backs where it may plug the lines, cause electric shorts, or be lost in the flashback water, or by being contaminated by impurities in make-up water by CO_2 from the air and hence require discarding. When the cell tank leaks, obviously a new gasket or other repairs are necessary. Many devices and designs have been made to remove the electrolyte from the gasses leaving the cells and return it to the cells. Some of these devices require the gas to be washed free from electrolyte by the pure make-up water which returns it to the cell. Others provide for the cooling of the gases as they leave the cells with the resultant condensation of water vapors which are used to wash the electrolyte back into the cells. This method also saves on make-up water. Some of the devices employ both these methods.

The electrolyte can be kept relatively pure or uncontaminated of obnoxious materials by using distilled water having a minimum or less than 5 parts per million of permanent hardness, especially iron sulphates and carbonates, and no chlorides. The amount of carbonates formed will, of course, depend upon the type of cell and whether or not paraffin is used on open cells.

The cell voltage may be kept at a minimum by using as pure an electrolyte as possible, at the density at which it has maximum conductivity, and by seeing that the anodes are kept nickel-plated and the cathodes either free from scale or cobalt-plated. The electrolyte conductivity will be greatest at a high electrolyte temperature and hence the temperature should be maintained as high as possible but not to exceed 165° F., since excess evaporation of water and attack on cell parts by the electrolyte will take place at higher temperatures.

The gas purities are the hardest items to control in cell operation. They are, however, of the greatest importance since hydrogen purities below about 92.5% and oxygen purities below about 91.5% constitute explosive mixtures. Impure gases are caused by any combination of faults, the main ones being:

(1) Holes in the diaphragms or leaks between compartments, which are large enough to permit the gases to inter-mix.
(2) Differences in pressures of the oxygen and hydrogen gases, which cause a flow of gas through the diaphragm; or, any small leaks which may exist.
(3) Shorting of an electrode to a diaphragm due to deposited impurities from the electrolyte in the case of asbestos; or, because of nickel used in the diaphragm, and thus act as an electrode.
(4) Acting of the diaphragm as a bipolar electrode, *if* it be conducting due to application of over twice the decomposition voltage to the cell.
(5) Reversed polarity of the cell due to reversed polarity of generator; or if generator voltage is less than back e.m.f. of cells; due to short circuiting of a cell upon itself.
(6) Too low a level of electrolyte, exposing porous diaphragm which would permit passage of gas because of loss of sealing effect due to liquid.

If the liquid level of the cell is maintained at the proper level, the diaphragms and gas seals are kept maintained at the proper level, the diaphragms and gas seals are kept free of leaks, pure electrolyte is maintained, gas holder pressures are balanced so that the cell gas pressures are equal, generator reverse current relays and undervoltage releases are used, plate warping is avoided by not overloading or overheating, good gas purities may be expected. If, however, the gas purities drop, the responsible cells must be located and removed from the electric circuit or vented to the outside air, until they are removed from the circuit. In the case of filter press type cells, the whole bank would perhaps require removal from service, since usually one cell cannot be vented or effectively removed from the electric circuit. The cells responsible for bad purities should be repaired as soon as possible, either to return to service or to act as standby equipment.

Since hydrogen diffuses more readily than oxygen and since it is produced in twice the quantities as oxygen, the oxygen purity will be lower than the hydrogen purity in all cases except when the cell oxygen gas pressure is greatest or when the anode shorts to the diaphragm.

If higher gas purities than are normally produced by the cells are required, the purities may be increased to any desired value by passing the gas through a purifier, which burns out the foreign gas by means of an electrically heated filament. In the case of oxygen, the life of any filament, except perhaps platinum, would be relatively short and hence the hydrogen is usually burned out in the presence of platinum chloride, deposited on an asbestos core, which acts as a catalytic agent.

This method of purification is wasteful of gas, especially where low purities are generated, since much of the gas is reconverted to water. However, it is the most practical. The better procedure is to use and maintain cells which will generate gas of the desired purity, there being cells on the market which will generate hydrogen of 99.8% and oxygen of 99.6% minimum purities.

