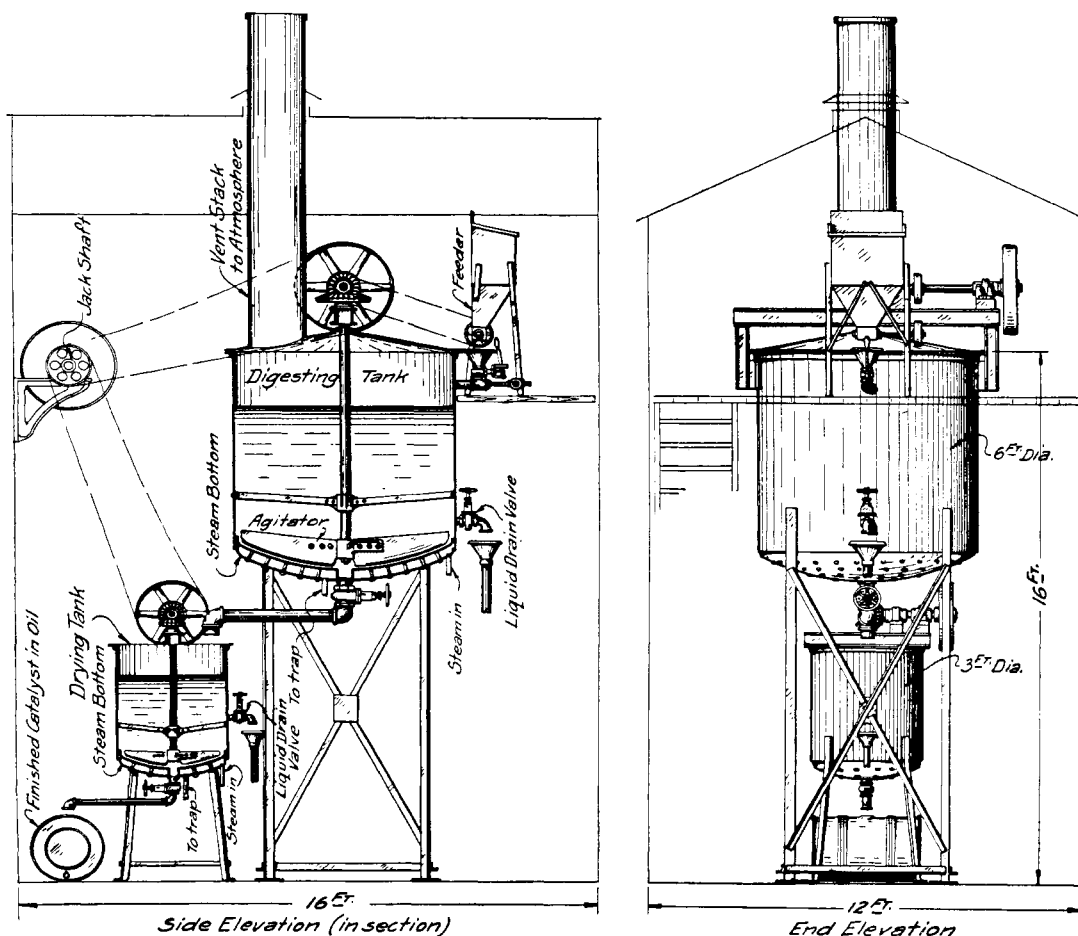


FIGURE 3. ARRANGEMENT OF EQUIPMENT FOR MAKING RANEY NICKEL CATALYST BY THE GRAVITY METHOD

not attack the catalytic material. Some alloys of this type are composed of nickel and aluminum. More complex alloys are made with two or more catalytic materials composing the insoluble portion. The soluble portion is conveniently either aluminum or silicon, or mixtures of the two. Aluminum, particularly, has the property of readily mixing with a number of metals to form alloys having proper characteristics for the production of catalysts. Aluminum alone or in combination with such catalytic metals as nickel, cobalt, copper, and silver is readily soluble in alkali solutions which do not attack the other metals.

