

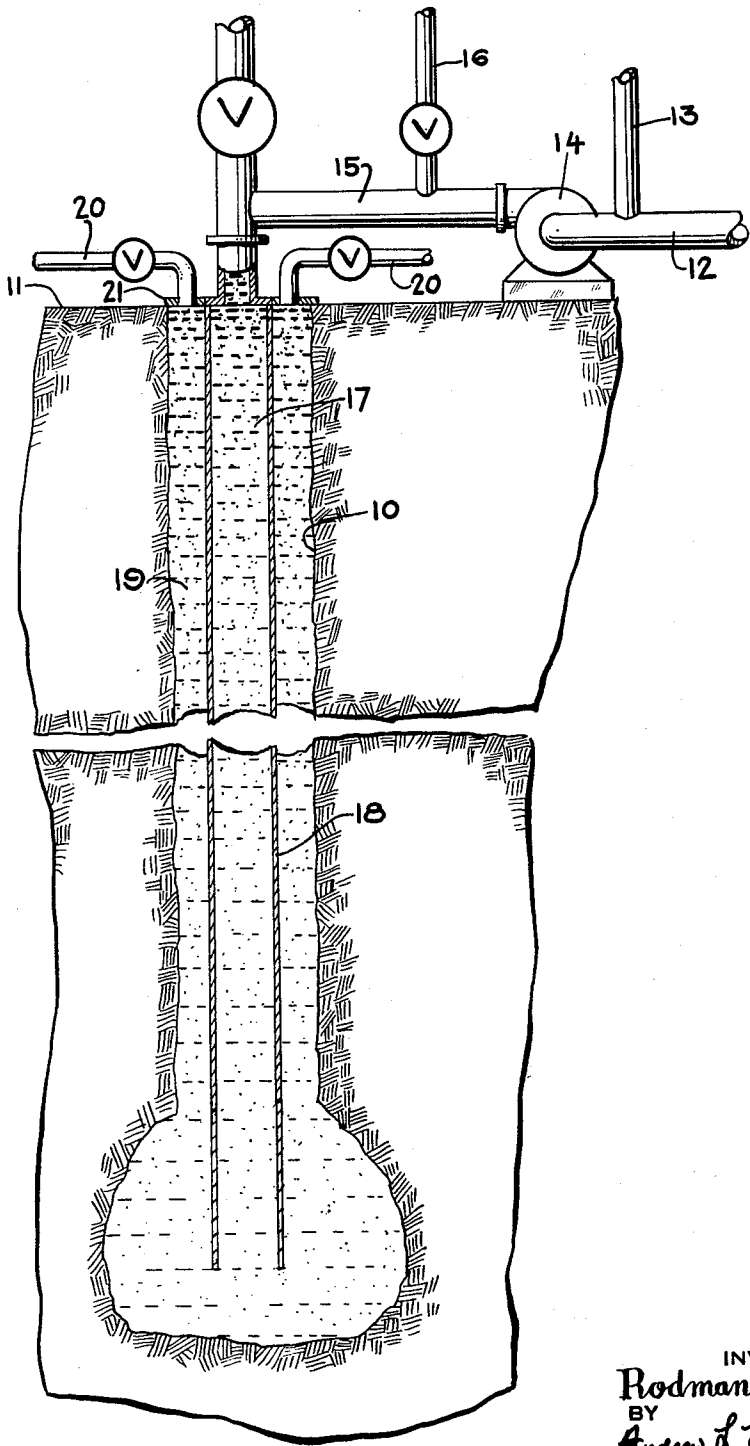
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UNDERGROUND HYDROGENATION

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UNDERGROUND HYDROGENATION

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1 Claim. (Cl. 208—108)

This invention relates to the hydrogenation of fluid hydrocarbons in the presence of hydrogenation catalysts to produce more valuable products.

The hydrogenation of fluid hydrocarbons, and more particularly the hydrocracking or destructive hydrogenation thereof, is a well-known operation that has been widely described in the literature. It has never found wide commercial acceptance in this country, however, for a variety of reasons, not the least of which is the high pressures that must often be employed to accomplish the desired reaction. These high pressures require that heavy walled reaction vessels be employed which, of course, are extremely expensive. In addition, there is always the danger that a small leak in the high pressure system might cause a very serious explosion.

There has now been discovered a technique for hydrogenation at higher pressures which avoids the need for the expensive heavy walled reaction vessels and conducts the reaction at a location where any explosion would not be a substantial safety hazard.

