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(54) HYDROCARBON SYNTHESIS

(54) SYNTHESE D'HYDROCARBURE

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|----------------------------|-------------------------------|
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The present invention relates to the synthesis of hydrocarbons by the catalytic reduction of carbon oxide with hydrogen and is more particularly concerned with the reactivation or regeneration of the catalyst used in the synthesis reaction and the upgrading of liquid hydrocarbons produced by the synthesis reaction.

In vapor phase processes for the production of hydrocarbons by the reaction of gaseous mixtures containing hydrogen and carbon monoxide in the presence of a catalyst, the reaction tends to deposit on the catalyst high-boiling reaction products or like carbonaceous material which progressively blocks the active surface of the catalyst and thus impairs the process. It is therefore usually necessary either continuously or periodically to revivify the catalyst.

Frequently, the revivifying reagents proposed are not economically available or have a detrimental effect upon the catalyst. It has been proposed to treat the synthesis catalyst with solvents of various types, but this is usually insufficient since some of the carbonaceous deposit is not removed and, in any case, catalyst poisons like sulfur compounds are not eliminated by such solvents.

In addition, when operating with a fluidized catalyst bed where the catalyst is in the form of a powder maintained in a turbulent state resembling a boiling liquid by the upflowing reactant gases, it is necessary to provide separating means in order to remove entrained catalyst particles from the gaseous reaction products. The separating equipment usually takes the form of filters, cyclones, electrostatic or magnetic separators or scrubbing means. The reaction gases almost invariably leave the synthesis zone

with at least small proportions of unreacted carbon monoxide and hydrogen present therein. If these gases are passed through a filter or cyclone separator to remove the entrained catalyst particles, the exothermic synthesis reaction tends to continue during the separation process so that run-away temperatures may ensue with deleterious effects on the reaction products and/or catalyst. If the gases are subjected to scrubbing to eliminate the entrained catalyst particles, expense is encountered in removing the scrubbing liquid from the catalyst and in drying the catalyst prior to the conventional regeneration process which involves treatment of the dry catalyst with a stream of hydrogen.

It is accordingly an object of the present invention to provide a catalytic synthesis process involving fluidization, wherein the entrained particles of catalyst are removed from the gaseous reaction products by scrubbing the gaseous stream with liquid hydrocarbons produced by the synthesis reaction to form a slurry or suspension of the catalyst in which form the revivification of the catalyst is advantageously carried out.

A further object of the invention is to provide a process wherein the catalyst revivification is carried out with a hydrogen-rich tail gas from the synthesis step so that the preparation of a special gas for revivification is accordingly obviated with corresponding economic advantages.

Other objects of this invention contemplate the operation of the scrubbing and revivification system in conjunction with a hydrocarbon fraction produced in the synthesis process; improvement in the quality of the hydrocarbon fraction by the action of the revivifying gas in the presence of

the catalyst; and the provision of a system for recovering catalyst escaping from the synthesis zone and for returning this catalyst after regeneration to the synthesis zone, which system is simple to operate because it involves handling the catalyst in the form of a liquid suspension.

In accordance with the present invention, the catalyst from the synthesis reaction zone is preferably continuously scrubbed from the entraining gaseous reaction products with a liquid hydrocarbon stream derived from the reaction products and the resulting slurry is treated with a hydrogen-rich gas under conditions to revivify the catalyst which is then returned to the synthesis reaction zone. It is advantageous to inject the revivified catalyst into the reaction zone while still suspended in the liquid hydrocarbon stream.

Generally, therefore, synthesis gas is passed in contact with a fluidized powdered catalyst at such a rate of flow that any desired proportion of the catalyst powder is swept outwardly with the reaction gases and passed in scrubbing relation with a liquid hydrocarbon fraction recovered from the synthesized products. The scrubbing liquid which now contains at least partially spent synthesis catalyst is directed to a catalyst revivification zone where the suspension is treated with hydrogen-rich gas. Simultaneously, under some conditions, the hydrogen acts in the presence of the suspended catalyst to hydrogenate and upgrade the liquid hydrocarbon fraction. Thus, for instance, where the synthesis reaction products contain an appreciable light oil fraction, this oil fraction may be utilized in accordance with this invention to remove the spent or partially spent catalyst particles from the suspending reaction gases and to facilitate regeneration of the catalyst

