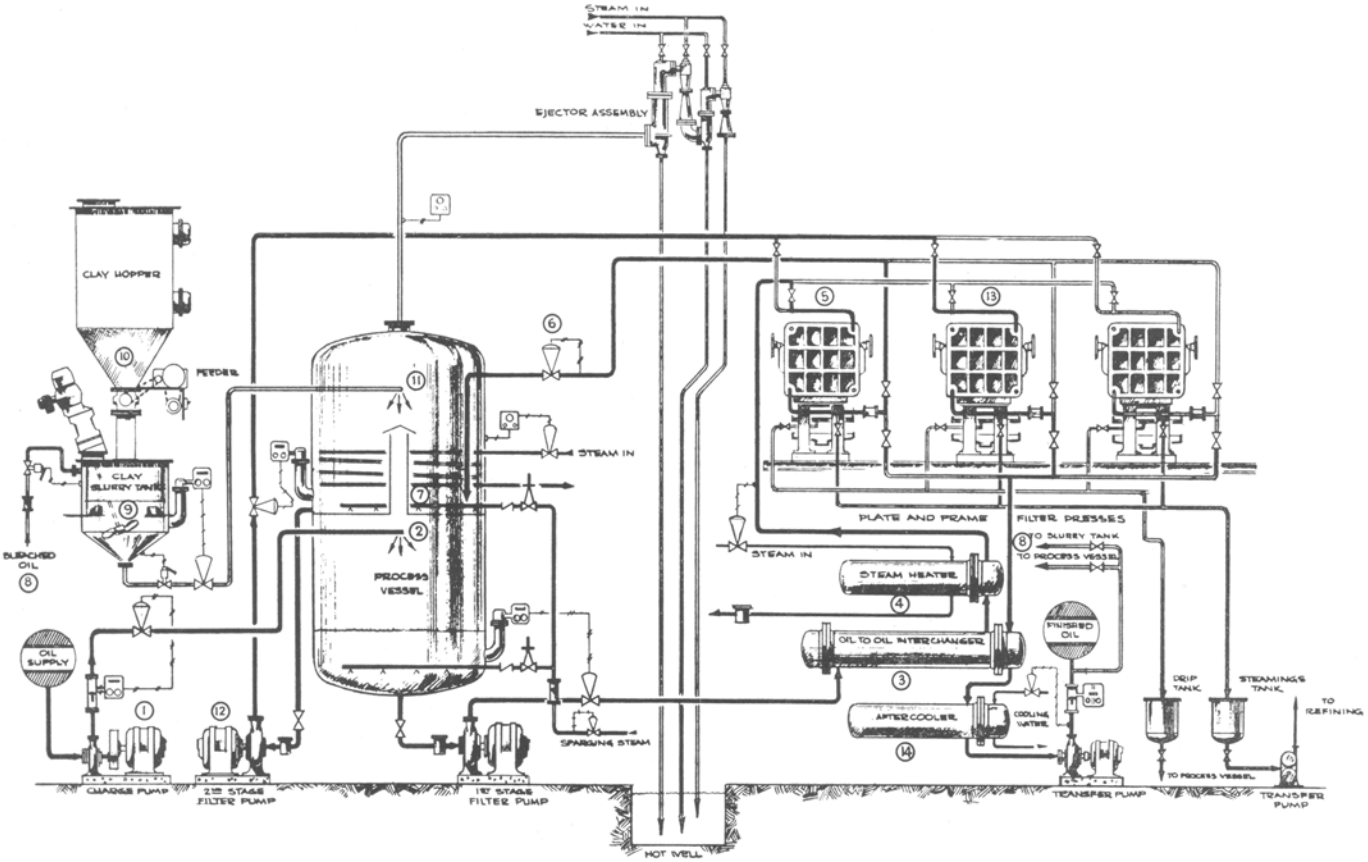

FIG. 10. Votator continuous counter current vacuum bleaching system

due to proper exclusion of oxygen, significant reduction in space requirements, especially in larger capacities, fully automatic operation from a centralized control station, cleanliness of plant, particular effectiveness in bleaching excessively dark oils, and approval of the B.A.I. for alternate use on animal and vegetable oils.