It is an object of this invention to provide a process for the hydrogenation of hydrocarbons which overcomes the above-described difficulties.

A specific object is to provide a method for hydrocracking liquid hydrocarbons efficiently and economically.

These and other objects from the invention will be apparent from the following discussion thereof.

Broadly, in this invention, a fluid hydrocarbon material is continually passed downwardly into a preformed underground cavity together with a finely divided catalyst and hydrogen. At least the lower section of the cavity is maintained at the desired reaction temperature and pressure to effect the hydrogenation reaction, thereby releasing the exothermic heat of reaction. The products of the hydrogenation are continuously removed from the cavity and the velocities of the fluid in the cavity are at all times maintained sufficient to keep the finely divided catalyst suspended in the fluid. The reaction conditions are likewise controlled so that the rate of reaction is sufficient to generate at least enough heat to compensate for the heat lost through the walls of the cavity.

This invention will be best understood by referring to the attached drawing, which is a diagrammatic illustration of one form of this invention.

In the drawing there is shown an underground cavity 10 extending downwardly from the earth's surface 11. This cavity may be one formed especially to practice this invention but more advantageously it might be an abandoned oil well or like cavity. The depth of the cavity required will, of course, be determined by the pressure desired at its lower end. It is required, however, that the cavity have a depth of at least one foot for each pound per square inch of pressure desired at its lower end, to maintain the desired pressure without rupturing the cavity walls. Preferably, for a hydrocracking reaction, the cavity should be within the range 2,000 to 15,000 feet deep.

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Cavity 10 is closed off at its upper end by a conventional closing member, such as those used to cap oil wells, designated 21. The fluid charge to be converted, generally in the liquid phase, enters the system through conduit 12. It is joined by hydrogen from a suitable source supplied through conduit 13. The quantity of hydrogen used will depend on the degree of hydrogenation required. For hydrocracking, a quantity of hydrogen within the range 1,000 to 15,000 standard cubic feet per barrel of charge is usually employed. Pump 14 forces the hydrogen and hydrocarbon mixture forward through conduit 15. A suitable hydrocracking catalyst is suspended in the flowing material entering through passage 16. This catalyst should normally be of a size within the range 20 to 200 mesh Tyler, so that it will remain suspended in the flowing fluid stream and still may be easily separated from the converted product. The hydrocarbon, catalyst and hydrogen then flow downwardly into a central region 17 of cavity 10, which central region is separated from the remainder of the cavity by an elongated conduit 18. The hydrocarbon reactant normally increases in temperature as it descends through passageway 17, reaching the desired reaction temperature in the lower section of the passageway. The desired reaction then occurs, releasing the exothermic heat of reaction. Liquid material, including the products of conversion, then flows upwardly through annular space 19 between the outer wall of cavity 10 and conduit 18. The product stream is removed from the cavity through passageways 20.

It is a feature of this invention that heat exchange occurs between the incoming reactant stream flowing through conduit 17 and the outgoing product stream flowing through annular space 19. Thus, the reactant need not be supplied at reaction temperature as it enters conduit 17, since a part of the heat required to bring it to that temperature will be received while it flows in the conduit. To improve heat transfer, fins may be provided along the length of conduit 17.

The product streams removed through conduits 20 may be handled in conventional manner to separate hydrogen and catalyst therefrom and separate the desired products such as gasoline and fuel oils from any other material. The hydrogen so removed will normally be recycled to the conversion system, entering through conduit 13. The catalyst separated may be discarded, or it may be reconditioned for re-use in the conversion, for example, by burning carbonaceous contaminants therefrom, and returned to the system through passage 16. With some catalysts it will be possible to continuously re-use the catalyst in the conversion reaction for substantial periods without reconditioning.

Any material heavier than fuel oil may be recycled to the conversion zone by merging it with incoming fresh charge in conduit 12.

In this invention it is necessary that the reaction which occurs be exothermic. Moreover, it is necessary that the reaction occur at a sufficient rate that the heat produced is at least equal to the heat lost through the walls of cavity 10. Preferably, the heat generated should exceed the heat losses so that a part of it may be used to preheat the charge in the manner illustrated in the drawing. For a hydrocracking conversion, the rate of reaction should be such as to convert at least 200 barrels (42 gal.) per day per 1,000 feet of cavity depth in order to prevent the cavity dropping below reaction temperature.