For all around cell operation where the desire for greater flexibility, better average gas purity, fewer forced outages, and better continuity of service overweighs the increased first cost and larger required floor space, the open tank cell will prove its merits.

Review of Hydrogenation

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IN the strict sense of the word the term hydrogenation should apply to those reactions in which hydrogen unites with an unsaturated compound to give a saturated one. Probably the best known industrial application of this procedure is the hardening of vegetable or other oils which are glycerides of oleic or other unsaturated carboxylic acids. As the name implies, the physical change which occur in many instances is the transformation of a liquid to a solid material, as for example, the changing of olein into stearin.

However, hydrogenation at present includes not only those reactions as mentioned above but also others in which reduction is predominate, as the conversion of gly-

Abstract

A brief review of hydrogenation as applied to hardening of vegetable oils, conversion of glycerides or other esters of fatty acids into alcohols of high molecular weights, reduction of carbon monoxide to hydrocarbons or to alcohols, and hydrogenolysis of petroleum. Some mention is made also of the types of catalysts as well as the operating conditions employed in each instance. In addition, a short outline of various methods for the commercial production of hydrogen, and also its purification, is included.

cerides of fatty acids (and also other esters) into alcohols having the same number of carbon atoms as the fatty acids. Another illustration of reduction is the manufacture of alcohols from carbon monoxide and hydrogen. Still further extension of the term hydrogenation includes those processes which depend upon a multitude of reactions, e.g., molecular decomposition, addition of hydrogen, polymerization, isomerization and cyclization, occurring simultaneously in the presence of hydrogen and which can be exemplified by the hydrogenation of petroleum.

Possibly the above-mentioned applications of hydrogenation are of the greatest interest in industrial developments in this country, and for this reason will be discussed briefly. Furthermore, since it is understood that succeeding papers will discuss in detail certain phases of operation, this review will be limited to a survey more from a chemical point of view.

It should be understood, however, that hydrogenation has proven applicable in many other fields, as for example, the conversion of phenolic bodies from coal tar into aromatic or hydroaromatic compounds. Other illustrations are hydrogenation of coal or of carbon monoxide or dioxide to hydrocarbons, processes which are of particular value in those countries having no readily available or only limited supplies of petroleum. Many other applications include those such as the manufacture of tetralin or decalin from naphthalene, hydrocarbons from aldehydes or ketones, aliphatic or paraffinic bodies from olefins, and aromatic amines from the corresponding nitro compounds.

Hydrogenation of vegetable oils, of carbon monoxide and of petroleum are alike in one respect, i.e., the use of a catalyst or catalysts is required. Preparation of the latter, maintenance of their activity, and recovery of them are important considerations. Some brief mention of these contact agents in connection with the various processes, therefore, is necessary. Another very important factor is an available and abundant supply of hydrogen of a high degree of purity. This latter factor will be considered more in detail later in this paper.

Hydrogenation of Vegetable Oils

Hydrogenation of vegetable oils, for the production of hardened fats to be employed in the manufacture of edible shortening or as soap stock, is essentially a liquid-phase operation in which hydrogen is intimately mixed with heated oil containing suspended or finely divided catalyst. Temperatures of 175° to 200° C. are suitable, and the hydrogen pressure may vary from substantially atmospheric to as much as 80 pounds. Generally, the higher the pressure the lower (within limits) the reaction temperature required. Reaction is continued until the oil is completely hydrogenated (or saturated) or until a product of the desired melting point and consistency is secured. Afterwards, separation of oil and catalyst is effected by filtration.

Hydrogenation at substantially atmospheric pressure is favored, since it is difficult to prevent loss of gas by leakage (e.g., in packing glands) in processes involving application of pressure. Although hydrogen is not costly when figured on a weight basis, as for example, in the conversion of olein into stearin because only about 1 per cent by weight is required, nevertheless when considered on a volume basis it becomes a much more active item of expense. This is indicated by the fact that about 2500 cu. ft. of gas per ton (2000 lb.) are required for complete hardening of cotton seed oil. The actual volume of gas necessary for a given weight of oil will vary, of course, with the iodine number of the latter, coconut oil needing less than, e.g., fish oil. Hydrogen is highly inflammable and this is another reason why hydrogenation under pressure is somewhat hazardous.