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while at the same time itself undergoing hydrogenation to yield a diesel oil of improved cetane number. This form of operation yielding a diesel oil of desirable quality is a preferred embodiment of the invention. All or part of the suspending liquid hydrocarbon may be returned with the  
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revivified catalyst to the synthesis reaction zone but it is generally desirable to withdraw part of the upgraded scrubbing liquid as a product stream. It is doubly advantageous to return revivified catalyst to the synthesis zone as a liquid  
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suspension because the controlled feeding of catalyst to the synthesis zone is thereby facilitated and the liquid entering the synthesis zone provides through flash evaporation a simple but effective means for cooling the highly exothermic synthesis reaction.

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The invention is of particular advantage in that the hydrogen-rich gas used for catalyst revivification may be a tail gas from the synthesis operation. As is known, most synthesis operations are carried out with a fresh feed gas containing about 1.5 to 3.5 mols of hydrogen for each mol of  
20  
carbon monoxide present in the fresh feed. As already mentioned, in practical operations, the gaseous reaction products are withdrawn from the synthesis zone while they still contain at least small proportions of the gaseous reactants. For example, in U. S. patent 2,629,729 it is disclosed that  
25  
there is considerable advantage in discharging from the synthesis zone the reaction gases when they contain about 1% to 3% by volume of carbon monoxide. In all cases where the synthesis reaction effluent contains unreacted hydrogen and carbon monoxide it is observed that

the carbon monoxide was consumed during the synthesis reaction in relatively greater proportions than the hydrogen with the result that after the various reaction products have been recovered from the reaction effluent there remains a tail gas containing chiefly hydrogen, carbon monoxide and dioxide, normally gaseous hydrocarbons, principally methane, and nitrogen. In general, the molar ratio of hydrogen to carbon monoxide in the tail gas is at least 9 and frequently at least 12. Such a tail gas is suitable as the revivifying gas in the process of this invention, tail gas with a hydrogen-to-carbon monoxide ratio of at least 12 being preferred. Since an appreciable quantity of carbon dioxide may produce interfering effects during the regeneration of the synthesis catalyst, it is advisable to maintain the content of carbon dioxide in the tail gas low enough so that the molar ratio of hydrogen to carbon dioxide is at least about 10. Where the tail gas contains an excess of carbon dioxide, the undesired carbon dioxide is readily and economically separated out by any of several known methods including the use of solid adsorbents or scrubbing with aqueous caustic soda or even with plain water.

In order to describe the invention more specifically, reference is now had to the attached drawing which forms a part of this specification and diagrammatically exemplifies one embodiment of the invention.

The synthesis reactor 10 is in the general form of a cylindrical vessel and holds a fluidized mass of powdered catalyst 11. The catalyst may comprise any of the known so-called Fischer catalysts, for example, metals of the iron group or ruthenium; iron catalysts are preferred. The

catalyst in finely divided form is maintained in a state of dense phase fluidization by a stream of synthesis gas introduced at the bottom of reactor 10 through conduit 12.

5 The mass of catalyst extending to the upper pseudo-liquid level 11A preferably surrounds a heat exchanger 13 for dissipating exothermic energy of the synthesis reaction. The exchanger 13 may take any conventional form, for example, a plurality of tubes joined by inlet and outlet headers 14 and 15, respectively, is preferably of streamlined configuration  
10 to prevent the incidence of dead spots in the fluidized catalyst mass. The heat exchanger is supplied with a suitable coolant, such as water or Dowtherm.

The synthesis gas having contacted the mass of catalyst 11 under reaction temperature and pressure for the  
15 required contact time emerges as a gaseous reaction effluent from the reactor 10 carrying partially spent catalyst particles by entrainment. The gaseous effluent and suspended catalyst particles are conducted through outlet pipe 16 to a scrubbing chamber 17 where the gases move upwardly countercurrent to  
20 a stream of liquefied reaction products introduced through pipe 18 and withdrawn through outlet pipe 19. The scrubbing tower 17 is provided with a multiplicity of vertically spaced, inclined, overlapping baffles to ensure that the entrained catalyst particles are removed from the gaseous stream and  
25 carried downwardly with the scrubbing liquid. The catalyst slurry or suspension draining from the bottom of the chamber 17 through line 19 is recirculated in part by pump 20 through branch pipe 21 back to pipe 18 to make the removal of catalyst powder from the reaction gases continuous.

