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HYDROCONVERSION OF LIGHT AND HEAVY HYDROCARBON FRACTIONS IN SEPARATE REACTION ZONES AND CONTACTING OF THE LIQUID PORTION OF THE HEAVY FRACTION HYDROCONVERSION PRODUCT WITH THE LIGHT FRACTION HYDROCONVERSION PRODUCT

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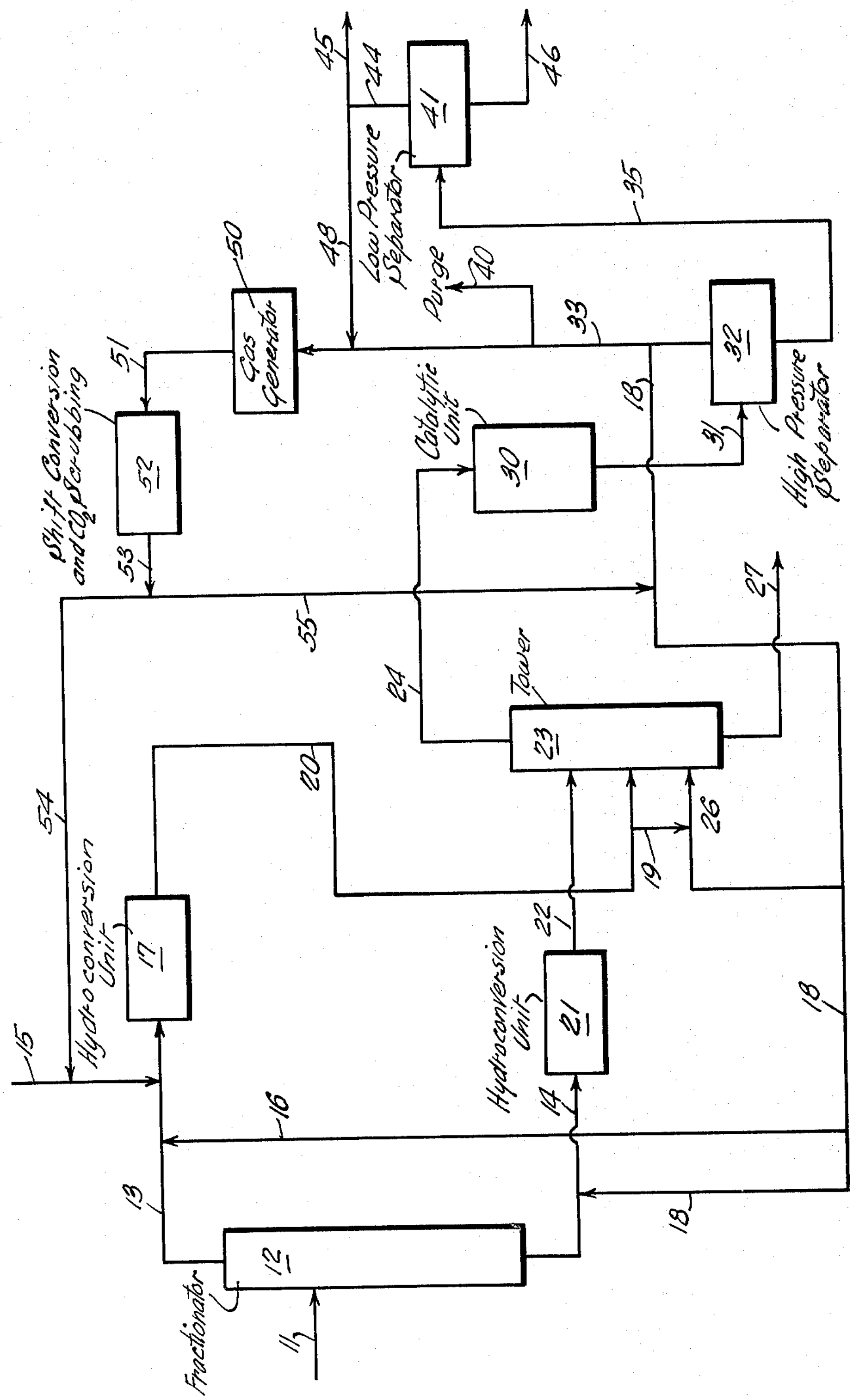

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HYDROCONVERSION OF LIGHT AND HEAVY HYDROCARBON FRACTIONS IN SEPARATE REACTION ZONES AND CONTACTING OF THE LIQUID PORTION OF THE HEAVY FRACTION HYDROCONVERSION PRODUCT WITH THE LIGHT FRACTION HYDROCONVERSION PRODUCT

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This invention relates to the treatment of hydrocarbons. More particularly it is concerned with the conversion of heavy hydrocarbons into light hydrocarbons. In its more specific aspect it pertains to the production of gaseous hydrocarbons suitable for use as LPG and to the production of liquid hydrocarbons suitable for use as fuel for internal combustion engines or for conversion into fuel for internal combustion engines.