Methods for maintaining oil, catalyst and hydrogen in intimate contact comprise (1) atomizing mixed oil and catalyst into an atmosphere of hydrogen, (2) passing fine streams of gas into a suspension of catalyst in oil, and (3) conducting hydrogen into a vigorously agitated mixture of oil and catalyst. Apparently operations resembling a combination of the last two procedures are employed. Thus, the mixture of oil and catalyst is sprayed into the top of a reaction chamber in which it comes into contact with an ascending stream of hydrogen entering the bottom of the chamber through a perforated conduit. The latter becomes coated with a liquid layer, due to condensation of the oil spray, and this is kept agitated by the fine streams of hydrogen gas passing through it. Hydrogen and oil are withdrawn separately and recirculated. Another type of operation comprises admitting a mixture of oil, catalyst and hydrogen through the top of a closed hydrogenator and conducting the mixture through a distributor located within and near the bottom of the reaction chamber whereby the mass of oil is broken up into fine streams and intimately contacted with the gas. The charge is withdrawn from the bottom of the hydrogenator and, after passing through an inductor in which more hydrogen is introduced into the system, again pumped into the reaction vessel through an opening in the top. Recirculation of oil and catalyst and simultaneous admission of hydrogen is continued until a product of desired melting point and consistency is secured.

Catalyst

Although many metals, as well as metallic compounds, have been suggested, metallic nickel is the most satisfactory from an economical and industrial point of view. Of the so-called noble or rare metals, those which are applicable include platinum, palladium, iridium, rhodium, ruthenium and osmium. In some instances the oxides of such metals are effective. Such catalysts appear to possess the property of bringing about hydrogenation at temperatures considerably lower than those required by nickel.

In the case of nickel, so many varied and different procedures have been developed for its use that only a few of these can be touched upon. Of the organic derivatives of this metal, the carbonyl and various esters (such as the acetate or oleate) have been employed. Nickel carbonyl is reported to give satisfactory results, but its use has not found favor, no doubt due to its toxic properties and expense involved in its manufacture, as well as to hazards arising from its unstable and other troublesome characteristics.

Two procedures, which have been designated as the wet and dry methods, are available for the preparation of a nickel catalyst. In the latter, a water-insoluble compound of the metal (such as the carbonate or hydroxide) is precipitated on or admixed with an inert carrier of a finely-divided character, for example, kieselguhr, clay, fuller's earth or infusorial earth. The resulting mass is washed with water, dried, and simultaneously ground and heated in a current of hydrogen. The temperature of the latter operation is generally about 300° to 325° C. At somewhat lower temperatures reduction of nickel oxide (resulting from decomposition of the corresponding carbonate or hydroxide) is incomplete, and at higher temperatures the effective life of the catalyst is impaired. Reduced nickel thus prepared is pyrophoric in character, because of the presence of nickel hydrides, and before incorporation with oil should be carefully protected from contact with air. Washing or sweeping out the container (in which reduction was effected) with nitrogen is an efficient method of freeing the metal of hydrogen.

In the wet process, which is used perhaps to a greater extent, thermal decomposition of nickel formate suspended in oil furnishes a finely-dispersed catalyst. In this instance a temperature of approximately 240° C. is employed, and simultaneously during the decomposition operation a current of hydrogen gas is conducted through the oil. Since a relatively high temperature is required, the liquid vehicle is more or less adversely affected thereby and, as a consequence, if the catalyst is to be used in the preparation of an edible product it should be filtered and washed free of the oil originally employed. If the catalyst is not employed in the hardening of edible fats, separation of the oil, of course, is unnecessary. As the latter is hydrogenated to some extent during reduction of the formate, on cooling the mixture of catalyst and oil may form a hard mass, the oil acting as a protective coating for the dispersed metal.