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Hydrogen Production

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THERE ARE MANY and varied ways of producing hydrogen for industrial use. However in the oil and fat industry there are only six sources of hydrogen that have been of any consequence and some of these to only a minor degree. These six sources are cylinder or compressed hydrogen, hydrogen produced as a by-product, hydrogen produced by the dissociation of ammonia, electrolytic hydrogen produced by the electrolysis of water, hydrogen produced by the steam-iron contact process, and hydrogen produced by catalytic steam hydrocarbon cracking. Practically all the fats and oils hydrogenated in the United States, Canada, and Mexico have been hydrogenated with hydrogen obtained from one of these six sources. The amount of hydrogen used from any one of these has been dictated by the size of the operation and economic considerations. Over the years the predominance of any one source has been almost entirely based on economic reasons alone. Emphasis on different methods of production has changed within the industry throughout the years.

Of the six methods of obtaining hydrogen in the oil and fat industry the so-called cylinder, bottled, or compressed hydrogen has played the smallest part by far. Cylinder hydrogen is almost always produced by one of the five other methods of hydrogen production already mentioned and actually is being marketed today from all the other five sources except dissociation of ammonia. The cylinder hydrogen produced by one of these methods of production is then compressed into steel containers to pressures of 2,000 to 2,200 p.s.i.g. Most of the hydrogen used in the industry is obtained in cylinders of approximately 200 cubic-foot capacity. In some instances a number of cylinders are put together to effect a larger container, and in other instances containers larger than the 200 cubic-foot capacity cylinders have been arranged on an independent trailer for more economical delivery. The use of cylinder hydrogen has for the most part been confined to situations where the total demand for hydrogen is so small that investment cost and operating labor for a hydrogen plant make it uneconomical to consider any of the other sources of hydrogen available to the industry. The companies who supply cylinder hydrogen must install and maintain a large inventory of containers. This means that the cost of hydrogen in cylinders is practically prohibitive to the oil and fat industry except for very small demands. Another factor which minimizes the use of cylinder hydrogen is that approximately 150 lbs. of steel in the cylinder must be transported round trip for every 1 lb. of hydrogen delivered. You can readily understand with present-day freight and hauling rates what an obstacle this presents. The companies offering cylinder hydrogen for sale usually have sliding price scales so that it is difficult to state definitely what hydrogen would cost at any one location in varying quantities. As a rule, cylinder hydrogen will cost from $6 to $12.50 per thousand cubic feet to the user plus the delivery cost. Considering these factors, it is easy to see why cylinder hydrogen has played its minor role in the oil and fat industry. The purity of cylinder hydrogen has always been satisfactory for the industry and is usually better than 99.5% hydrogen with the impurities varying with the method of producing the hydrogen.

The use of by-product hydrogen, when it has been used, has almost always been a marriage of convenience. A company may have a supply of hydrogen which is of very little value to them. Nearby there may be a demand for hydrogen which justifies payment of a price sufficient to make it attractive for the producer of this by-product hydrogen to sell it. The factor already mentioned concerning the cost of transporting hydrogen confines the producer and user of surplus hydrogen to the same general locality. Through the use of pipe-line transfers the distance between the producer and user can be lengthened economically. Most all by-product hydrogen is obtained from the chemical or petroleum industry. It is produced as a by-product in the manufacture of chlorine and as a result of chemically or thermally cracking hydrocarbons. As a general rule, the purity of the by-product hydrogen is satisfactory for the oil and fat industry, but if not, the very simplest of treatments will make it so. While there have been large quantities of by-product hydrogen available to the industry, its use has not been large as a whole. The chief reason has been geographical as usually the supply has been located where it is not practical or economical to locate an oil and fat processing plant and the cost of transporting hydrogen for any distance is prohibitive. There have been a few instances within the industry where the producer and user have found themselves side by side and the marriage of convenience has been arranged, but the increasing use of hydrogen by the chemical and petroleum industries will probably rule out by-product hydrogen as a source of supply to the industry in the future. Costwise, by-product hydrogen has probably been the most attractive source of hydrogen because to its producer the only worth has usually been in its heating value which is very low, having a B.t.u. content of about 320. Prices of by-product hydrogen vary with individual situations. The cost has varied over the years in the $.75 to $2.50 per 1,000 cubic-foot range. However the single fact that the user of by-product hydrogen is dependent on an outside source for one of his most important raw materials often out-weighs the low cost feature.

