

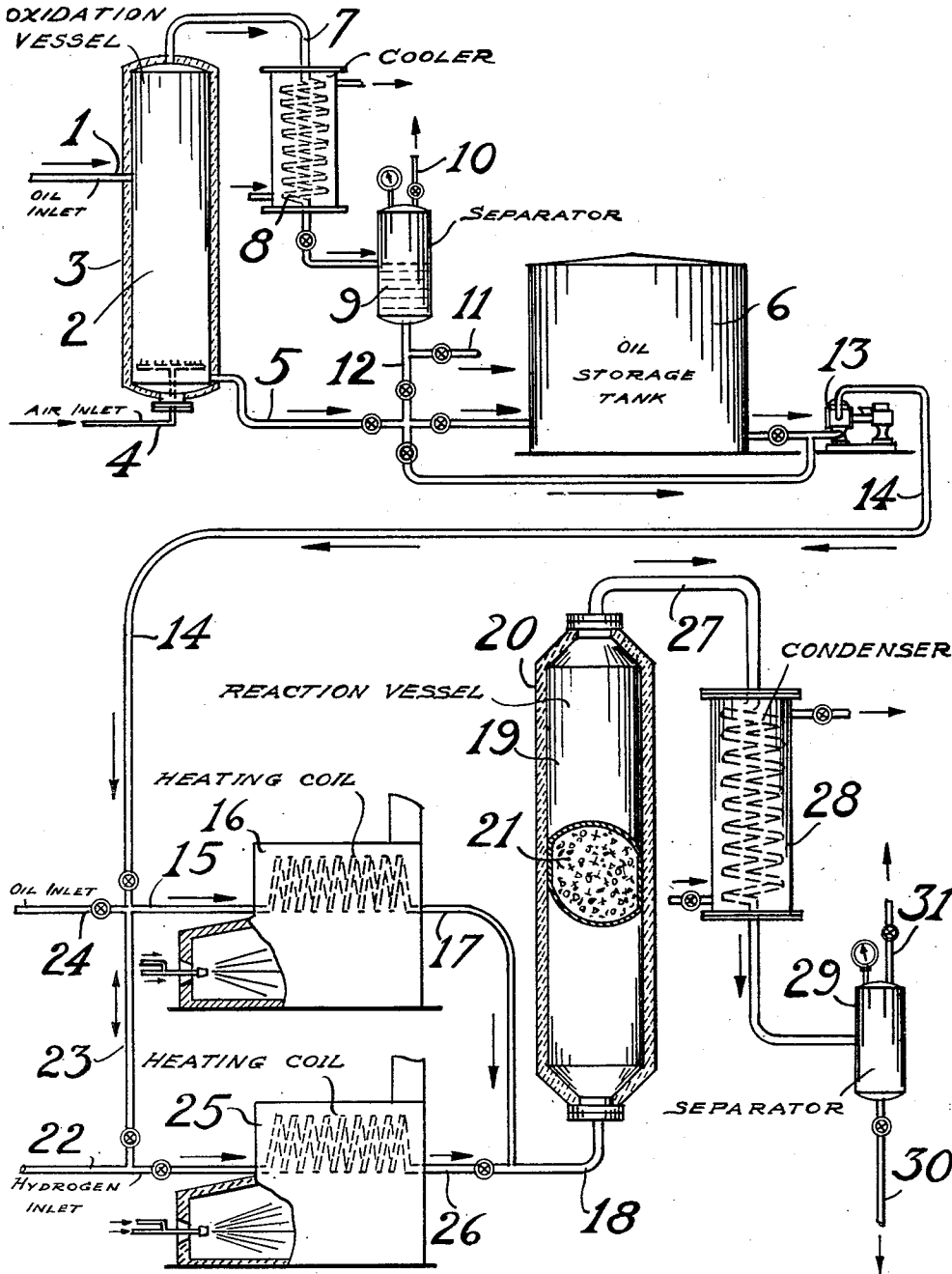
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PROCESS OF TREATING HYDROCARBON OILS

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PROCESS OF TREATING HYDROCARBON OILS

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This invention relates to the hydrogenation of hydrocarbon oils. It is already known that the deoxygenation of an oxidized hydrocarbon by hydrogen is an exothermic reaction. Now I have found that the heat of deoxygenation may be effectively utilized in the hydrogenation of hydrocarbon oils by a process which will be fully understood from the following description.

A hydrocarbon oil is first oxidized in any suitable manner. This may be done by blowing air or other oxygen-containing gas through the oil while maintaining it at temperatures of above 250° F. and preferably 350° F. or higher. A number of materials may be used to catalyze this oxidation, among which are manganese stearate, zinc stearate, comminuted hard coke, manganese dioxide and potassium permanganate in quantities varying from .1 to 5%, although it will be understood that a catalyst is not essential. Oxidation is generally carried out under normal atmospheric pressure, but higher pressures may be used. It is generally desirable to provide means for cooling the oil, such as a jacket or cooling coil, for example, because the oxidation reaction is exothermic.