A cooler 22 is provided in line 21 so that the scrubbing liquid may be sufficiently cooled to induce condensation of some of the reaction products in the gaseous effluent which is scrubbed with the cooled liquid. The reaction products which are thus liquefied compensate for the portion of the scrubbing liquid which is not recycled by pump 20 to the top of chamber 17. The scrubbed and catalyst-free reaction gases leave chamber 17 through pipe 24.

Part of the catalyst slurry draining into line 19 is forced by pump 23 into the catalyst regenerating chamber 27. The catalyst slurry or suspension flows downwardly over a suitable packing or interior arrangement of baffles or trays to promote good contact with an upward flow of hydrogen-rich gas introduced at the distributing head 28 in the lower portion of vessel 27. Distributing head 28 is supplied by pipe 29. Regenerator 27 is usually provided with a jacket 27A or heat transfer tubes for the passage therethrough of a heat transfer medium to maintain the desired regeneration temperature.

The liquid carrying the regenerated catalyst particles flows down into outlet pipe 30 and thence is discharged through valved branch pipes 33 leading to the interior of the reaction chamber 10. A cooler 32 in pipe 30 serves to lower the temperature of the catalyst slurry passing to the reactor 10 and thus permits control of the amount of cooling to be effected in reactor 10 by means of the flashing liquid. Part of the liquid passing through regenerator 27 may be discharged as product through valved branch pipe 31, the catalyst particles being separated from the liquid which is withdrawn as product.



In short, the entrained catalyst powder is scrubbed out of the gaseous reaction stream leaving the synthesis reactor by some of the liquid products made in the reactor and the resulting slurry is treated with hydrogen at elevated temperature and pressure, and the treated slurry is returned to the fluidized mass in the synthesis reactor where the suspended liquid reaction products are revolatilized and absorb some of the reaction heat thus facilitating close control of the reaction temperature.

The catalyst slurry flowing from hydrogenation vessel 27 into pipe 30 is inherently recycled at least in part to vessel 27 because the hydrogenated or improved oil and catalyst removed from vessel 27 via pipe 30 and introduced as a slurry via pipes 33 into synthesis reactor 10 eventually leave reactor 10 via outlet pipe 16, are caught in scrubber 17 and are returned by pipe 19 and pump 23 to hydrogenation vessel 27. Catalyst-oil slurry issuing from vessel 27 may be recycled directly to vessel 27 via valved pipe 45 discharging into pipe 19 on the inlet side of pump 23.

The gaseous reaction effluent which has been scrubbed of entrained catalyst particles by the liquid reaction products flowing down over the baffles in scrubber 17 passes through pipe 24 to the products recovery and separation plant 25. Plant 25 conventionally separates the reaction effluent into an oil fraction issuing from pipe 35, a gasoline fraction from pipe 36, reaction water and water-soluble oxygenated hydrocarbons from pipe 37, carbon dioxide and like undesirable gases from pipe 38, and from pipe 39 a hydrogen-rich gas usually containing some normally gaseous hydrocarbons and carbon monoxide in addition to hydrogen.

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Part of the hydrogen-rich gas leaving by way of pipe 39 is conveyed by compressor 40 and pipe 29 to the catalyst regenerator 27.

5           The reaction gases discharging from the top of regenerator 27 pass through pipe 41 to recovery plant 25 wherein hydrocarbon vapors may be separated from these gases. Alternatively, the reaction gases may flow through valved branch pipe 42 to any desired treatment or utilization plant.

10           Depending upon the character of the oil fraction issuing at pipe 35, it may be desirable to treat part or all of this oil in regenerator 27 to effect its upgrading through hydrogenation. In such case, the oil is forced by pump 43 through pipe 44 and pipe 18 into scrubber 17. The oil and catalyst slurry reaching outlet pipe 19 may not require  
15           recycling to the top of scrubber 17 through pipe 21 (pump 20 being stopped) but, in any event, will enter regenerator 27 where simultaneously the suspended catalyst is revived and the oil is upgraded. Where oil from pipe 35 is pumped to scrubber 17 and regenerator 27, an upgraded oil product is  
20           withdrawn from valved branch pipe 31. Catalyst particles are strained or otherwise separated from the oil withdrawn at pipe 31. Catalyst particles separated from the oil withdrawn via pipe 31 may be added to the slurry flowing through pipe  
25           45 or pipes 33. This will give a catalyst slurry for recycling purposes which is heavier than the slurry issuing from hydrogenation vessel 27. It is evident that the proportions of catalyst and hydrogenated oil which are recycled may be changed at will.