The hydrocarbon liquids use in the process of this invention generally have a wide boiling range and may include materials ranging from naphtha through kerosene, gas oil, tar and asphalt. Suitable starting materials include the various whole crudes such as Arabian crude and, depending on the type of products desired, topped crude. If it is desired to produce large amounts of gaseous hydrocarbons, the feed ordinarily will include naphtha. If it is desired to produce large amounts of motor fuel, the feed will be composed primarily of hydrocarbons boiling above the naphtha range. Generally, there is no upper limit on the boiling range of the feed stock.

In the first step of the process the feed stock is fractionated into a light fraction and a heavy fraction. Ordinarily the separation will be made between about 300 and 650° F. The actual cut point will be determined to a large extent by the particular feed stock and the amount of different products desired. The process is flexible and can be made to produce maximum yields of different products such as LPG or motor fuel or middle distillates by varying the cut point and the operating conditions. For example, for a high yield of LPG a high cut point such as 400–500° F. would be used whereas for a high yield of aromatics a low cut point such as about 280° F. would be used.

The overhead from the initial fractionator or as referred to previously the light fraction is combined with hydrogen in an amount between 1,000 and 100,000 standard cu. feet per barrel (s.c.f.b.), heated to a temperature between 800 and 1,500° F. and subjected to hydroconversion by being passed through a first tubular reaction zone under conditions of highly turbulent flow. Residence time in the zone will range from two seconds to two hours. Generally the turbulence level or the ratio of the average apparent viscosity to the molecular or kinematic viscosity should be at least 25. Preferably the hydroconversion of the light fraction is carried out at a temperature between 850 and 1,100° F., a pressure between 1,000 and 10,000 p.s.i.g. and a turbulence level of at least 50. Hydrogen rates of 2,000 to 20,000 s.c.f.b. and residence times of 5 to 200 seconds are also preferred.

The bottoms from the initial fractionator or heavy fraction as mentioned above is also mixed with hydrogen in an amount between 1,000 and 100,000 s.c.f.b. and the mixture subjected to hydroconversion conditions by being passed through a second tubular reaction zone under conditions of highly turbulent flow at a temperature between 750 and 950° F. and a pressure between 500 and 20,000 p.s.i.g. Residence time in the second tubular reaction zone ranges from two seconds to one hour and the turbulence level is at least 25 and generally is in excess of 50.

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Preferably the temperature is maintained between 800 and 925° F. and the pressure between 1,000 and 10,000 p.s.i.g. Residence times of 5 to 100 seconds, hydrogen rates of 2,000 to 40,000 s.c.f.b. and turbulence levels of at least 100 are also preferred. Advantageously the pressure in the first tubular reaction zone is substantially the same as the pressure in the second tubular reaction zone.

Effluent from the second tubular reaction zone comprising a mixture of hydrogen, vaporous hydrocarbons and liquid hydrocarbons, the last being in the form of mist-like droplets suspended in the gas phase, is then separated into a gaseous portion and liquid portion. This is accomplished by passing the effluent into the upper section of a tower where, as a result of a reduction in the velocity of the effluent, the suspended liquid settles from the gaseous stream.

The disengaged liquid is then contacted with the effluent from the first tubular reactor. Advantageously, the effluent from the first tubular reactor which is composed of unreacted hydrogen, gaseous and vaporous hydrocarbons is introduced into the intermediate section of the tower and is brought into countercurrent contact with the disengaged liquid as the latter descends through the tower. During this contacting some dissolved and entrained vaporous hydrocarbons are removed from the descending liquid and transferred to the upwardly flowing gaseous stream.

