

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Method and apparatus for Effecting Reactions of Flowing Reactants

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of No. 30, Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved method and apparatus for effecting reactions of flowing reactants in the presence of solid contact material, and is more specifically directed to a novel method for effecting catalytic reactions in the presence of hydrogen while permitting a particular control of the residence time of the reactants within the reaction zone containing solid catalytic material. Processes which involve catalytic hydrogenation and catalytic desulfurization are particularly benefited through the adaptation of the present invention thereto.

Catalytic hydrogenation reactions, and most catalytic desulfurization reactions must, of necessity, be effected in the presence of an excessive quantity of hydrogen. The hydrogen is often present as a necessary reactant, and in many instances, is required for the purpose of suppressing undesirable side reactions, whereby the useful, effective life of the catalyst is substantially increased. Investigations have indicated that hydrogen and/or other normally gaseous material is necessary, in many processes utilizing a solid contact or catalyst mass, in order to prevent the formation of coke or other carbonaceous material, and the deposition of the same on the catalyst. The concentration of carbon or carbonaceous material on the catalyst can rapidly attain the

degree at which the activity and stability of the catalyst is effectively nullified, and the catalyst must be either regenerated, or, in a non-regenerative process, replaced.

As hereinbefore stated, the presence of excessive quantities of hydrogen, in a catalytic hydrogenation or desulfurization process, will suppress the tendency for coke or carbonaceous material to be formed and deposited on the catalyst, and, within practical limits, the higher the ratio of the mols of hydrogen to the mols of hydrocarbon or other organic reactant in the reaction zone, the more effective the suppression of the formation and depositing of said coke or carbonaceous material. The high mol ratio hydrogen to charge stock has been customarily provided, in the majority of hydrogenation processes, employing an external compressive recycle of gas for the purpose of providing sufficient hydrogen within the atmosphere which surrounds the catalyst, and to replace that hydrogen which is consumed by the process. With proper selection of the catalyst and its disposition in the reactor, as hereinafter described, it is possible, through the utilization of the method of the present invention, either to avoid entirely, or decrease substantially the amount of compressive external recycle of hydrogen to the reaction zone.

Heretofore, it has been necessary to maintain the mol ratio of hydrogen to hydrocarbon or other charge stock to be treated with hydrogen at a high level by means of recycling hydrogen with the aid of compressors at a sufficiently high rate to prevent undesirable side reactions. This recycling has certain inherent disadvantages: first, such recycling is necessarily accomplished at elevated process pressures, requiring all of the additional re-

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cycle process equipment to be designed to withstand such pressures; secondly, the high rate of recycle requires compressors of sufficient capacity to maintain the necessary hydrogen flow, which compressors must also be designed to withstand the elevated process pressures; and, thirdly, there exist severe fluctuations in the residence time in regard to the hydrogen, which fluctuations effect a varying internal ratio between the hydrogen and the charge stock being processed within the system. Efficient control of the ratio (generally expressed in terms of molar quantities) of hydrogen, or other normally gaseous material, to the normally liquid material being charged, is extremely important in those instances wherein the hydrogen is constantly being reacted with various components of the charge stock, thereby increasing the quantity of product components, decreasing the quantity of charge stock components and decreasing the quantity of available hydrogen. These latter considerations are simplified in regard to a continuous process, and particularly those processes involving catalytic hydrogenation wherein the molar concentrations of charge stock and hydrogen, with respect one to the other, tend to influence the efficiency of the process.

As hereinabove stated, the required quantity of hydrogen was heretofore maintained by means of external hydrogen recycle utilizing a compressor capable of withstanding the conditions of operation. Aside from the initial cost of the compressors, there exists the added cost of power and maintenance. Also, in the event of a power failure to the compressors, the cessation of the recycle gas flow may cause coke or carbonaceous matter to form on the catalyst immediately, and in such degree that the process is rendered inoperable until such time as the catalyst is regenerated or replaced. The carbon or carbonaceous material may, in fact, build up to such a degree on the catalyst that the catalyst cannot be regenerated in a normal manner, if at all. For these reasons it is highly desirable to eliminate the compressive recycle gas system and its necessary appurtenances, while continuing to maintain a sufficient quantity of hydrogen within the reaction zone. The utilization of our invention makes possible the elimination of, or substantial reduction in, the recycle gas compression while maintaining an effective mol ratio of gaseous reactant to charge stock within the reaction chamber, and permitting control of the residence time of the gaseous reactant and its molar relationship with the charge stock.