It will be observed that dark-colored, gummy compounds form during the oxidation, but since these will disappear in the subsequent hydrogenation, the oxidation may be carried to any extent desired without danger of permanently impairing the oil. If preferable, however, a substantial amount of a separately oxidized hydrocarbon, such as paraffin wax, may be added to the hydrocarbon oil. In any case what I desire to obtain is a hydrocarbon oil containing an appreciable quantity of oxy-compounds which may be deoxygenated by hydrogen.

The oxidized hydrocarbon oil or oil containing oxy-hydrocarbons is then passed through a heating zone, preferably in admixture with hydrogen, wherein it is heated to a temperature not substantially greater than 650° F. The mixture may be heated rapidly in the heating zone to a temperature above 500° F. but below that at which substantial deoxidation occurs, and may then be discharged into a reaction chamber containing a hydrogenating catalyst, whereby deoxidation proceeds with evolution of heat sufficient to raise the temperature of the reacting materials to above about 750° F. The heated mixture is discharged into a reaction chamber maintained under a pressure in excess of 25 atmospheres, and preferably 200 atmospheres, wherein the mixture is raised to a temperature of about 750° F. to 850° F. principally by the heat evolved in the deoxygenation of the oxy-hydrocarbon compounds. The reaction chamber is adapted to withstand high temperature and pressure, is resistant to attack by the reacting materials, and preferably contains a suitable hydro-

genating catalyst, immune to sulfur poisoning, such as mixtures of chromium and molybdenum oxides, tungsten and molybdenum oxides or oxides of other metals of the sixth periodic group which may be combined with magnesium oxide or zinc oxide or oxides of other metals of the third and fourth periodic groups. The hot materials flow out of the reaction chamber in heat interchange relationship with cold incoming feed to a condensing and separating drum in which the liquid products are separated from uncondensed gases and from which the product may be drawn off.

The drawing is a diagrammatic sectional elevation of an apparatus suitable for conducting one modification of this process and indicates the flow of materials.

Referring to the drawing, an oil or paraffin wax is supplied by line 1 to oxidation vessel 2, which is preferably insulated with lagging 3 to prevent loss of heat. The vessel may be equipped with suitable heating and cooling means (not shown) for initiating and controlling the reaction. Air or other suitable oxidizing gas is supplied preferably in a suitably pre-heated condition by line 4. The partly oxidized oil is withdrawn by line 5 and may be passed to storage tank 6 or directly to the hydrogenation process to be described below, depending upon whether the oxidation step is conducted as a continuous or batch process. The gases leaving vessel 2 are conducted by line 7 through cooler and condenser 8 to separator 9 from which uncondensed gases may be vented by line 10. The condensate may be withdrawn by line 11 or, preferably after separation of water therefrom, may be passed by line 12 into line 5 in admixture with the oxidized products therein.

The oxidized products are forced by high pressure pump 13 through lines 14, 15, fired coil 16, and lines 17 and 18 into a reaction vessel 19 suitably designed to withstand the elevated temperatures and pressures used for high pressure hydrogenation and the corrosive effects of the reactants. This vessel may be insulated with lagging 20 and may be packed with lumps of suitable hydrogenation catalyst 21.

Hydrogen or gases rich in hydrogen are supplied under pressure by line 22 and may be passed by lines 23 and 15 through coil 16 admixed with the oxygen containing oils already described. Suitable carbonaceous material such as a portion of the hydrocarbon oil supplied to the oxidation step or other hydrocarbon oil may be supplied under high pressure by line 24 and may also be passed through line 15 and coil 16 in admixture with the oxygen containing oil. Hydrogen or a mixture of hydrogen and hydrocarbon oil may also be passed through heating coil 25 and line 26, and admixed with the pre-

heated oxygen containing materials entering the hydrogenation zone in line 18.

The hydrogenated products are withdrawn from the hydrogenation zone by line 27 and may be cooled in the cooler and condenser 28 and passed to a separator 29 from which liquids and uncondensed gases are separately withdrawn by lines 30 and 31 respectively. The liquid products may be passed to storage, fractionated, subjected to additional or repeated treatments and worked up into desired products by any suitable means. The uncondensed gases may be purified and recycled in the hydrogenation process by suitable means known to the art.

The following example is presented to illustrate a preferred method for operating this process.