The descending liquid is then further contacted with a gas rich in hydrogen, usually recycle hydrogen, which results in removal of most of the remaining entrained and dissolved vaporous hydrocarbons from the descending liquid. Some additional hydrogenation takes place during this contacting as is evident from a slight increase in temperature as the liquid descends through the tower. The contacting tower is operated at a pressure substantially identical with the pressure of the first and second tubular reaction zones. Also, if desired, either or both streams from the first and second tubular reaction zones may be subjected to heating or cooling before being introduced into the tower.

The gaseous portion of the effluent from the second tubular reactor, the effluent from the first tubular reactor containing vaporous hydrocarbons removed from the descending liquid and the hydrogen rich gas containing additional vaporous hydrocarbons removed from the descending liquid are combined and the combined stream is contacted with a hydrogenation catalyst under hydrogenation conditions. Advantageously the combined stream is cooled prior to contact with the catalyst to a suitable temperature. Oridinarily the stream will be cooled to a temperature between about 600 and 900° F. In the catalytic hydrogenation zone unsaturated hydrocarbons are converted to more saturated hydrocarbons. Other reactions taking place in the hydrogenation zone are the conversion of organic sulfur to H_2S and the conversion of organic nitrogen to NH_3.

Suitable hydrogenation catalysts include the oxides and/or sulfides of cobalt, nickel, or molybdenum used alone or in combination with each other or with other compounds such a s sulfides or oxides of tungsten. The catalysts may be used per se or may be supported on a base such as silica, alumina, magnesia, or mixtures thereof.

The amount of catalyst in the hydrogenation zone is sufficient to provide a space velocity of between 0.1 and 10 volumes of normally liquid hydrocarbon per hour per volume of catalyst in the catalyst bed. Preferably the amount of catalyst will provide a space velocity of between 0.75 and 3 v./v./hr. Hydrogen rates, as will be obvious to those skilled in the art, are considerably higher than customarily used in a catalytic hydrogenation zone and under preferred conditions range upwards from

5,000 cubic feet per barrel of liquid hydrocarbon liquid introduced into the initial fractionation zone.

The catalytic hydrogenation product is then cooled rapidly and sent to a high pressure separator maintained at substantially the same pressure as the catalytic hydrogenation zone. From the high pressure separator a gas rich in hydrogen is removed overhead. The composition of this gas will depend to a large extent on the temperature. Desirably, the product from the catalytic reaction zone is cooled to a temperature sufficient to provide a gas having a hydrogen concentration between 60 and 70 percent. Normally this can be accomplished by cooling the effluent from the catalytic hydrogenation zone to a temperature between about 100 and 200° F. The overhead from the high pressure separator may be recycled to the tubular reaction zones. Ordinarily the bulk of this hydrogen rich overhead gas in introduced into the contacting tower and lesser amounts are returned to the tubular reaction zones.

When the hydroconversion conditions are severe or when the high pressure separator is maintained at a temperature or a pressure which does not provide a gas having a satisfactory hydrogen concentration for the various hydrogenation reactions, a portion or all of the hydrogen rich overhead gas from the high pressure separator may be sent to a gas generation zone in which the hydrocarbons present in the hydrogen rich gas are subjected to partial combustion to produce a synthesis gas composed for the most part of hydrogen and carbon monoxide. This gas is converted by a water gas shift conversion followed by CO_2 removal in a manner well-known in the art to produce a gas consisting essentially of pure hydrogen. This latter gas may then be recycled to the tubular reaction zones and the contact zone or when only a portion of the overhead from the high pressure separator is subjected to combustion, may be used as make-up hydrogen and introduced as fresh hydrogen to the first tubular reactor.

The hydrogen concentration of the overhead from the high pressure separator may be increased by recycling a portion of the product liquid obtained from the high pressure separator or the low pressure separator described below to either the inlet to the catalytic unit or the inlet to the high pressure separator. The increased ratio of liquid to gas resulting from this operation causes the dissolution of more of the light hydrocarbons in the liquid leaving the bottom of the high pressure separator with a resulting higher purity recycle hydrogen stream being obtained overhead from the high pressure separator.

It is also possible to obtain higher purity recycle hydrogen by an autorefrigeration technique which involves rapidly expanding at least a portion of the bottoms from the high pressure separator and passing the expanded product into indirect heat exchange with the feed to the high pressure separator.