While the present specification is primarily directed to the catalytic hydrogenation and desulfurization of hydrocarbons, especially as practised within the petroleum industry, it is understood that the process and apparatus of the present invention may be used to effect

other reactions, which reactions must be performed in the presence of a normally gaseous substance such as hydrogen, and/or reactions in which one of the products may be in the liquid form or liquefied by condensation within the reaction vessel.

In one embodiment, the present invention provides a process for effecting reactions which comprises continuously introducing a charge stock to a reaction zone containing a mass of solid contact material, also continuously introducing to said reaction zone an excess of a normally gaseous reactant, reacting a portion thereof with said charge stock in the presence of the solid contact material, maintaining a pool of liquid reaction product in the lower portion of said reaction zone, thereby forming a gas seal and preventing gas loss from said zone, removing from said pool and from said zone a liquid product stream containing, at most, only the small amount of gas that is soluble in said liquid product, continuously withdrawing a portion of said normally gaseous reactant from said zone at a point above said pool of liquid reaction product, and retaining substantially all of the remaining unreacted gas within said reaction zone without compressive recycle of the gas phase.

In a more specific embodiment of this process, a portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point above and adjacent the pool of liquid reaction product and is returned without external compression to the upper portion of the reaction zone and into contact with the charge stock and contact material therein. Advantageously, a portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point below the contact material therein and above the pool of liquid reaction product and is returned without external compression to the upper portion of the reaction zone at a point above the contact material therein while another portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point above the pool of liquid reaction product and then discharged from the process.

When the reaction product in the present process is formed substantially in the liquid phase, at the temperature and pressure maintained within the reaction zone, the liquid seal in the form of a pool of liquid reaction product in the lower portion of the reaction zone is readily obtained. When the product in the reaction zone is substantially in the vaporous state, the present invention provides for condensation of the reaction product within the lower portion of the reaction zone, preferably within a heat-exchange zone in-between those portions of the reaction zone which contain the catalyst and the pool of liquid reaction product, respectively.

A particularly advantageous embodiment of this invention is constituted by the application of the present process to the reaction of a hydrocarbon material as charge stock with a
5 gaseous reactant comprising hydrogen at elevated temperature and superatmospheric pressure in the presence of a catalytic contact material promoting the reaction of the hydrocarbon material with hydrogen. In one
10 specific mode of thus applying the present invention the hydrocarbon material is introduced in the liquid state into the reaction zone and the reaction is effected at a pressure at which substantial vaporization of the hydro-
15 carbon material is prevented. In another specific mode of thus applying the present invention a normally liquid hydrocarbon material is introduced in the vaporous state into the reaction zone, and the hydrogenated
20 normally liquid product is condensed in the lower portion of the reaction zone.

The apparatus provided by the present invention and suitable for use in carrying out the present process comprises, in combination,
25 a vertically arranged chamber, supporting means for a mass of solid, contact material in the upper portion thereof, an indirect heat exchange means disposed below and spaced from said supporting means and occupying a
30 substantially smaller space than the space provided for said mass of solid contact material in said upper portion of the chamber, an inlet conduit connecting with the upper portion of the chamber, a liquid-collector
35 section in the lower portion of the chamber below said indirect heat exchange means, a liquid discharge conduit extending from the liquid-collector section, and a gas withdrawal conduit connecting with the chamber at a
40 point above said liquid-collector section. This apparatus in a preferred form, is provided with a gas recirculation conduit which has one end thereof in open communication with the chamber between the collector section and
45 the heat exchange means while the other end of this conduit is in open communication with the chamber at a point above the mass of contact material. The upper portion of this apparatus, moreover, is preferably of a sub-
50 stantially larger cross-sectional area than that of the lower portion, perforate means for supporting the mass of solid contact material being provided in the chamber portion of enlarged cross-sectional area, while the in-
55 direct heat exchange means is disposed in the chamber portion of smaller cross-sectional area.

