

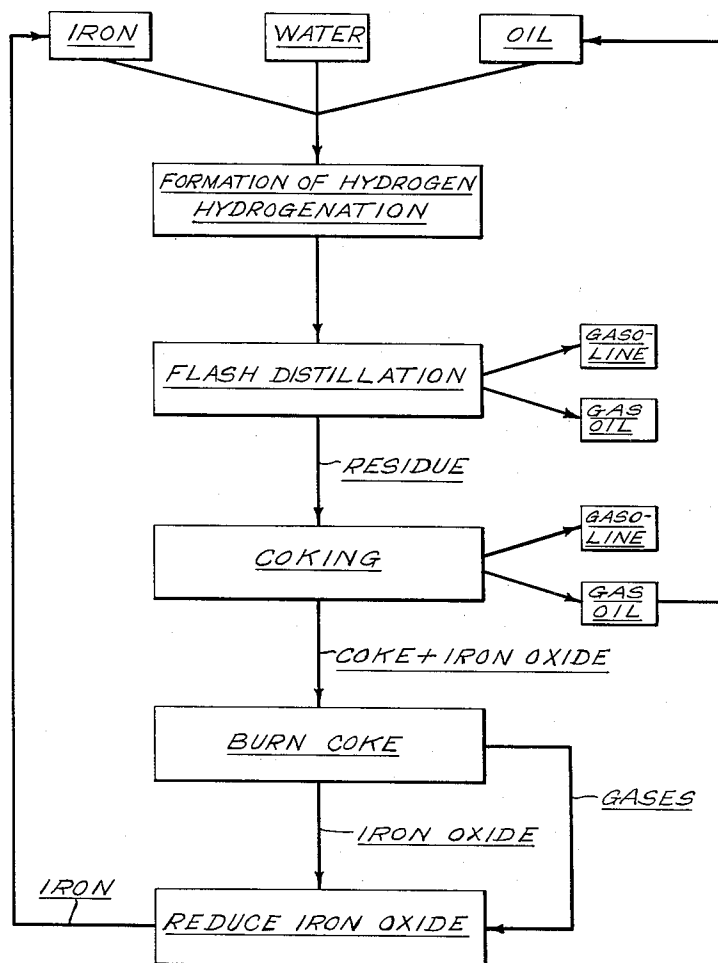
March 27, 1956

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2,739,929

RECOVERY OF CATALYST IN THE HYDROGENATION OF HYDROCARBON OILS

Filed Aug. 24, 1951



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1

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Application August 24, 1951, Serial No. 243,505

1 Claim. (Cl. 196—53)

This invention relates to that method of hydrogenating hydrocarbon oils in which the hydrogen is produced in situ by means of the reaction between finely divided iron and steam. The invention is concerned with certain improvements in the recovery and utilization of the products of such hydrogenation.

In this hydrogenation process a mixture of iron, water and oil is subjected to elevated temperatures such as 720–950° F. under high pressures in excess of 200 atmospheres ordinarily around 4,000 to 5,000 pounds per square inch. The iron and steam react under these conditions to generate hydrogen which simultaneously hydrogenates the oil, producing lighter hydrocarbons such as gasoline and intermediate constituents such as kerosene and gas oil. The process is exemplified in the Uhde process, which is disclosed in the Bayer U. S. Patent No. 1,936,819 and in the Pfärrmann U. S. Patents 2,057,971 and 2,088,214.

In this hydrogenation process the iron is oxidized to form iron oxides. The present invention is directed to certain improvements in the treatment of the reaction products for separating the iron oxide from the products of reaction and for reducing the oxide to the metal for reuse in the hydrogenation process. The invention also has in view a better utilization of the hydrocarbon oil products of the hydrogenation in the production of additional quantities of light products such as gasoline.

In accordance with the invention, the reaction products of the hydrogenating step are flash distilled to separate gaseous and vaporous products from a residue which contains iron oxide. This residue is subjected to coking to effect conversion into lighter products such as gasoline and gas oil and produce a coke residue containing the iron oxide and this coke is burned so as to obtain an ash or slag consisting essentially of the iron oxide. Prior to the present invention it has been sought to separate the iron oxide from the hydrogenation residue by centrifuging followed by filtering in a filter press. The present invention thus presents an improvement in the recovery of the oxide from the hydrogenation residue in that such expensive operations as centrifuging and filtering are eliminated and replaced by a coking operation which not only functions to yield additional lighter hydrocarbons but also places the iron oxide in a condition in which it is readily separable by mere burning of the coke.

The accompanying drawing is a flow diagram which illustrates a preferred embodiment of the invention.