Nickel catalysts can be made also in the following manner. The metal is alloyed with either silicon or aluminum and afterwards the alloy treated with an aqueous solution of sodium hydroxide. As a result, silicon or aluminum is dissolved, leaving finely-divided nickel as a residue. This process has become quite popular.

Not only may nickel be employed as finely-divided or dispersed particles, but it may be used also in massive form. In one process involving a catalyst of the latter type, turnings or small pieces of nickel wire are enclosed in a long perforated cylinder, and through the center of the catalytic mass is inserted a rod of nickel which serves as an electrode. The small masses of metal (while in the cylinder) are subjected to anodic oxidation, whereby they are coated with a thin film of oxide. Afterwards the cylinder, through which hot oil admixed with hydrogen is allowed to flow, is transferred to the reaction zone. During the hydrogenation operation nickel oxide is reduced and thus furnishes a surface of active nickel which is the catalytic agent for hydrogenation of the oil.

Reduction of Glycerides to Alcohols

Although the reduction of glycerides, or other esters, of fatty acids to alcohols of high molecular weights has been known for a long time, it is only within the last decade that such reactions have assumed an industrial importance. In the search for new detergent and wetting agents it was noted that the alkali salts of the acid sulphates of alcohols of high molecular weights (e.g., lauryl or higher alcohols) exhibited unusual properties. Thus, not only were they effective as detergent agents in hard water but also in slightly alkaline or acid water. As a result, the preparation of these sulphate materials has become of considerable importance.

In the hydrogenation of liquid fats if both the temperature of operation and the hydrogen pressure be increased not only are the unsaturated fatty acid radicals hydrogenated, but simultaneously there is a rupture of the oil molecule and the formation of glycerol (or other low-molecular alcohols) and alcohols containing the same number of carbon atoms as the fatty acid radicals. Although the optimum conditions for alcohol production will vary with the catalyst and the oil employed, nevertheless temperatures of about 320° C. and hydrogen pressures of approximately 200 atmospheres are applicable. Above 350° C., for example 400° C., these alcohols are reduced and hydrocarbons are the main products.

This reduction to alcohols, however, is not limited to glycerides of fatty acids and as a consequence to liquid-phase operation, but may be effected also in the vapor phase. In the latter instance, of course, the more volatile esters, such as the methyl or ethyl, must be employed.

Catalysts for the preparation of alcohols by hydrogenation of esters include not only nickel but also copper as well as the so-called mixed catalysts, as for example, nickel-zinc chromate.

In this connection it is interesting to note that electrolysis of soaps dissolved in water containing small proportions of ethyl alcohol and potassium bicarbonate furnishes alcohols. In this case, however, the alcoholic body possessed one less carbon atom than the acid from which the soap is derived.

Hydrogenation of Carbon Monoxide

In the reduction, or hydrogenation, of carbon monoxide the reaction may proceed in one of two ways, to give hydrocarbons or to yield alcohols. The factors which control the course of the reaction are temperature, pressure and catalyst, but more particularly the last two. For the production of hydrocarbons, relatively low pressures (from atmospheric to about 30 atmospheres) and temperatures (200° to 250° C.) are required. Catalysts containing iron, nickel, thorium or cobalt or mixtures of these elements appear to be the most generally applicable. However, as indicated previously, such a process cannot compete with the large quantities of petroleum hydrocarbons available in this country. In some European countries, particularly Germany, in which fuels are needed at almost any cost, the hydrogenation of carbon monoxide has been developed and exploited to a considerable extent. In those localities where coal is available in sufficient quantity, water gas can be produced and from it in turn gasoline or other hydrocarbon fuels.