The primary feature of the present invention involves independent withdrawal of liquid
60 reaction product and gaseous material from the reaction zone, rather than withdrawal of the total reaction product and excess gaseous material in a single stream. The liquid reaction product will, of course, include small
65 amounts of dissolved gaseous material. How-

ever, by maintaining continuous and separate withdrawal of a predetermined quantity of gaseous material for the purpose of controlling the residence time within the reaction zone, the normally gaseous substances are not
70 withdrawn inevitably at the same rate as the liquid product, but rather are retained for the desired period of time within the reaction zone as reactants or as material designed to prevent undesirable side reactions. The rate
75 of withdrawal of gaseous material will, of course, depend upon charge rate, extent of reaction, change in charge quality or product specification and the like. But, the essential feature of this invention is that withdrawal
80 is continuous and separate, not intermittent. In some reactions, there is often formed a gaseous light paraffin, for example methane, which is not completely soluble in the liquid product being withdrawn, and which has the
85 tendency to build up and dilute the principal reactant gas such as hydrogen, or which, in and of itself, exhibits the tendency to counteract the desired reaction or promote the formation of coke and/or other carbonaceous
90 material. It is within the scope of our invention to include continuous but separate withdrawal of such insoluble gas from the reaction zone for the purpose of eliminating these undesirable gases, decreasing thereby the
95 dilution of the reactant gas and the tendency to retard desirable reactions. The amount of gas thus vented from the reaction zone may be small. Substantially, only a liquid product, and a separately controlled quantity of gas
100 is withdrawn, and it is possible thereby to regulate the amounts of the substances in the reaction zone and thus, within the catalyst bed itself. For example, in a process for hydrogenating a gas-oil over a chromia-alumina
105 catalyst, while charging the gas-oil into the reactor in the liquid state at a hydrogen pressure of 68 atmospheres and a temperature of about 343°C., the gas-oil remains substantially in the liquid phase. Some of the hydro-
110 gen is immediately dissolved in the hydrocarbon oil, and is available for effecting hydrogenation. An excess amount of hydrogen must be made available so that the hydrogenating reaction may continue. The thin film
115 of liquid oil that surrounds the catalyst has hydrogen dissolved therein initially, and more hydrogen is supplied from the surrounding hydrogen-rich atmosphere as the hydrogenating reaction proceeds. Therefore, the gas-oil is
120 passed downwardly through the body of catalyst at such a rate that excess hydrogen is always present in the catalyst bed, including the hydrogen in the catalyst, in the oil, and the hydrogen in the voids and closely
125 surrounding atmosphere of the catalyst particles. By maintaining a liquid seal on the exit line, only a small amount of dissolved hydrogen is ~~withdrawn~~ with the liquid. By maintaining a continuous but separate bleed
130



withdrawn

of hydrogen and light gaseous hydrocarbons, it is possible to control the residence time of the hydrogen with respect to the residence time of the liquid hydrocarbon charge. Hydrogen is added only in the amount necessary to maintain the pressure, and it is possible to maintain an appreciably higher mol ratio of hydrogen to hydrocarbon throughout the reaction zone and catalyst bed than is maintained in the materials being continuously introduced into the reaction zone. By maintaining a cooler in the lower portion of the reaction zone, the process may be used even though the products are in the vapor phase at reaction conditions.

When the process is used for the desulfurization of a sulfur-containing hydrocarbon oil charge stock, a sulfur-resistant catalyst, such as cobalt sulfide and/or molybdenum sulfide, supported on a suitable refractory carrier material such as alumina, is employed within the reaction zone. Any of the well-known desulfurization catalysts may be utilized. Similarly, when the process is used for hydrogenation, any suitable hydrogenation catalyst such as, for example, nickel-kieselguhr may be employed. The scope of the present invention is not intended to be limited to any particular catalyst.