Control of the temperature in the cavity can be achieved in a variety of ways. Most obvious of these is the control of the charge inlet temperature; others include varying the quantity of product recycled and varying the quantity of hydrogen.

When starting up the reaction system it will be necessary to employ some means to raise the cavity tempera-

ture up to reaction temperature. One way in which this can be accomplished is to lower an electric heater into the cavity and utilize heat from this source until the reaction rate is sufficiently high to sustain the temperature. Another technique is to circulate hot gases through the cavity until it is heated to the reaction temperature and then introducing heated charge to the cavity.

The catalyst used must remain suspended in the fluid reactant at all times in the process of this invention. The fluid velocities needed to accomplish this will, of course, be a function of the size and density of the solids and the fluid viscosity. For example, with conventional catalysts of a size within the range 32 to 60 mesh Tyler, the velocity of liquid hydrocarbon material should be above 3 feet per minute and preferably above 10 feet per minute. Due to the irregular shape of most cavities there will be some small regions where the velocity will drop below the velocity needed to maintain the catalyst suspended. It is not intended to exclude from the scope of this invention operations where such regions exist, provided that their volume is relatively minor compared to the volume of the cavity in which the velocity is high enough to maintain the catalyst suspended.

As indicated above, this invention will find particular favor with the hydrocracking of liquid hydrocarbons. Suitable hydrocracking catalysts for use in this process will usually have both a hydrogenation component and a cracking component. The hydrogenation component might be nickel, molybdenum, platinum, palladium, ruthenium, iron, tungsten or cobalt or the oxides or sulfides thereof. The cracking component might be silica and alumina or magnesia. One catalyst that might be successfully used in the present invention is iron on coke.

In hydrocracking, the temperature in the cavity where the reaction is to occur should normally be within the range 800° F. to 950° F. and the pressure within the range 2,000 p.s.i. to 10,000 p.s.i. Where heat exchange between reactant and product streams is accomplished in the manner shown in the drawing and the rate of reaction exceeds 200 barrels (42 gal.) per day per 1,000 feet of cavity depth, the reactant might be supplied at a temperature within the range 100° F. to 200° F.

Example

Employing this invention, a 40 percent Kuwait residual stock having an initial boiling point of 700° F. might be hydrocracked using an iron on coke catalyst. The catalyst might be of a size within the range 32 to 60 mesh Tyler. The catalyst-oil slurry might be supplied to an abandoned oil well at a temperature of about 200° F. and at a rate of 10,000 barrels (42 gal.) per day. Hydrogen would also be supplied at a rate of 4,000 standard cubic

feet per barrel of charge stock. At the bottom of the well, which might be 3,000 feet deep, the temperature might be 850° F. and the pressure 3,000 p.s.i. The well could be roughly 7 inches in diameter and conduit might be 4 inches in diameter. At the lower end of the well it would be desirable to produce a cavity 30 feet in diameter. This could be done by shooting the well with nitroglycerine. It would be desirable to circulate a clay suspension through the cavity before start-up to remove small particles of rock, etc.

It is intended to cover herein all changes and modifications of the examples of the invention herein chosen for purposes of disclosure which do not constitute departures from the spirit and scope of the invention.

I claim:

A continuous process for the catalytic hydrocracking, at elevated pressures, of a liquid hydrocarbon charge to produce lower boiling products, which comprises: suspending a hydrocracking catalyst of a size within the range about 20 to 200 mesh Tyler in the liquid hydrocarbon charge and flowing said suspension downwardly through an elongated, preformed, underground cavity having walls that are substantially non-reactive with hydrogen at the temperature and pressure of the hydrogen flowing therethrough and having a depth within the range about 2,000 to 15,000 feet; maintaining a reaction temperature in the lower section of said cavity within the range about 800 to 950° F. and maintaining the rate of supply of said charge to said cavity sufficient to maintain the desired reaction pressure at the lower end thereof, said reaction pressure being less than one pound per square inch per foot of depth of said cavity whereby said hydrocracking reaction occurs; maintaining the reaction conditions in said cavity such that at least 200 barrels per day of charge are reacted per 1000 feet of cavity depth, thereby maintaining said cavity at the reaction temperature; supplying liquid hydrocarbon charge to the upper end of said cavity at a temperature below the desired reaction temperature and passing the product of conversion upwardly out of the lower end of said cavity at a velocity of at least three feet per minute in heat exchange relationship with incoming charge to heat the charge to the desired reaction temperature prior to the charge reaching the lower end of the cavity.

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