By increasing the temperature (300° to 350° C.) and the pressure (to 200 atmospheres) and employing catalysts consisting of mixtures of metallic oxides, the product is mainly methanol. In most instances the oxides comprise those of basic metals, such as zinc, cadmium or magnesium, admixed with those of acidic metals, as for example, chromium or vanadium. The proportion of basic oxides should be greater than that of the acidic oxides. Although nickel, cobalt and iron seem to be specific agents for hydrocarbon formation, nevertheless they may be employed when methanol is the desired product, especially when they are mixed with the so-called non-reducible oxides, magnesia, zinc oxide, etc., and a metallic halide, e.g., zinc chloride or vanadium chloride.

At still higher temperatures (400°to 425° C.) and in the presence of strongly basic contact agents, not only methanol but also higher alcohols (ethyl, propyl, isopropyl, butyl and isobutyl) are obtained. In addition, other oxygenated hydrocrabons, e.g., aldehydes, ketones and acids, are formed in small proportions. Catalysts, in this instance, differ from those employed in the methanol synthesis in that a considerable proportion of a strongly basic substance, for example, the oxide, carbonate or hydroxide of potassium, is incorporated.

The composition of the reacting gases also should not be overlooked, since a slight excess of hydrogen over carbon monoxide increases the formation of hydrocarbons, and excess of the monoxide over hydrogen favors a larger yield of ethanol and higher alcohols.

Hydrogenation of Petroleum

Treatment of petroleum with hydrogen at temperatures of 800° to 900° F., pressures of about 200 atmospheres, and in the presence of appropriate catalysts brings about molecular changes probably far more deep-seated than any of those previously discussed. Such an operation affords means for converting so-called low-grade stocks into gasolines of higher antiknock value, into kerosenes of improved burning qualities, and into lubricating oils of high grade. Even heavy asphaltic or tar-like materials secured on the distillation or cracking of petroleum fractions can be hydrogenated to light-colored or almost colorless liquid bodies. Since the lower-boiling distillates (up to about 450° to 500° F.) from these hydrogenated products contain large proportions of benzene-like or cyclic hydrocarbons, in many instances they are equal to or superior in solvent power to analogous fractions from coal tar.

Other changes taking place during hydrogenation, or hydrogenolysis, of petroleum oils are elimination of oxygen from such bodies as phenols or carboxylic acids, nitrogen as ammonia from complex nitrogen-containing compounds, and sulphur as hydrogen sulphide from mercaptans, thioethers and other sulphur-containing substances present in petroleum. Since sulphur or organic sulphur compounds are poisons for many contact agents, hydrogenation of petroleum oils involves the use of sulphactive catalysts, i.e., those not affected by this element or its derivatives. Suitable contact agents are the oxides of molybdenum, tungsten and chromium, with which may be admixed those of copper, zinc, manganese, aluminum and vanadium.

As indicated by the foregoing very brief discussion, hydrogenation of petroleum includes two separate and distinct phases, hydroforming and hydrofining. The first of these, or hydroforming, involves considerable disturbance or reconstitution of the hydrocarbon molecules in the oil undergoing treatment. The other, or hydrofining, results in no substantial change or extensive alteration in the structure of the oil molecules but rather a replacement of elements such as oxygen, nitrogen or sulphur by hydrogen.

Maintenance of Catalytic Activity

Although theoretically a catalyst should remain active for an indefinite period, nevertheless it is well known that its activity does decrease and eventually becomes substantially negligible. This undesirable effect is attributed to catalysts poisons or inhibitors, present in small proportions in the oil or gaseous mixture undergoing treatment or in the hydrogen gas employed. Inhibitors presumably exert their effect either by mechanically coating the catalyst and thus preventing it from coming into contact with the reacting substances, or by being adsorbed on the surface of the contact agent, thereby preventing its proper functioning, or by reacting with the catalyst, thus converting the latter into compounds which exert little or no catalytic effect.

In the case of liquid fats, e.g., vegetable oils, refining and bleaching prior to hydrogenation eliminates catalyst poisons to a substantial degree. Pretreatment with spent catalyst, particularly of fish oils, is effective in removing undesirable inhibitory bodies. Hydrogen and carbon monoxide mixtures may be conducted over a spent catalyst before being brought into contact with an active one.