Hydrogen produced by the electroylsis of water at one time played a large part in the hydrogenation of fat and oil and is still used to a small extent in the industry, probably in greater proportion, to the total use of hydrogen, in Canada and Mexico than in the United States. The installation of electrolytic hydrogen plants in the United States in the early days of oil and fat hydrogenation was called for more because of the crudeness of other methods of production and the purity of the hydrogen produced by other methods than for any other reason. Outside of the Western Hemisphere the lack of raw materials for any other method of production has usually been the determining factor. Starting in the early 1930's, when methods of producing hydrogen by other processes were fully developed in the United States and purity requirements of the industry were met by these new processes, the use of electrolytic hydrogen gradually diminished until today it is a minor factor and will probably disappear entirely within the industry in the Western Hemisphere as soon as the remaining plants are obsolete. Another factor in the early days of electrolytic hydrogen use which made it attractive was the fact that one-half as much oxygen was produced as hydrogen, and usually this oxygen could be sold to companies engaged in the distribution of welding supplies. Often this sale of oxygen almost offset the cost of producing the hydrogen required. In later years the development of liquid oxygen manufacturing and distributing techniques brought the cost of oxygen down to the point where the collection and compression of by-product oxygen from the electrolytic process was not economically feasible. The purity of electrolytically produced hydrogen has always been satisfactory for the industry. There has been some question as to what effect the approximate 0.2% oxygen present in electrolytically produced hydrogen has in the hydrogenation of fat and oil. This is however a useless discussion as it is a simple matter to remove catalytically even the last trace of oxygen at practically no cost.

The cost of producing electrolytic hydrogen is tied directly to two things: the cost of power and the prevailing wage rate. Other costs such as distilled water and maintenance, etc., while a factor, represent a minor part of the total cost. There are a number of different types of electrolytic cells on the market;

however, generally, most of the cells require approximately 150 k.w.h. of power to produce 1,000 cu. ft. of hydrogen. It is possible to operate small electrolytic plants without operator attendance, yet most owners of electrolytic plants as well as insurance companies feel that it is advisable to have an operator on hand. Under present competitive methods of hydrogen production it is felt that the use of electrolytic plants in the Western Hemisphere, where suitable raw materials for other methods of production are available, will play very little part in the oil and fat industry. The only possible exception might develop where the total daily demand is so low as to be below the sensible operating level of other processes and therefore cheaper in original installation cost. The initial investment on electrolytic plants *versus* capacity is nearer to a straight line curve than the cheaper operating processes.

The use of hydrogen produced from ammonia by thermal or catalytic dissociation has only in recent years played any part in the hydrogenation of oils and fats. To a student of economics it would not seem sensible to go to the trouble and expense to make hydrogen and combine it with nitrogen to make ammonia and then take the ammonia and break it down to obtain the hydrogen. Why make the ammonia? However if you look at the cost of transporting hydrogen in steel containers, maybe it does make sense to make the ammonia as a vehicle to transport the hydrogen. This actually is true to a certain extent. The use of hydrogen produced from dissociated ammonia originally came into use in the oil and fat industry for the hydrogenation of animal fats where the amount of hydrogen to be used was small and its use was not complicated. The capital investment of a dissociator itself was relatively low, and if the demand were small and the actual cost of the hydrogen not too important, cylinder ammonia could be used and the total installation cost could be small. In these conditions the cost of the hydrogen produced would be extremely high and could not be competitive. For larger installations where ammonia storage in tank car quantities is required and hydrogen compression and storage are needed, the installation costs would soon approach the initial cost of a more conventional method.