The catalyst bed may be situated such that gases can readily move therethrough; that is, the bed arrangement may be such that it has high porosity even in the presence of flowing liquid charge or products. To accomplish this, it is preferred that the catalyst particles be sufficiently large to prevent extremely close packing of the particles, and the interstices thereof from being completely filled by liquid. The catalyst is selected in shapes that facilitate relatively large void spaces; examples of suitable shapes are spheres, solid cylinders, as well as hollow cylinders, rings, saddles; mixtures of irregular shapes and sizes may also be used. To further aid in contacting the reactants with the catalyst, non-catalytic material, such as ceramic balls, may be mixed with the catalyst. The catalyst also may be disposed in thin layers in the reactors, and the space between the beds may be used as a re-distribution zone wherein the reactants may be re-distributed to afford more uniform contact with the next bed of catalyst. For example, it may be desirable to collect all the liquid which may have concentrated at the walls of the reaction chamber, re-distributing such liquid across the mass of catalyst. In the type of situation hereinabove described, the external gas recirculation or so-called recycle conduit, which is described hereinafter in detail with reference to the attached drawings, is not required to obtain efficient "recycle" of the gases, and the process is effected through the utilization of "internal recycle" within the reaction zone. The elimination of this external recycle conduit is within the

broad embodiments of the present invention.

The novelty and utility of the present invention are illustrated further in the accompanying drawings. Figure 1 illustrates one possible flow of the process; in Figure 1, most of the valves, heat exchangers, coolers, controls and similar appurtenances have been either limited, or omitted entirely from the drawing: these are well known in the art, and are not essential to the complete understanding of the particular embodiment illustrated. Figure 2 diagrammatically indicates, in an elevated view, one form of apparatus which is preferred for use with the method of the present invention.

Referring to Figure 1, a hydrocarbon charge stock to be hydrogenated is introduced into the process through line 1, is picked up by pump 2 and discharged into line 3. The hydrogen entering the process through line 4 is picked up by compressor 5 and discharged into line 6. The oil in line 3 and the hydrogen in line 6 are commingled in line 7, and this mixture is passed into heater 8. The temperature of the mixture is raised to the desired level and the mixture is discharged into line 9. The heated oil and hydrogen are passed in a downward flow into reactor vessel 11 through a spray nozzle 10. The spray nozzle is a convenient means for distributing the hydrocarbon oil and hydrogen evenly over the top of the catalyst bed. In the case herein illustrated, since the process of this invention is particularly adaptable to fixed-bed types of operation, the catalyst is shown deposited as a fixed bed in reactor 11. In reaction vessel 11, the hydrogenated product, containing dissolved hydrogen, is collected in liquid collector zone 12, and is withdrawn through line 13 and cooler 14 into separator 15.

Reaction vessel 11, as hereinbefore stated, is maintained at a temperature and pressure required to inhibit excessive vaporization of the oil. In reactor 11 there is also a high concentration of hydrogen, and, by controlling the flow of the oil into reactor 11, a high hydrogen to hydrocarbon mol ratio may be maintained therein. The maintenance of a liquid seal in the liquid collector 12 may be accomplished through the use of a U-tube arrangement, or preferably by locating a valve in line 13 that is controlled by a liquid level-sensing instrument connected to the collector 12; the gas is thereby sealed in vessel 11. Compressor 5 is preferably on pressure control; that is, the compressor operates to maintain the pressure in the reaction vessel 11. Compressor 5 does not act as a recycle compressor, but merely serves the function of adding as much hydrogen as is necessarily consumed in the process.