Substances such as sulphur (either elemental or in the sulphide form), halogens, carbon monoxide (in the case of oil hardening), arsenic, sulphur dioxide and phosphorus are classed as poisons. Sulphur is probably the most commonly occurring one and is remarkably active on nickel. Some of these are found in the gases used in hydrogenation operations, and their removal or elimination is highly desirable. Brief mention, therefore, will be made of the preparation of hydrogen and also of mixtures of this gas and carbon monoxide.

In this connection it is interesting to note that in some instances the activity of hydrogenating catalysts (for example those of copper and chromium) may be regulated by incorporation of poisons or inhibitors, e.g., sulphur, phosphorus or compounds containing these elements. Such poisoned catalysts are reported capable of effecting hydrogenation of unsaturated fatty acids to wax-like esters. The latter may be saponified afterwards to obtain unsaturated alcohols.

Production of Hydrogen

The more widely employed methods for the production of this gas are (1) electrolysis of water, (2) decomposition of water by iron, (3) decomposition of water by carbon or the water-gas reaction, (4) thermal decomposition of hydrocarbons and (5) interaction of water and hydrocarbons. The first of these (i.e., electrolysis of water) has served for the production of large quantities of hydrogen for the oil-hardening industry due, no doubt, that the gas made in this manner is less contaminated with impurities than that obtained by some other procedures. Furthermore, hydrogen is secured as a by-product in electrolytic operations intended for the manufacture of oxygen or chlorine. However, processes based on the decomposition of water (or steam) by iron, e.g., the Messerschmidt process, have met with much favor.

Electrolysis of Water

This operation comprises subjecting an aqueous solution of an alkali, sodium or potassium hydroxide, or of sulphuric acid to the action of an electric current and collecting separately the gases (hydrogen and oxygen) which are evolved. Aqueous caustic soda and electrodes of iron or nickel-plated iron are commonly used. The electrodes must be separated by a diaphragm to prevent mixing of hydrogen and oxygen, and this often has caused considerable difficulty, particularly in the case of high-pressure cells.

Developments in the types of electrolyzers have included the so-called bipolar and multi-polar cells as well as those capable of delivering the gases at pressures as high as 120 to 150 atmospheres. These improvements have been brought about for two reasons: first, a demand for less floor space requirements for the cells, and second, the elimination of compressors needed in some cases when hydrogen escapes from the cells at substantially atmospheric pressure.

Factors in favor of production of hydrogen by electrolysis of water are ease of manipulation, low labor costs, and cheapness of materials. However, depreciation charges are reported to be somewhat high.

Steam-Iron Process

This is essentially oxidation of iron by steam, and the reaction taking place can be represented by $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$ In practice three steps are required to secure a complete cycle of operation. These are, reduction of iron ore (iron oxide) at a temperature of 650° to 900° C. with water gas, purging the reaction chamber with steam, and lastly oxidizing the iron with steam.

Hydrogen produced in this manner contains small proportions (totaling about 2.5 per cent) of carbon dioxide, carbon monoxide, hydrogen sulphide and nitrogen. Washing the gas with water will remove extraneous matter such as dust particles and some carbon dioxide. Further treatment of the gas with iron oxide and lime effects removal of hydrogen sulphide and carbon dioxide, respectively.

Carbon monoxide is said to be eliminated in the final gaseous product if carbon dioxide is added to the reducing gas (water gas) so that the proportion of dioxide to monoxide is about 2:1. This prevents decomposition of the monoxide to carbon and deposition of the latter during the reducing step. As a consequence reaction of carbon with steam to give carbon monoxide (during the oxidation step) is avoided.

Water Gas

This gaseous mixture of hydrogen and carbon monoxide is produced by subjecting incandescent coke to the action of steam, the temperature of reaction being about 1000° C. In practice a cycle consists of two operations, first subjecting heated coke to a blast of air to secure the proper temperature, and then conducting steam through the heated bed of coke, the gases from both operations being stored separately. This gaseous mixture is not applicable for the hardening of oils or the production of alcohols by reduction of fatty glycerides or esters but rather as a source of hydrocarbons or alcohols resulting from the hydrogenation of carbon monoxide.