One of the largest single objections to dissociated ammonia for hydrogenation is that the hydrogen is present in only 75% concentration. In the hydrogenation process the 25% nitrogen inert accumulates and has to be removed from the process. Methods have been derived continuously to bleed the nitrogen from the system, but it is not practically possible to do so to the exclusion of hydrogen. Not too much data are available, but it is reasonable to assume from what is known that the total hydrogen utilization will only average 80–85% as compared to 93–95% utilization from hydrogen produced in high purity plants. Very little information is available on the effect of 25% nitrogen dilution in the selective hydrogen procedures now being practiced by the industry, but it is believed that efficiently to use this 75–25 mixture a new approach would have to be made to the hydrogenation techniques. The cost of producing a 75% hydrogen–25% nitrogen mixture from ammonia depends to a great extent on the cost of ammonia delivered to the plant. When using cylinder ammonia at 13–15 cents per pound, the cost of the hydrogen would be prohibitive for any operation in the fat and oil field. When using tank car ammonia at 4–6 cents per pound delivered, the cost of utilized hydrogen will appear in the $2.50 to $4 per thousand cubic-foot range without amortization of investment, which can vary over wide limits. While there are several users of dissociated ammonia in the industry, the majority being in the animal fat field, nothing has been disclosed to indicate that this method of production will compete with more conventional methods of producing hydrogen except in highly specialized instances.

The steam-iron contact process is the means of producing hydrogen most widely used in the fat and oil industry. This process was introduced into this country in 1926, in the early stages of its present development, with the installation of a so-called continuous Bamag Generator in Atlanta, Ga. Before this time the steam-iron process had been used in the industry in a more or less batch method. The batch methods were cumbersome to operate and most unreliable. After the continuous generator was proved successful, the industry moved steadily to steam-iron contact until soon a majority of fats and oils hydrogenated in the United States, Canada, and Mexico were processed with steam-iron hydrogen. The steam-iron process consists essentially of reducing a mass of iron oxide, usually in the form of iron ore, with a suitable reducing gas to free iron at a temperature of 1,600–1,700°F. and then contacting the hot iron with steam which oxidizes the iron to iron oxide and liberates hydrogen from the steam. The raw materials for the production of the reducing gas used in reducing the iron oxide to iron originally consisted of coke or coal processed in a conventional water gas generator to produce a gas having approximately equal parts of hydrogen and carbon monoxide. In recent years in many instances coal and coke have been replaced as raw materials by hydrocarbons such as methane, ethane, propane, or butane, which are cracked catalytically with steam over a nickel catalyst to produce a mixture of hydrogen and carbon monoxide and this mixture is used as a reducing gas. Any processed or by-product gas having a total reducing component as low as 25–35% can successfully be used as a reducing gas. This flexibility of raw materials makes the steam-iron process suitable for installation in practically any location. The hydrogen as produced from a steam-iron generator usually has an analysis of 99.1% hydrogen, 0.3% nitrogen, 0.3% carbon monoxide, and 0.3% carbon dioxide. Practically all steam-iron produced hydrogen is contacted with caustic to remove any traces of hydrogen sulphide and the carbon dioxide present. In the late 1930's with the introduction of low-temperature, low-pressure selective hydrogenation in the oil and fat industry it became apparent that for many companies the 0.3% carbon monoxide present in steam-iron hydrogen might be detrimental. Means were then introduced to remove this carbon monoxide.

One of the methods consists of a two-stage catalytic removal unit. The first stage oxidizes the carbon monoxide to carbon dioxide with steam in the presence of a catalyst and removes the carbon dioxide with caustic. This oxidation process is reversible so that only about 90% of the carbon monoxide can be removed in this way. The final traces of carbon monoxide are then converted to methane by the reaction of carbon monoxide and hydrogen to form methane and water. Usually a nickel catalyst is used for this reaction. As a general rule, most companies do not find detrimental the small amount of carbon monoxide left after the first stage catalyst, so the final stage is omitted. In fact, some companies consider it unnecessary to remove any of the 0.3% carbon monoxide found in unpurified steam-iron hydrogen. A new development in carbon monoxide removal in the steam-iron process consists of converting all the carbon monoxide to methane in a single stage with suitable catalyst. This method of eliminating the carbon monoxide is cheaper than the two-stage method as no steam is required and there is no carbon dioxide formed to be removed. The resultant purity of the hydrogen with this method is 99.4% hydrogen, 0.3% methane, and 0.3% nitrogen. As both methane and nitrogen in these concentrations are inert in the hydrogenation process and at the single stage methanation at the temperatures operated results in practically complete removal of the carbon monoxide, this single-stage purification is the more desirable of the two. The cost of manufacturing and the low cost of installation make the steam-iron hydrogen process one of the two cheapest methods available to the fat and oil industry.