Reaction vessel 11, as shown, is also equipped with a gas recirculation line 20 containing control valve 21, and when the process

is operating to the extent that more hydrogen circulation, in excess of the "internal recycle" within the reaction zone is desired, valve 21 may be opened and such hydrogen will circulate upwardly through line 20 without the aid of a compressor in this line. Line 20 is preferably connected with the lower portion of the reaction vessel at a point above the liquid level in collector 12 and below the catalyst bed, and is connected with the upper portion of the reaction vessel at a point above the catalyst bed. As hereinbefore stated, the catalytic material deposited within reaction zone 11 may be disposed in a manner which facilitates the free flow of gaseous material through the catalyst bed. Thus, the method of the present invention may be effected, in such instances, without the utilization of the external recycle gas line 20. This scheme relates to one of the embodiments of the present invention, that is, the present invention is sufficiently broad to encompass a process utilizing the special apparatus with internal recycle of hydrogen through catalyst voids alone, in which process, line 20 is not in existence. The reaction vessel may also be equipped with lines 22 and 23 which may be used for the introduction of hydrogen into the reaction zone at selected points, and this hydrogen may be obtained from line 6. A gas bleed connection 24, containing valve 25 is also provided on the reaction vessel and may be used for bleeding off a predetermined minor portion of normally gaseous material as hereinbefore stated. In an advantageous mode of operation a larger amount of gaseous material is recirculated through line 20 and control valve 21 without external compression than is discharged from the process through line 24 and control valve 25.

In separator 15, the liquid hydrogenated product is separated from the dissolved hydrogen. The hydrogenated product is withdrawn from separator 15 through line 18 containing valve 19, and the small amount of dissolved hydrogen is withdrawn through line 16 containing valve 17. The hydrogen may be sent back to the suction side of compressor 5 to be re-introduced to reactor vessel 11.

Referring now particularly to Figure 2, there is illustrated as a reactor, a vertically disposed reaction chamber 26, comprising an enlarged cross-sectional area upper shell portion 27, which is usually fabricated of steel and constitutes a principal housing and structural support for the apparatus. This shell may be provided with any of the well-known insulating materials and/or insulating cements to protect the steel walls from the high temperatures that may be employed in the reaction zone. Insulating materials may also be placed between outer shell 27 and a thin inner metal lining. This particular embodiment is not, however, herein illustrated. A fluid

material, usually a heated oil and/or a heated gas, is passed into the reaction chamber through conduit 28 located in a center axial position in respect to the reaction chamber. The outer shell 27, with its insulating material defines a cylindrical chamber 29 adapted to contain a mass or bed of catalytic material, usually pellets such as spheres or pills 30. The catalyst particles 30 are held by a supporting means such as perforated plate 31. Perforated plate 31 may be a metal plate in which suitable size holes have been stamped or drilled and likewise, the perforated plate may comprise larger holes covered by a screen of suitable mesh, or the plate may comprise screening that is strengthened by metal rods or bars immediately under the screen. In the embodiment herein illustrated, the supporting grid 31 is held in place by supports 32 which are welded or otherwise fastened to the walls of the shell 27. In the illustration, supports 32 are shown as short pieces of angle iron.

Hydrogen (or other gaseous reactant) may be introduced above the catalyst bed 30 via conduit 33 and likewise hydrogen may be introduced below the catalyst bed 30 via conduit 34. Conduits 33 and 34 may be connected by a common line not illustrated in the drawing. Depending upon the type of operation, conduits 33 and 34 may be provided with suitable valves, and it is within the scope of this invention to use either one or both of the conduits or to use them alternately. In some modes of operation, moreover, the conduits 33 and 34 may be closed by valves while gaseous reactant is introduced together with the charge stock through the inlet 28. The reaction chamber 26 is reduced along its length in reducing section 35, so that the lower portion of chamber 26 will comprise the smaller cross-sectional lower portion in which is disposed an indirect heat exchanger.