The actual composition of the alloy in the most useful range is complex, and is probably made up of several combinations of nickel and aluminum, with perhaps traces of free nickel and aluminum. Since in the final production of the catalyst the aluminum is substantially removed and wasted, it is desirable from a cost standpoint to produce a pound of nickel with the use of as little aluminum as possible. However, other factors enter into the final cost, and for a given use all the factors are taken into consideration in selecting the most suitable alloy. Many alloys within the practical working range produce equally efficient catalysts. Some of the most useful proportions of nickel and aluminum for the alloy are: 50 per cent Ni-50 per cent Al, 42 Ni-58 Al, and 30 Ni-70 Al. These percentages would correspond approximately to the nickel-aluminum compositions NiAl_2 , NiAl_3 , and NiAl_5 , respectively. The latest studies of the nickel-aluminum system (2) indicate the existence of Ni_3Al , NiAl , Ni_2Al_3 , and NiAl_5 , but not of NiAl_2 or NiAl_5 . The best previous work

(7) had suggested the existence of NiAl_2 , as well as NiAl_3 and NiAl . It is interesting to note that the composition NiAl is a hard tough alloy, only slightly soluble in 20 per cent sodium hydroxide solution.

Catalyst alloys seem to have little if any other uses. A 50-50 nickel-aluminum alloy, for example, which would be employed for a finely divided catalyst, has few of the physical properties of nickel or aluminum. It is not ductile or malleable, has little tensile or compressive strength, but, in common with aluminum, is not magnetic. It has a high melting point, cools rapidly, and would be difficult to cast in a mold except in the simplest form. It is very friable, and is easily crumbled and reduced to a fine powder.

Figure 2 (left) shows the pouring of a nickel-aluminum catalyst alloy on the cooling table. The incandescence of the molten alloy indicates the high temperature. This is further emphasized by the appearance of molten aluminum when poured from a crucible (Figure 2, right).

Catalyst alloys comprise a regular commodity, and are available in any quantity in the form of fine powders and larger particles. These forms provide a starting material from which highly active, uniform, and efficient catalysts may be prepared with great ease. Both the equipment and procedure required for processing the catalyst alloy are simple and need no highly technical supervision. In any case, only two plain atmospheric-type agitator tanks are required. In some cases the entire preparation may be completed in one tank. There are no filter presses and no hydrogen or other reducing apparatus.

Processing a Catalyst Alloy

Figure 3 shows the typical arrangement of the two tanks. The large one is the digesting tank, and the small one the drying tank. In the digesting tank the catalyst alloy is treated with an alkali solution, usually 20 per cent sodium hydroxide, to dissolve the aluminum. The sodium hydroxide solution may be prepared directly in the tank or pumped into it from some other source. After the solution is ready, the catalyst powder is introduced either by the feeder shown or simply by throwing it through an opening in the top of the tank. The solution need not be heated to start, because the catalyst powder reacts readily with the cold solution, liberates hydrogen gas, and generates sufficient heat to bring the solution to the boiling point quickly.

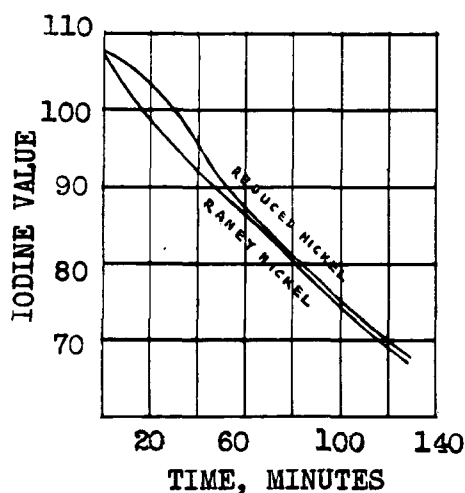


FIGURE 4. COTTONSEED OIL SATURATION CURVES

The digesting tank is designed to process 600 pounds of powder, and this amount may be conveniently fed into the tank within one hour. Because of the fact that hydrogen and steam are generated during the digesting operation, the digesting tank must be vented to the outside of the building. This is done by the stack shown, without any escape of hydrogen and steam into the room. During the time the powder is being introduced into the tank, it is necessary to add water to make up for evaporation and to keep the density of the solution about constant. After all the powder is in the tank, steam is turned on the jacketed bottom, and the digestion, with occasional addition of water, is continued for 2 or more hours, at a temperature of 245–250° F.