True water gas contains approximately equal proportions of hydrogen and carbon monoxide, as well as small proportions of carbon dioxide, hydrogen sulphide, nitrogen and hydrocarbons (e.g., methane). Before being used for the purpose mentioned above, water gas must be freed of impurities and the proportion of monoxide to hydrogen adjusted either by partial removal of or the addition of one or the other of these gaseous compounds, as the case may be.

Elimination of carbon dioxide and hydrogen suphide is effected by treatment with lime and iron, respectively. Organic compounds which contain sulphur, and are often present, are a much more difficult problem. One procedure comprises selective hydrogenation of the latter compounds to hydrogen sulphide employing a catalyst of copper oxide and lead chromate supported on silica and temperatures of 300° to 400° C. To remove more completely hydrogen sulphide than is possible with iron oxide, alkaline solutions of oxides of arsenic or antimony or of phenolic bodies may be employed. Suspensions of iron or managese oxides in aqueous alkali also have proven effective. Incorporation of 5 to 10 per cent of alkali carbonates with iron oxide and subjecting water gas to the action of this composition at elevated temperatures is reported to eliminate organic sulphur compounds.

Thermal Decomposition of Hydrocarbons

Carbon and hydrogen are the ultimate products of the thermal decomposition of hydrocarbons, though in any operation the proportion of these elements and other products secured will depend upon two factors, the temperature employed and the period of heating. High temperatures of the order of 1200° to 1400° C. are required. The heating period will vary considerably with the hydrocarbon employed and the temperature. Thus, methane at 1000° to 1200° C. with a contact time of about 0.1 second is converted mainly into ethylene and aromatic oils. When the contact time is increased to 40 or 45 seconds and the temperature to 1100° C., substantially complete decomposition of methane into its elements is secured. At 1250° C. about 5 seconds' heating is required to obtain carbon and hydrogen.

Catalysts such as nickel or iron or their oxides have been suggested. Their value may be doubtful, however, since in many instances their effectiveness is soon diminished due to carbon deposition, and the necessity of frequent removal of the latter by steam or air. For this reason thermal decomposition of hydrocarbons is carried out generally in the presence of refractory material or carbon (coke), which has the effect of increasing the heating area.

In technical processes involving decomposition of hydrocarbons to carbon and hydrogen the former element is utilized as a fuel. To illustrate, decomposition (which is endothermic) is effected in the presence of highly heated refractory material or incandescent coke until the temperature falls below that required for pyrolysis. The flow of hydrocarbon gases or vapors then is stopped and the carbon burned by means of an air blast, thus raising the temperature of the refractory mass or coke to that necessary for thermal decomposition of the hydrocarbons. These successive cycles of heating and dissociation constitute the basis for the well known Rincker-Walter and other processes.

Hydrogen from Hydrocarbons and Steam

Interaction of hydrocarbons with steam at elevated temperatures furnishes hydrogen together with carbon monoxide and dioxide. The proportion of these two oxides depends upon the quantity of steam employed, the larger the proportion of the latter the more dioxide will be formed. Although higher hydrocarbons may be employed, industrial interest centers about the use of methane and its immediate homologues (e.g., natural gas or still gases) as the initial material. If we select methane as the example of the hydrocarbon, then the two reactions taking place may be represented by

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

As in the case of purely thermal pyrolysis, reaction of hydrocarbons with steam requires high temperatures (about 900° to 1000° C.). In addition, catalysts may be used, since, as indicated by the above equations, no carbon is formed, and, as a result, fouling of the contact agent by this element is substantially eliminated.