30           The temperature and pressure maintained in the synthesis zone will vary, as is known, with the selected

catalyst and the type of hydrocarbons desired as product. In general, the synthesis temperature will fall in the range of about 350° to 750°F., preferably about 550°F. to 700°F., while the pressure will range up to about 500 lbs. per square inch gage. With the preferred iron catalysts, it is advisable to operate the synthesis reactor at a temperature of about 600° to 675°F. and a pressure of about 200 to 500 lbs. per square inch gage.

In contrast to the vapor phase operation of the synthesis zone, the catalyst regenerator is made to function on a liquid phase which is assured by the control of the pressure and temperature maintained in the regenerator. The pressure of the regenerator should be at least 200 lbs. per square inch higher than that of the synthesis reactor. Pressures in the range of about 500 to 1000 lbs. per square inch gage are generally desirable for the catalyst revivifier. Regeneration of the catalyst and simultaneous upgrading of liquid hydrocarbons used as suspending medium are usually effected at temperatures in the range of about 500° to 900°F.

As a specific example of the embodiment of the invention represented by the drawing, an installation designed to produce approximately 8,000 barrels per day of liquid hydrocarbons (C<sub>3</sub> and higher hydrocarbons) will be considered. In this case, the reactor 10 contains a fluidized mass 11 of catalytic iron powder of 40 mesh and finer, about 40% passing through a 100-mesh screen. Synthesis gas containing hydrogen and carbon monoxide in the ratio of 2.7 mols of hydrogen per mol of carbon monoxide is passed upwardly through fluidized catalyst mass 11 at a linear velocity of 1 foot per second, reactor 10 being maintained at a gauge pressure of 400 pounds

per square inch and a temperature of 650°F. Pseudo-liquid level 11A is 20 feet above feed gas conduit 12.

5 The gaseous reaction effluent leaving reactor 10 by way of line 16 carries in suspension entrained catalyst particles at the rate of 0.003 pound of catalyst per cubic foot of gaseous effluent. While the plant is designed to produce approximately 8,000 barrels per day of liquid hydrocarbons, principally boiling in the boiling range of gasoline, 13% of this liquid is in the form of diesel oil and heavier  
10 oil fractions. In passing through scrubbing tower 17, the gaseous reaction effluent from reactor 10 is cooled so that part of the heavy oil fractions of the liquid hydrocarbons produced in reactor 10 are liquefied and partly recycled to the top of tower 17 by pump 20 and line 21 and partly introduced by pump 23 into catalyst regenerating chamber 27.  
15 The heavy oil fractions which are condensed in scrubbing tower 17 correspond in quantity to 4% of the total liquid products synthesized in reactor 10 plus the quantity of liquid injected into reactor 10 through branch pipes 33. The temperature control necessary for effecting condensation of the  
20 heavy oil fractions in the reaction effluent passing through tower 17 is afforded by passing the recirculated oil through cooler 22 before it is reintroduced into the top of tower 17. The oil flowing down through tower 17 countercurrently to the reaction effluent containing entrained catalyst  
25 particles scrubs the effluent so that it passes through line 24, free of suspended catalyst particles, to recovery plant 25. The resulting catalyst-in-oil slurry, which eventually is conveyed by line 19 and pump 23 into regenerating chamber 27, is therein subjected to countercurrent flow contact with  
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a hydrogen-rich gas introduced at the distribution head 28. Chamber 27 is maintained at a gauge pressure of 750 pounds per square inch and a temperature of 700°F. The hydrogen-rich gas supplied by line 29 is a tail gas recovered from the reaction effluent and contains hydrogen and carbon monoxide in the ratio of 15 mols of hydrogen per mol of carbon monoxide; the carbon dioxide normally present in this tail gas is largely eliminated by conventional absorption so that the tail gas introduced into regenerator 27 has at least 12 mols of hydrogen per mol of carbon dioxide. The hydrogen-rich gas is charged into regenerator 27 at a rate to maintain a hydrogen partial pressure of 150 pounds per square inch. Under these conditions, the synthesis catalyst is maintained in a state of high activity and the cetane rating of the oil which is condensed in tower 17 is raised from a value of 45 to 60. Of the liquid which is condensed in scrubbing tower 17 and is upgraded by treatment in regenerator 27, a portion corresponding to 4% of the total liquid products synthesized in reactor 10 is recovered by condensation and separation from the gaseous stream discharging from line 41 and by withdrawal through valved line 31. Treated oil withdrawn by way of line 31 is strained to remove suspended catalyst particles.