The hydrogenation process is most advantageously applied to the treatment of heavy stocks such as topped or reduced crude petroleum. The heavy oil is mixed with finely divided iron and water and the slurry is subjected to temperatures and pressures such as above indicated to effect the reaction between the iron and steam to form hydrogen and to hydrogenate the hydrocarbon material. The reaction is usually conducted in the presence of certain promoters, such as small amounts of nickel oxide, copper oxide, zinc oxide, zinc chromate, zinc chloride, aluminum hydrate, thallium, and chromium chloride, and tin and bromine. The reaction products are passed

2

through a pressure reducing valve or other pressure reduction means into a flash chamber wherein the products are flash distilled preferably under low pressures such as atmospheric or thereabouts.

The flashed vapors are fractionated to obtain the fractions desired such as gasoline and gas oil. The latter constitutes a good charge stock for a catalytic cracking operation. The residue produced in this distillation is a heavy hydrocarbon material containing the iron oxide.

The essential feature of the present invention is the coking of this flashed residue. It is preferably subjected to a delayed coking operation by being passed through a heating coil wherein it is heated to temperatures of the order of 900° F. and then directed into a coking chamber wherein it is converted to coke at temperatures such as around 825° F. to 875° F., while under relatively low pressures, usually below 100 pounds per square inch. In the coking step additional quantities of gasoline are produced as well as intermediate products such as gas oil. The gas oil is advantageously recycled, being mixed with the heavy residual stock that is being subjected to hydrogenation.

The coke with contained iron oxide produced in the coking step is subjected to oxidation of burning with resultant segregation of the iron oxide as an ash or slag from the burning.

In one method of utilizing the coke, it is pulverized and employed as a powdered fuel to supply heat for the coking step and for generating steam for the process. In this method the coke is burned in closed chambers in which the iron oxide slag is readily collected. In an alternative method the coke is blasted with air and steam to effect burning of the coke and separation of the iron oxide ash or slag.

The iron oxide, recovered by the burning of the coke, is reduced to the metal by contacting with hydrogen, producer gas, water gas, or other suitable reducing agent. In the preferred operation, the coke burning and iron oxide reducing steps are integrated by blasting the coke with air and steam in one chamber to produce gases rich in carbon monoxide, the iron oxide is withdrawn and directed to a subsequent reducing step in which the gases rich in carbon monoxide produced in the burning of the coke are utilized to effect the reduction of the iron oxide.

In an example of the invention reduced crude oil is subjected to reaction with finely divided iron and steam to produce hydrogen and simultaneously subject the oil to hydrogenation. The reaction products under a pressure of 5,000 lbs. per square inch and at a temperature of 840° F. are passed to a flash drum operating under reduced pressure to separate gases and vapors from a liquid residue containing iron oxide. The residue is subjected to delayed coking at temperatures of about 850° F. in the coke drum. The coke product is pulverized and passed to a gas generating chamber wherein it is subjected to burning in the presence of air and steam. The effluent is shock chilled with water to obtain the iron oxide ash or slag in pulverulent form. This ash is delivered to a subsequent chamber and the iron oxide is reduced by being contacted at elevated temperatures with the gases including carbon monoxide produced in the preceding chamber in which the coke is burned. The reactivated metal is sent back to the hydrogenating step for further use in the reaction.

Although a preferred embodiment of the invention has been described herein, it will be understood that various changes and modifications may be made therein, while securing to a greater or less extent some or all of the benefits of the invention, without departing from the spirit and scope thereof.

I claim:

In the hydrogenation of heavy petroleum stocks where-

3

in said petroleum stock, steam and finely divided iron are subjected to reaction at elevated temperature and pressure to effect formation of hydrogen and iron oxide and simultaneous hydrogenation of the oil producing lower boiling constituents including gasoline and gas oil and the resultant products of reaction including the iron oxide catalyst are subjected to flash distillation separating gaseous and vaporous products from a liquid residue containing the iron oxide; the process that comprises heating said liquid residue containing iron oxide to a temperature of the order of 900° F.; passing said heated liquid residue into a coking chamber at a temperature of about 825 to 875° F. and at a pressure of about 100 pounds per square inch effecting conversion of said liquid residue to gaseous hydrocarbons, additional quantities of gasoline and gas oil, and a solid coke residue containing the iron oxide catalyst; recycling gas oil from said coking step to the aforesaid hydrogenation step; subjecting said coke residue to oxidation by blasting with air and steam producing

4

gases rich in carbon monoxide and iron oxide substantially free of coke; reducing at least a part of said iron oxide to metallic iron in a separate reducing zone with said gases rich in carbon monoxide, and directing metallic iron thus produced to the hydrogenation step.

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