Perhaps the greatest difficulty encountered in making hydrogen from hydrocarbons and steam is the heating of large masses of catalytic materials, since the reaction is highly endothermic. Addition of air or oxygen to the reactants and therefore internally heating the reaction system through partial oxidation of methane, for example, to carbon monoxide and hydrogen (which is an exothermic reaction) does not appear particularly advantageous. In the first place, unless a very considerable proportion of methane is oxidized, insufficient heat is introduced to counterbalance the endothermic interaction of hydrocarbon and steam. Secondly, if air is employed as the oxidizing agent, an extraneous gas (nitrogen) is introduced into the system. Third, some types of catalysts appear to be poisoned by this extraneous gas. One method of overcoming these objectionable features is the burning of hydrocarbon gases in heat-exchange relation to but out of contact with the reacting gases.

Instead of effecting production of hydrogen in one operation, two-stage processes may be employed. For example, cracking gas and steam may be reacted at 870° C. in the presence of a catalyst, the products being mainly carbon monoxide and hydrogen. More steam is introduced into the mixture and further reaction effected at 455° C., whereby carbon monoxide is converted into carbon dioxide. Compression of the resulting gaseous mixture under 240 lbs. per sq. in., followed by washing with water and with triethanolamine yields a gas containing about 97 per cent hydrogen.

As a catalyst, nickel appears to be universally accepted as the best. When admixed with other metallic oxides, such as those of aluminum, zinc, molybdenum, manganese and even those of a highly basic character, e.g., potasium oxide, its catalytic effect is said to be enhanced. Cobalt and iron are reported to be good contact agents, though less effective than nickel. At temperatures above 1000° C., zirconia and thoria are stated to be particularly active catalysts.

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ABSTRACTS

Oils and Fats

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Polymerization of fat IV. Polymerization of drying fat with the influence of sulphur chloride. H. P. Kaufmann and S. Funke. *Fette u. Siefen 45*, 670-4 (1938). A theory of polymerization with SCl is graphically presented.

Review of properties and types of air oxidized linseed oil. T. Crebert. *Fette u. Seifen 45*, 674-6 (1938). Oil emulsions in paint technic. H. Wigner. *Ibid.* 676-80 (1938).

Simple method of determining unsaponifiable and its constituents in food fats. J. Groosfeld. *Z. Untersuch. Lebensm. 76*, 513-30 (1938). Methods for detg. unsapon. matter using 50 and 200 cc. of petrol. ether and method for detg. phytosterol are described. The cholesterol in butterfat, hardened whale, linseed, peanut and olive oil and cacao-butter was similar in amt. to that in lard. In coconut fat there was a larger amt. Results on phytosterols were similar. In tests without fat the extn. losses of cholesterol and phytosterol did not depend on the amt. of alc. Coco fat soap has a greater retaining capacity for the sterols than other soaps. Equation for calcg. the amt. of sterols and hydrocarbons and total unsapon. in fats is presented. Data for the equation are obtained by detg. unsapon. by 2 methods.

Oil hardening with copper-nickel catalyst. W. Norman. *Fette u. Seifen 45*, 664-9 (1938). A hydrogenation app. made with laboratory glassware is illustrated and described in detail. The data on the activity of Ni-kieselguhr, Ni-Cr, Ni-formate and severeal Ni-Cu catalysts are tabulated and plotted. The curves show the rate of H uptake. The results are discussed from the standpoint of Cu improving the Ni-catalyst by acting as a carrier or it may, according to other investigators, prevent sintering of the Ni. The hardening odor of fats hardened with Ni-Cu is weaker and somewhat different from those with Ni, catalyst, but the odors increase rapidly on standing in air.

The fatty acids and glycerides of solid seed fats. VI. Bornee tallow. W. J. Bushell & T. P. Hilditch. *J. Soc. Chem. Ind. 57*, 447-9T (1938). The chief glycerides in the fat were "oleo"-distearins (about 40%), "oleo"-palmitostearins (about 31%) and stearodi-"oleins" (about 13%), with about 8% of "oleo-"dipalmitins and about 5% of fully-satd. glycerides.

Studies of the essential unsaturated fatty acids in their relation to the fat-deficiency disease of rats. E. M. Hume, L. C. A. Nunn, I. Smedley-Maclean and H. H. Smith. *Biochem. J. 32*, 2162-77 (1938). It is concluded that the ability of unsatd.