The remaining portion of treated catalyst-in-oil slurry passes through line 30 and cooler 32 which lowers the temperature of the slurry to 600°F. and then discharges through branch pipes 33 into reaction chamber 10. Thus, the catalyst particles inevitably carried out of reactor 10 by entrainment in the gaseous reaction effluent have been recovered by scrubbing the effluent with oil separated from the liquid synthesis products, have been revived and

5 returned to reactor 10 along with the scrubbing oil which  
has been upgraded by treatment with hydrogen and which upon  
introduction into reactor 10 vaporizes to afford cooling of  
the exothermic synthesis reaction as well as compensation of  
the volumetric contraction arising from the reaction of the  
gaseous reactants introduced by way of conduit 12. The com-  
pensation of the volumetric contraction of the reactants  
provided by the injected oil slurry is highly desirable in  
maintaining uniform fluidization along the vertical dimension  
10 of reactor 10.

Those skilled in the art will visualize many  
variations of the invention without departing from its spirit  
and intent. Accordingly, the foregoing disclosure should be  
interpreted as being illustrative of the invention and not  
15 restrictive; only such limitations should be imposed as are  
indicated in the appended claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the treatment of hydrocarbon oil with hydrogen in the presence of a hydrogenating catalyst in solid particle form, the steps comprising mixing said catalyst with said oil to form a slurry of catalyst and oil, continuously flowing a stream of said slurry downwardly over packing in a hydrogenation zone maintained under hydrogenating pressure and temperature while countercurrently contacting said slurry flowing over said packing with hydrogen, and withdrawing from said hydrogenation zone the treated stream of said slurry after flowing downwardly over said packing.

2. The treatment of hydrocarbon oil according to claim 1 wherein at least part of the oil and catalyst in the withdrawn slurry is recycled to said hydrogenation zone for flow downwardly over said packing.

3. The treatment of hydrocarbon oil according to claim 2 wherein part of the oil in the withdrawn slurry is separated therefrom for recovery as treated oil product.

4. The treatment of hydrocarbon oil according to claim 1 wherein the hydrogenating pressure is at least about 500 lbs. per square inch gage and the hydrogenating temperature is below 900°F.

5. The treatment of hydrocarbon oil according to claim 1 wherein the hydrocarbon oil boils in the range of diesel and heavier oils.

6. The treatment of hydrocarbon oil according to claim 5 wherein the hydrogenating pressure is in the range

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of about 500-1000 lbs. per square inch gage and the hydrogenating temperature is below 900°F. but not below about 700°F.

7. In the vapor phase process of synthesizing liquid hydrocarbons by passing hydrogen and carbon monoxide into contact with suspended particles of synthesis catalyst in a reaction zone maintained at reaction temperature and pressure, which process involves the discharge from said reaction zone of a gaseous reaction effluent containing entrained particles of said catalyst, the improvement which comprises scrubbing said gaseous effluent with relatively cool liquid hydrocarbons synthesized by said process and recovered from said gaseous effluent thereby forming a slurry of said entrained particles in said scrubbing liquid hydrocarbons, continuously flowing a stream of said slurry downwardly over packing in a hydrogenation zone maintained under hydrogenating pressure and temperature while countercurrently contacting said slurry flowing over said packing with hydrogen-rich gas recovered from said gaseous effluent so as to revivify the catalyst and to hydrogenate the liquid hydrocarbons in said slurry, withdrawing from said hydrogenation zone the treated stream of said slurry after flowing downwardly over said packing, and injecting into said reaction zone at least part of the withdrawn, treated slurry containing revivified catalyst and hydrogenated liquid hydrocarbons.