A fraction of petroleum oil of 35° A. P. I. gravity is subjected to a limited oxidation until the combined oxygen content of the oil is about 4 to 6% by weight. This oxygenated oil is then raised to a pressure of about 3000 pounds per square inch and is heated rapidly in an externally fired coil to a temperature of about 650° F. The heated oil is then mixed with hydrogen gas at substantially the same pressure and temperature in a proportion of about 6000 cu. ft. of hydrogen per barrel of oil and the mixture is passed directly into a hydrogenation vessel containing a suitable hydrogenation catalyst, such as a mixture of oxides and sulfides of heavy metals of group VI. The temperature of the oil and gas mixture rises rapidly to about 750° F. due to heat liberation accompanying the formation of water by reduction of the oxygenated components of the oil. The oil and gas mixture is passed continuously through the reaction vessel and is withdrawn, cooled, condensed and separated into uncondensed gases and suitable oil fractions. A large proportion of gasoline, or a larger proportion of improved heavier oils of increased purity may be obtained depending on the rate of throughput and the time permitted for destructive hydrogenation to proceed.

In the ordinary process for hydrogenating hydrocarbon oils it is necessary to heat the oil substantially to a temperature at which hydrogenation will take place before discharging into the reaction chamber. This temperature is generally above about 750° F. and may be as high as 850° F., 950° F. or higher. It is true that the hydrogenation reaction itself is exothermic, but the amount of heat evolved in this way is only sufficient to raise the temperature of the reacting materials 20 to 60° F. depending upon the type of oil used. By a preliminary oxidation of the hydrocarbon oil it is possible to supply a considerably greater quantity of heat directly to the reacting materials, because deoxygenation and hydrogenation may proceed simultaneously. It will be understood that the amount of heat evolved by deoxygenation may be regulated by the quantity of oxidized compounds present in the oil. I have found that temperature rises of 100° F., 150° F. and more may be readily obtained.

This invention is not limited to the use of oxidized hydrocarbon oils or oils to which an oxidized hydrocarbon has been added, but may conceivably apply to an oil to which an oxygen-containing compound has been added, the deoxygenation of which by hydrogen in the subsequent hydrogenation will evolve a substantial

quantity of heat. Nor is it limited by the specific details of operation given, nor by any theory of the mechanism of the reaction, but only by the following claims in which I wish to claim all novelty inherent in this invention.

I claim:

1. In a process for the hydrogenation of hydrocarbon oil with hydrogen under pressure above 20 atmospheres and at temperatures above 750° F., the steps of partially oxidizing a portion of the oil whereby sufficient oxygen-containing compounds are produced therein to furnish upon their deoxygenation sufficient heat to materially assist in attaining and maintaining the temperature required for hydrogenation, heating the oil with hydrogen to a temperature above 500° F., but below that at which substantial hydrogenation begins, then discharging the hot oil and said oxidized portion thereof into a reaction zone containing a sulfactive catalyst, wherein the oxygen-containing compounds are deoxygenated and the heat evolved thereby raises the oil to a temperature at which hydrogenation of the oil occurs.

2. Process for the hydrogenation of hydrocarbon oils which comprises rapidly heating a mixture of hydrocarbon oil, containing a quantity of partially oxidized petroleum hydrocarbons sufficient to furnish upon their deoxygenation heat required to materially assist in raising the oil from an incipient hydrogenation temperature to a temperature at which hydrogenation occurs and thereafter to maintain such temperature, to a temperature at which the partially oxidized hydrocarbons may be reduced by hydrogen in an exothermic reaction, then discharging the heated mixture and hydrogen under a pressure above 20 atmospheres into a reaction zone containing a sulfactive hydrogenation catalyst wherein the oxygen compounds are reduced and the heat liberated thereby raises the temperature of the mixture to above 750° F., and hydrogenating the hydrocarbon oil at the temperature thereby attained.

3. Process for the hydrogenation of oils, which comprises passing hydrocarbon oil containing a quantity of partially oxidized petroleum hydrocarbons sufficient to furnish upon their deoxygenation heat required to materially assist in raising the oil from an incipient hydrogenation temperature to a temperature at which hydrogenation occurs and thereafter to maintain such temperature, with hydrogen at a pressure in excess of 20 atmospheres, rapidly through a heating zone wherein the mixture is heated to a temperature above 500° F. but below that at which the partially oxidized hydrocarbons are substantially reduced, then passing the heated mixture into a reaction zone containing a sulfactive hydrogenation catalyst maintained at a pressure above 20 atmospheres, wherein the temperature of the reactants is raised above 750° F., principally by the deoxygenation of the partially oxidized hydrocarbons and hydrogenating the hydrocarbon oil at the temperature thereby attained.

4. Process according to claim 1 in which the said oxygen compounds are obtained by the limited oxidation of paraffin wax.

5. Process according to claim 1 in which the said oxygen compounds are obtained by a preliminary limited oxidation of the said hydrocarbon oil with free oxygen.

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