When the digesting operation is completed, the active catalyst remains in the tank as a sludge. After being washed free from alkali, it is ready for use without further treatment. Washing takes place in the digesting tank, preferably with cold water. It is desirable to draw off as much as possible of the strong sodium aluminate solution through the opening shown before starting the washing. Then with the agitator running, the tank is filled with water. The agitator is then stopped, the catalyst is allowed to settle, and the wash water is drained off. The washing operation is repeated as often as may be necessary to reduce the residual alkali content to the desired level. Large quantities of sulfates and chlorides in the wash water apparently do not signify inferior quality in the catalyst.

If the catalyst is to be used in a saponifiable oil, it is better to transfer it to the drying tank for removing the water. This is done through the opening in the bottom of the digesting tank, using a hose to wash off any that may have settled

on the agitator or supports. After the catalyst is in the drying tank, it is allowed to settle, and as much water as possible is drained off. The drying oil is then added, steam turned on the jacket, the agitator started, and heating continued until drying is complete. The catalyst suspended in oil may then be run from the bottom of the drying tank into any suitable container.

During the digesting and washing operations the catalyst must be kept covered with the digesting solution or water. When transferring the catalyst from water to some other compound, it must be kept covered by whatever compound is used for the purpose. The preparation procedure may be modified by varying the kind and amount of alkali used, the density of the solution, and the temperature and time at which the digesting is carried out. Covert and Adkins (5) describe a procedure which gives a highly satisfactory catalyst for a number of hydrogenations for which it has been used. With a given catalyst powder the same procedure will always produce the same type of catalyst.

Catalytic Properties

It is not clear just how the catalytic property is developed in nickel from alloys. However it is done, it is apparently not in the same way that develops the catalytic property in nickel when prepared by other methods.

Reduced nickel catalyst, for example, is basically one thing—the product of the action of hydrogen or some other reducing agent on a nickel compound. Differences in the methods for preparing reduced nickel usually lie in the preparation of the nickel compound and in the application of the reducing agent. The action of hydrogen on nickel oxide, for example, seems to be simply the union of the hydrogen with the oxygen in the oxide to form water and nickel mixed with different oxides of nickel. Seldom is the reduction carried to completion. Good reduced catalysts are often made up of 33 per cent nickel and 67 per cent of various nickel oxides. This proportion does not always remain constant during the life of the catalyst, because under some conditions of use, reduction of the oxide continues. After the catalyst is spent, the proportion will be reversed; that is, the nickel content will amount to 67 per cent or more of the total, and the balance will be nickel oxides. Reduced catalysts are usually in a state of extremely fine division, smaller than 325 mesh. Some of them are not pyrophoric at normal temperatures.

The preparation of nickel catalysts from alloys of nickel and aluminum is not similar in any respect to the preparation of reduced nickel catalysts. Except for possible minute quantities picked up during processing, there are no oxides in nickel-aluminum catalyst alloys. These are precluded by the powerful reducing action of the aluminum under the conditions of manufacturing the alloy. The action of sodium hydroxide on the catalyst alloy is to combine with the aluminum in the alloy to produce sodium aluminate and hydrogen gas. The hydrogen on and in the alloy particle at the moment of liberation is in the atomic state and, no doubt, has all the active qualities of such a gas. Under the circumstances there are ideal reducing conditions, but there is nothing to reduce, unless the nickel can be thought of as being in the atomic state also, and in this condition being first oxidized by the water and then immediately reduced by the atomic hydrogen. Such action seems improbable. Whatever the action is, no nickel oxide exists in the nickel catalyst prepared from nickel-aluminum alloy.