8. The process of claim 7 wherein the hydrogenating pressure is at least 200 lbs. per square inch higher than the reaction pressure.

9. The process of claim 8 wherein the hydrogenating pressure is not higher than about 1000 lbs. per square inch gage and the hydrogenating temperature is below 900°F.

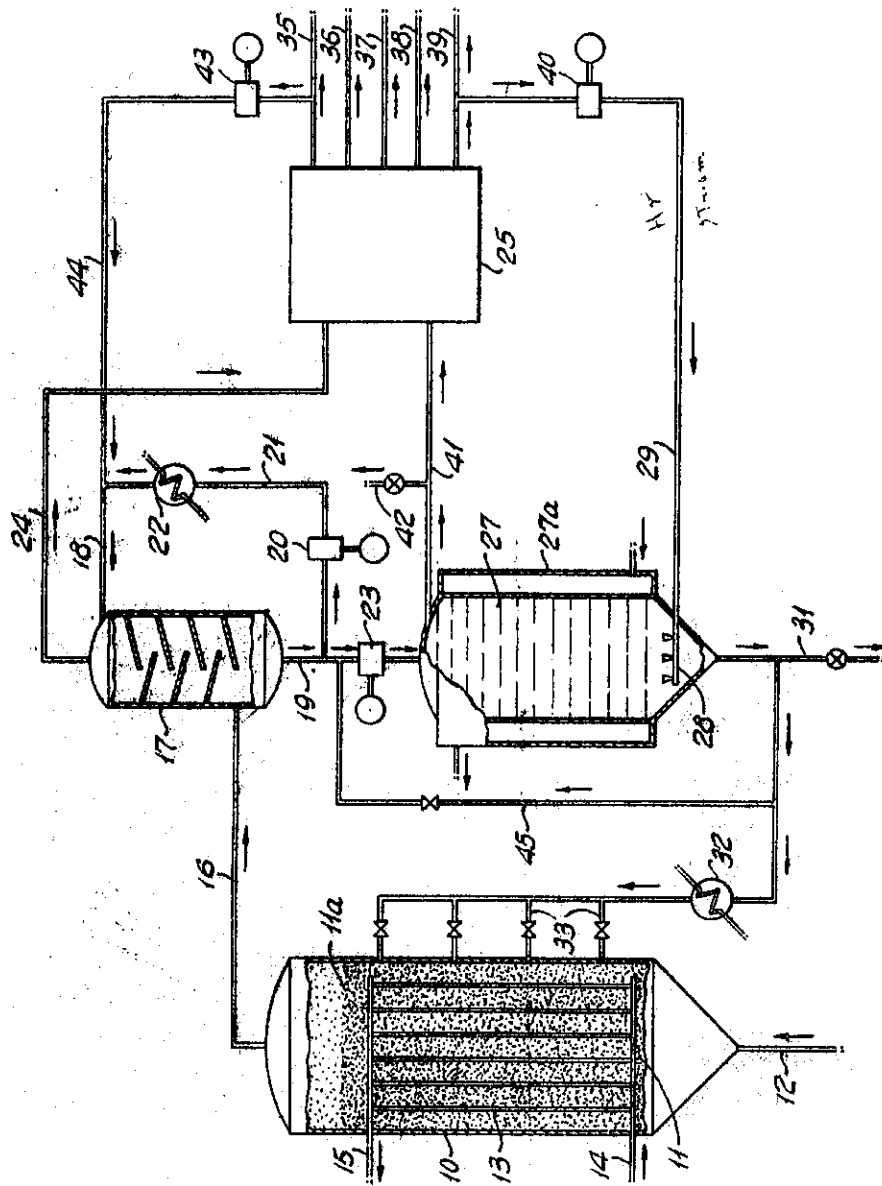


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10. The process of claim 7 wherein the hydrogen-rich gas is supplied to the hydrogenation zone at a rate to maintain therein a hydrogen partial pressure of at least about 150 lbs. per square inch.

11. The process of claim 7 wherein the relatively cool liquid hydrocarbons boil in the range of diesel and heavier oils.

12. The process of claim 7 wherein part of the slurry is recycled for scrubbing the gaseous reaction effluent.



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