The heat exchanger is herein illustrated as constituting a plurality of tubes 36. In normal operation, the product from the catalytic reaction flows downward through tubes 36 which are enveloped by a cooling fluid enclosed in shell 37. The cooling fluid enters through conduit 38 and is discharged through conduit 39. The cooler may be supplied with suitable baffling to insure proper distribution of the heat transfer fluid throughout the heat exchanger. Any indirect type of heat exchanger may be used with the cooling fluid in the tubes or in the shell. The tubes may be horizontal, or vertical as illustrated, or they may be diagonal. The heat exchanger is chosen so that the free space through the openings or tubes is relatively small. This type of heat exchanger is preferred since the process and apparatus of our invention operates much more efficiently when the heat exchanger or condenser operates somewhat as

a diffusion pump. Although we do not intend our invention to be limited to this theory, it appears that the reaction products condense and push or seem to pump the gases down through the condenser and thus to give an internal pumping effect which circulates the light gas, such as hydrogen, throughout the system. The heat exchanger or cooler thus should preferably offer some restriction to the downward gas flow so that the condensing vapors of the large molecules may better direct the light gaseous molecules downward. It is also within the scope of this invention to use a cooler that is especially adapted to act as a diffusion pump.

Below the cooling chamber is located the liquid collector section 40, which section narrows down to outlet conduit 41. The liquid collector section 40 is illustrated as having a liquid level device 42 which operates valve 43. The liquid level device 42 and valve 43 operates so as to maintain a liquid level in liquid collector section 40. In the illustration, a level controller of the type employing a float is shown; however, any of the well-known level sensing devices may be used. Above liquid collector section 40 and below the cooling chamber is located a gas recirculation conduit 44. In this particular embodiment, conduit 44 is illustrated as entering the reaction chamber above the catalyst bed, and this is the preferred location. However, the conduit may re-enter the reaction chamber in the catalyst bed or below the catalyst bed. In operation valve 45 may be opened or may be closed. In an operation in which hydrogen is consumed rapidly, sufficient hydrogen may be introduced through conduit 33 and in this case valve 45 is closed and the hydrogen is circulated completely within the reaction chamber 26, as hereinbefore set forth in the description of Figure 1. Line 46 containing valve 47 is the bleed connection on the system which is operated as hereinbefore discussed, to permit control of the residence time of the hydrogen within reactor 26. Thus, the gas recirculation line 44 and control valve 45 may be used in conjunction with the bleed line 46 and valve 47 in the same manner as described above for the gas recirculating line 20 and bleed line 24 of Figure 1.

By suitable modifications, reactor 26 of Figure 2 may be used for the reaction vessel 11 of Figure 1.

When a cooling means is employed in the lower section of the reaction chamber, the conditions in the catalyst may be such that there may be complete vaporization of the charge stock and/or products, and, in fact, when a cooler is employed, the charge may be introduced in the vapor phase. In the hydrogenation process, the pressure employed is above atmospheric pressure, and preferably above about 13 atmospheres. Pressures as high

as 680 atmospheres may be used; however, pressures below about 135 atmospheres are preferred. When the process is used for the hydrodesulfurization of a sulfur-containing hydrocarbon oil, the conditions are substantially the same as for the hydrogenation reaction. However, when the process is used for hydrodesulfurization, a sulfur-resistant catalyst is preferably employed.

From the foregoing description it can be seen that we have provided a new method and apparatus for effecting reactions of flowing reactants in the presence of solid contact material, such as the reaction of hydrocarbon materials with hydrogen in the presence of a solid catalyst. The foregoing specific illustrations were intended to show the advantages of a particular embodiment of the herein disclosed process, and a particular apparatus in which to effect the same. The specific operations described may be modified in minor details within the scope of this invention.

WHAT WE CLAIM IS:—

1. A process for effecting reactions which comprises continuously introducing a charge stock to a reaction zone containing a mass of solid contact material, also continuously introducing to said reaction zone an excess of a normally gaseous reactant, reacting a portion thereof with said charge stock in the presence of the solid contact material, maintaining a pool of liquid reaction product in the lower portion of said reaction zone, thereby forming a gas seal and preventing gas loss from said zone, removing from said pool and from said zone a liquid product stream containing, at most, only the small amount of gas that is soluble in said liquid product, continuously withdrawing a portion of said normally gaseous reactant from said zone at a point above said pool of liquid reaction product, and retaining substantially all of the remaining unreacted gas within said reaction zone without compressive recycle of the gas phase.