There is evidence that the nickel is in the form of nickel hydride, NiH_2 . A carefully weighed sample which has been dried in acetone and gently warmed will flash. Weighing again shows that the sample has lost weight. This loss

corresponds to that which would be shown by the decomposition of NiH_2 to leave nickel and drive off hydrogen. The particle size is about 167 mesh. It is pyrophoric at normal temperatures.

Figure 4 shows that catalysts having different physical characteristics may have practically equal catalytic characteristics. Duplicate samples of cottonseed oil were hydrogenated. In one sample 0.5 per cent of nickel by weight of reduced nickel was used, in the other, 0.5 per cent of nickel by weight of Raney nickel. The reduced nickel was finer than 325 mesh. The Raney nickel was about 167 mesh. The reduced nickel was not pyrophoric, the Raney nickel was. The maximum hydrogenating temperature was 385–390° F., and the pressure 15 pounds per square inch. The graphs show that the saturation of the oil proceeded at practically the same rate. Characteristics of the hydrogenated oil at critical points on the curves were substantially the same.

Uses

Nickel catalysts from alloys usually referred to as Raney nickel find use in the many reactions for which nickel is a catalyst. Adkins, in his comprehensive work with copper-

chromium oxide and nickel catalysts (1), gives numerous examples of the adaptability, selectivity, and general use of Raney nickel.

Recent patents describe its utilization in the hydrogenation of rosin (3) and in the hydrogenation of aliphatic nitro compounds (8). Its use in the hydrogenation of indene-coumarone resins was recently described (4). An important use is the synthesis of sex hormones (10).

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HYDROGENATION OF PETROLEUM

The present status of high-pressure hydrogenation of petroleum is discussed as to theory and commercial application. Particular reference is made to the production of aviation gasoline, motor fuel, aviation blending agents, and Diesel fuel, and the conversion of heavy asphaltic fractions. Yields and inspection data on these operations are included. Economics are discussed, and it is shown that for a 30 per cent spread between crude and fuel oil price, hydrogenation in competition with thermal cracking for production of motor fuel will show a 20 per cent return on the added investment for hydrogenation.

FROM the time of Sabatier until the middle of the third decade of this century, commercial hydrogenation was practiced to a limited extent under very restricted conditions. Effective catalysts, composed mainly of reduced nickel, were available, but impurities in the feed or hydrogen, such as sulfur and arsenic, tended to deactivate them rapidly. Since coal and oil usually contain such substances, these limitations made it impossible to hydrogenate carbonaceous materials of mineral origin. The industrial application of hydrogenation was therefore limited for many years to the treatment of fats and oils of animal and vegetable origin.

Early attempts to convert coal into liquid hydrocarbons by subjecting it to high hydrogen pressures were not too satisfactory. However, when the research organization of the I. G. Farbenindustrie discovered sulfur-resistant catalysts, hydrogenation of carbonaceous materials of mineral origin assumed commercial possibilities, although the use of pressures of the order of 3000 to 4000 pounds per square inch was

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required. In 1927 the Standard Oil Development Company joined in the further development of the hydrogenation process. As a result of this work the hydrogenation process has been adapted to the following applications:

High-octane-number aviation gasoline production from kerosene and gas oil fractions.

Motor gasoline production from gas oils.

Aviation blending agent production by saturation of branched-chain polymers.

Production of high-grade Diesel fuels from low-quality gas oils.

Production of water-white paraffinic kerosenes from inferior-quality distillates.

Production of high-viscosity-index lubricating oils from poor-quality lubricating distillates.

Refining (or "hydrofining") of gasolines to low sulfur content and high stability.

Conversion of asphaltic crudes and refinery residues into lower boiling gas oils of increased paraffinity.

Preparation of low-aniline-point high-solvency naphthas.

Preparation of high-flash high-octane-number safety fuels.

The theoretical background of the above adaptations is discussed briefly, and the commercial applications of the more important are presented in some detail. At present, commercial hydrogenation for lubricating oils, solvents, and kerosenes has been superseded by solvent extraction methods. No commercial application of hydrofining has been made. These