The cost of purified hydrogen, when using coal or coke at $20 per ton, would be, per thousand cubic feet, coal or coke $.60, caustic $.04, power at 1 mill $.03, iron ore $.02, 250 lbs. steam, at $.60 per 1,000 lbs., $.15, 750 gallons of water $.06. This gives an operating cost of about $.88 per thousand cubic feet. When using natural gas instead of coal or coke, approximately 950 cubic feet of gas are used per 1,000 cubic feet of hydrogen produced and only 200 lbs. of steam are required.

The steam-iron process as installed today is completely automatic and can be run continuously seven days a week or can be run intermittently with very little sacrifice in operating costs. The plants can be shut down completely for an hour or a week-end.

The steam hydrocarbon cracking process for producing hydrogen has been used extensively in the chemical and petroleum industry for years. However it was only in the early '40's that it was introduced into the fat and oil industry. Prior to that time the plant designs were of too large capacity to fit the demands of the industry. Since the first installation a number of plants have been installed throughout the country.

This process consists of cracking a saturated hydrocarbon, usually methane, with steam over a nickel catalyst. The catalyst is usually contained in a high nickel alloy tube or tubes and heated in a suitable furnace. The furnace temperatures required are 1,800°F. to 2,000°F. The methane and steam react to give a mixture of carbon monoxide and hydrogen. The product gas has an approximate analysis of 18–22% carbon monoxide, 74–78% hydrogen. The product gas is conducted over an oxidation type of catalyst with steam where the carbon monoxide reacts with the steam to form carbon dioxide and hydrogen. This reaction is reversible, and only about 90% of the carbon monoxide present is converted. The gas is cooled, and the carbon dioxide is removed usually through the use of one of the amines. This leaves a gas, with a carbon monoxide content of 1.5 to 2%, which is then heated and conducted over a second-stage oxidation catalyst with steam where the same reaction takes place as before and the carbon monoxide content is reduced to .15 to .2%. This residual carbon monoxide can be further reduced by a third-stage oxidation catalyst or can be converted to methane over a suitable methanation type catalyst. In addition to methane, ethane, propane, or butane can be successfully used as a raw material for producing hydrogen in the steam hydrocarbon cracking process. The heavier hydrocarbons usually contain small amounts of organic sulphur which, if allowed to remain in the gas, could reduce the efficiency of the nickel-cracking catalyst and therefore are usually removed by converting to hydrogen sulphide in a vapor phase reaction. The hydrogen sulphide is removed from the gas by treatment with caustic.

The process itself is continuous and fully automatic, and plants have been installed in the oil and fat industry in capacities from 100,000 cu. ft. per day and up.

The purity obtained from this process is satisfactory from all stand-points for the hydrogenation of fats and oils and is usually 99.8% or better.

The cost of producing hydrogen in the steam-hydrocarbon cracking process is approximately the same as the cost of producing by the steam-iron contact process. The steam hydrocarbon cracking process will use less natural gas, requiring about 600 to 700 cu. ft. against 900 to 950 cu. ft. for the steam-iron process while the steam hydrocarbon cracking process requires more steam, 375 to 400 lbs. against 200 lbs. for the steam-iron process. Power and chemical cost of the two processes are approximately the same.

Although all six of the methods of obtaining hydrogen have been, and to some extent still are in use in this country, practically all of the hydrogenation in the industry is done with either the steam-iron contact process or the steam-hydrocarbon cracking process.