2. The process of claim 1, characterized in that a portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point above and adjacent the pool of liquid reaction product and is returned without external compression to the upper portion of said reaction zone and into contact with the charge stock and contact material therein.

3. The process of claim 1, characterized in that a portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point above the pool of liquid reaction product and is discharged from the process and another portion of said normally gaseous reactant is continuously withdrawn from the reaction zone at a point below the contact material therein and above the pool of liquid reaction product and is returned without external compression to the



a diffusion pump. Although we do not intend our invention to be limited to this theory, it appears that the reaction products condense and push or seem to pump the gases down through the condenser and thus to give an internal pumping effect which circulates the light gas, such as hydrogen, throughout the system. The heat exchanger or cooler thus should preferably offer some restriction to the downward gas flow so that the condensing vapors of the large molecules may better direct the light gaseous molecules downward. It is also within the scope of this invention to use a cooler that is especially adapted to act as a diffusion pump.

Below the cooling chamber is located the liquid collector section 40, which section narrows down to outlet conduit 41. The liquid collector section 40 is illustrated as having a liquid level device 42 which operates valve 43. The liquid level device 42 and valve 43 operates so as to maintain a liquid level in liquid collector section 40. In the illustration, a level controller of the type employing a float is shown; however, any of the well-known level sensing devices may be used. Above liquid collector section 40 and below the cooling chamber is located a gas recirculation conduit 44. In this particular embodiment, conduit 44 is illustrated as entering the reaction chamber above the catalyst bed, and this is the preferred location. However, the conduit may re-enter the reaction chamber in the catalyst bed or below the catalyst bed. In operation valve 45 may be opened or may be closed. In an operation in which hydrogen is consumed rapidly, sufficient hydrogen may be introduced through conduit 33 and in this case valve 45 is closed and the hydrogen is circulated completely within the reaction chamber 26, as hereinbefore set forth in the description of Figure 1. Line 46 containing valve 47 is the bleed connection on the system which is operated as hereinbefore discussed, to permit control of the residence time of the hydrogen within reactor 26. Thus, the gas recirculation line 44 and control valve 45 may be used in conjunction with the bleed line 46 and valve 47 in the same manner as described above for the gas recirculating line 20 and bleed line 24 of Figure 1.

By suitable modifications, reactor 26 of Figure 2 may be used for the reaction vessel 11 of Figure 1.

When a cooling means is employed in the lower section of the reaction chamber, the conditions in the catalyst may be such that there may be complete vaporization of the charge stock and/or products, and, in fact, when a cooler is employed, the charge may be introduced in the vapor phase. In the hydrogenation process, the pressure employed is above atmospheric pressure, and preferably above about 13 atmospheres. Pressures as high

as 680 atmospheres may be used; however, pressures below about 135 atmospheres are preferred. When the process is used for the hydrodesulfurization of a sulfur-containing hydrocarbon oil, the conditions are substantially the same as for the hydrogenation reaction. However, when the process is used for hydrodesulfurization, a sulfur-resistant catalyst is preferably employed.

From the foregoing description it can be seen that we have provided a new method and apparatus for effecting reactions of flowing reactants in the presence of solid contact material, such as the reaction of hydrocarbon materials with hydrogen in the presence of a solid catalyst. The foregoing specific illustrations were intended to show the advantages of a particular embodiment of the herein disclosed process, and a particular apparatus in which to effect the same. The specific operations described may be modified in minor details within the scope of this invention.

WHAT WE CLAIM IS:—

1. A process for effecting reactions which comprises continuously introducing a charge stock to a reaction zone containing a mass of solid contact material, also continuously introducing to said reaction zone an excess of a normally gaseous reactant, reacting a portion thereof with said charge stock in the presence of the solid contact material, maintaining a pool of liquid reaction product in the lower portion of said reaction zone, thereby forming a gas seal and preventing gas loss from said zone, removing from said pool and from said zone a liquid product stream containing, at most, only the small amount of gas that is soluble in said liquid product, continuously withdrawing a portion of said normally gaseous reactant from said zone at a point above said pool of liquid reaction product, and retaining substantially all of the remaining unreacted gas within said reaction zone without compressive recycle of the gas phase.

2. The process of claim 1, characterized in that a portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point above and adjacent the pool of liquid reaction product and is returned without external compression to the upper portion of said reaction zone and into contact with the charge stock and contact material therein.

3. The process of claim 1, characterized in that a portion of the normally gaseous reactant is continuously withdrawn from the reaction zone at a point above the pool of liquid reaction product and is discharged from the process and another portion of said normally gaseous reactant is continuously withdrawn from the reaction zone at a point below the contact material therein and above the pool of liquid reaction product and is returned without external compression to the

upper portion of the reaction zone at a point above the contact material therein.

4. The process of claim 1, characterized in that a stream of the normally gaseous reactant is withdrawn from the reaction zone at a point above and adjacent the pool of liquid reaction product, a minor portion of said stream thus withdrawn is discharged from the process, and the remaining larger portion of said stream is continuously returned without external compression to the upper portion of said reaction zone and into contact with the contact material therein.

5. The process of any one of the claims 1 to 4 characterized in that it is applied to the reaction of a hydrocarbon material as charge stock with a gaseous reactant comprising hydrogen at elevated temperature and superatmospheric pressure in the presence of a catalytic solid contact material promoting the reaction of said hydrocarbon material with hydrogen.

6. The process of claim 5, characterized in that the hydrocarbon material is introduced in the liquid state into the reaction zone and the reaction is effected at a pressure at which substantial vaporization of said hydrocarbon material is prevented.

7. The process of claim 5, characterized in that a normally liquid hydrocarbon material is introduced in the vaporous state into the reaction zone, and the hydrogenated normally liquid product is condensed in the lower portion of the reaction zone.

8. A reactor suitable for use in effecting the process of any of the claims 1 to 7, which comprises in combination a vertically arranged chamber, supporting means for a mass of solid contact material in the upper portion thereof, an indirect heat exchange means disposed below and spaced from said supporting means and occupying a substantially smaller space than the space provided for said mass of solid contact material in said upper portion of the chamber, an inlet conduit connecting with the upper portion of said chamber, a liquid collector section in the lower portion of the chamber below said indirect heat exchange means, a liquid discharge conduit extending from said liquid-collector section, and a gas withdrawal conduit connecting with the chamber at a point above

said liquid collector section.

9. Apparatus as claimed in claim 8, characterized by a gas recirculation conduit having one end thereof in open communication with the chamber between the collector section and the heat exchange means and having its other end in open communication with the chamber at a point above the heat exchange means, said gas recirculation conduit being preferably provided with a valve for controlling the flow of gas therethrough.

10. A reactor as claimed in claim 8, characterized by an elongated vertically disposed chamber having an enlarged cross-sectional area upper portion and a smaller cross-sectional area lower portion, perforate supporting means for a mass of solid contact material in the upper portion of said chamber, and an indirect heat exchange means disposed in said smaller cross-sectional area lower portion of the chamber below said perforate supporting means.

11. A reactor as claimed in one of the claims 8 to 10, characterized by a gas recirculation conduit having one end connected to the chamber between the collector section and the heat exchange means and having its other end connected to the chamber at a point above the solid contact material therein.

12. A reactor as claimed in claim 11, characterized in that a gas discharge conduit is connected to the gas recirculation conduit at a point between the lower end of the latter and a flow control valve in said gas recirculation conduit.

13. A reactor as claimed in claim 8 or 10, characterized by a second inlet conduit connecting to said chamber between the supporting means and the heat exchange means.

14. The process for effecting reactions of flowing reactants in the presence of solid contact material substantially as described with reference to the attached drawings.

15. The apparatus for effecting reactions of flowing reactants in the presence of solid contact material substantially as described with reference to the attached drawings.

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