The recycle hydrogen may be also purified by contacting same with a molecular sieve having a uniform cell structure with 4 Angstrom unit openings. This treatment results in the adsorption of the hydrocarbons whereas the hydrogen present in the recycle stream pass through the unit. Subsequent desorption of the unit removes the adsorbed hydrocarbons and eventually restores the sieve to its initial capacity.

Bottoms from the high pressure separator are then transferred to a low pressure separator where the product is separated into an overhead fraction suitable for use as fuel gas or the production of LPG and a bottom fraction which contains hydrocarbons suitable for use as a motor fuel or suitable for conversion into a motor fuel. If desired, a portion of the overhead from the low pressure separator may be used in conjunction with the overhead from the high pressure separator as feed for the gas generator.

Reference is now made to the accompanying drawing which illustrates diagrammatically a flow scheme for the practice of the invention and in connection with which the following example is given:

Arabian crude is introduced into the system through line 11 and passes into crude fractionator 12 where it is separated into a light fraction having an end point of 560° F. removed overhead through line 13 and a heavy fraction having an IBP of 560° F. removed through line 14. By making the separation at 560° F. in this example, the light fraction is substantially equal in volume to the heavy fraction. Fresh hydrogen at the rate of 2000 standard cubic feet per barrel of overhead and recycle hydrogen also at the rate of 2,000 standard cubic feet per barrel of overhead are introduced into the overhead stream through lines 15 and 16 respectively and the combined stream introduced into hydroconversion unit 17 through which it is passed under conditions of highly turbulent flow at a temperature of 1,000° F., a pressure of 1200 p.s.i.g. and for a residence time of 15 seconds. Effluent from the hydroconversion unit 17 is removed therefrom through line 20. The effluent amounts to 4,200 standard cubic feet per barrel of light fraction.

The heavy fraction withdrawn from fractionator 12 through line 14 is mixed with recycle hydrogen from line 18 at the rate of 5,000 s.c.f. per barrel of heavy fraction and the mixture is introduced into hydroconversion unit 21 at a temperature of 925° F. and a pressure of 1,200 p.s.i.g. The mixture of hydrogen and hydrocarbons from line 14 passes through hydroconversion unit 21 under conditions of highly turbulent flow. The residence time is 30 seconds. Effluent from the hydroconversion unit 21 then passes through line 22 to the upper disengaging section of tower 23. The effluent is in the form of a gaseous phase containing suspended mist-like droplets of liquid phase.

In the upper section of tower 23 the liquid phase of the effluent from hydroconversion unit 21 is disengaged from the gaseous phase which passes overhead through line 24. The disengaged liquid portion of the effluent because of the reduced velocity of the stream settles downwardly through tower 23. In so doing the liquid phase countercurrently contacts first the effluent from hydroconversion unit 17 introduced into the intermediate section of tower 23 through line 20. This countercurrent contacting serves to remove from the descending stream entrained and dissolved lighter hydrocarbonaceous material. In its further descent through the tower the residual liquid is then countercurrently contacted with a stream of recycle hydrogen introduced into the lower section of tower 23 through line 26 at a rate of 6,800 s.c.f. per barrel of feed to hydroconversion unit 21. This contacting serves to remove residual entrained or dissolved gaseous hydrocarbonaceous material from the descending liquid. The remaining liquid is withdrawn as heavy oil from tower 23 through line 27.

Overhead from tower 23 comprising hydrogen and the gaseous products from hydroconversion units 17 and 21 passes through line 24 to catalytic unit 30 which contains a cobaltmolybdenum-alumina catalyst. Catalytic unit 30 is maintained at a temperature of 775–800° F. and the reactant stream is passed through the unit at the normal pressure of the system and at a space velocity of 1–2 volumes of original Arabian crude feed per volume of catalyst per hour. The reactant stream is then transferred through line 31 to high pressure separator 32 from which a gas containing 67% hydrogen is removed through line 33. 6,900 cubic feet of this gas per barrel of original Arabian crude feed is recycled to the system through line 18 and the balance is removed through line 40. Bottoms from high pressure separator 32 is transferred through line 35 to low pressure separator 41 from which normally gaseous hydrocarbons are removed through lines 44 and 45 and normally liquid hydrocarbons are removed through line 46. The C_4 and lighter hydrocarbon stream produced in a yield of

23.13 wt. percent basis crude feed has a heating value of 2258 B.t.u./ft.³ and has the following composition:

	Mol percent
H_2	4.53
CO	.70
A	.12
CH_4	7.43
C_2H_6	21.03
C_3H_8	40.39
iso-C_4H_{10}	8.76
n-C_4H_{10}	14.54
H_2S	2.50

The debutanized liquid hydrocarbon stream has the following composition:

Component:	Wt. percent
iso-C_5	1.55
n-C_5	5.56
C_6+	92.89
Gravity °API	41.6
Wt. percent basis crude	41.88

Fresh hydrogen may be obtained from any satisfactory source and may be introduced into the system through line **15**. Advantageously, however, the fresh hydrogen may be obtained from the gaseous material which is normally removed from the system. This can be done by introducing excess recycle gas containing approximately 67% hydrogen from line **33** into gas generator **50** where the light hydrocarbons contained therein are subjected to partial combustion with a free oxygen containing gas to produce a gas composed of carbon monoxide and hydrogen with minor amounts of CO_2. The partial combustion product gas is sent through line **51** to shift conversion and CO_2 scrubbing zone **52** where the gas is contacted with an iron oxide shift conversion catalyst at a temperature of about 700° F. in the presence of about 4 to 5 parts of steam per part of carbon monoxide. The gas produced by the shift conversion is then scrubbed for the removal of CO_2 and the resulting gas, which is approximately 98% hydrogen, is sent to hydroconversion unit **17** through lines **53**, **54**, **15** and **13**.

It is also possible to increase the purity of the recycle hydrogen by sending all of the overhead from the high pressure separator to gas generator **50** and then sending the partial combustion reaction product through line **51** to shift conversion and CO_2 scrubber zone **52**. A portion of the hydrogen so produced is sent to tower **23** through line **53**, **55**, **18** and **26** and another portion is sent to hydroconversion unit **21** through lines **53**, **55**, **18** and **14**. In this case, essentially pure hydrogen would be used in each of the reactors. However, in most instances satisfactory operation is obtained by recycling a gas containing from 60 to 85% hydrogen.

It is also possible to direct some or all of the light hydrocarbons from line **44** through lines **48** and **33** to gas generator **50**. The hydrogen so produced may be used in the system for hydrogenation, may be used to reduce the heating value of the gas withdrawn through line **45**, or may be removed from the system for external use.

In another embodiment of the invention effluent from hydroconversion unit **17** may be passed through lines **20** and **19** and introduced with the recycle hydrogen through line **26** into the lower portion of the tower. The combined stream is passed in countercurrent flow with the disengaged liquid reactant stream descending through the tower **23**.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the conversion of a wide boiling range hydrocarbon liquid into lighter hydrocarbons which comprises fractionating said hydrocarbon liquid into a light fraction having an end boiling point between about 300 and 650° F. and a heavy fraction having an initial boiling point between about 300 and 650° F., passing said light fraction through a first tubular reaction zone at a temperature between about 800 and 1,500° F. and a pressure between about 500 and 20,000 p.s.i.g. in the presence of added hydrogen under conditions of turbulent flow to produce a first effluent comprising hydrogen and vaporous hydrocarbons, passing said heavy fraction through a second tubular reaction zone at a temperature between about 700 and 950° F. and a pressure between about 500 and 20,000 p.s.i.g. in the presence of added hydrogen under conditions of turbulent flow, removing from the second tubular reaction zone a second effluent comprising hydrogen, vaporous hydrocarbons and non-vaporous hydrocarbons, separating said second effluent into a first gaseous stream comprising hydrogen and vaporous hydrocarbons and a liquid stream comprising non-vaporous hydrocarbons, contacting the separated liquid stream with said first effluent from said first tubular reaction zone, recovering from the contacting zone a second gaseous stream comprising hydrogen and vaporous hydrocarbons and combining said first and second gaseous streams.

2. The process of claim **1** in which the combined stream is passed into contact with a hydrogenation catalyst.

3. The process of claim **1** in which the separated liquid stream is countercurrently contacted with said first effluent from the first tubular reaction zone.

4. The process of claim **2** in which the effluent from the catalytic treating zone is passed to a high pressure separation zone where a gas rich in hydrogen is separated from a liquid rich in hydrocarbons.

5. The process of claim **4** in which a portion of the gas rich in hydrogen is introduced into the contacting zone with said first effluent from the first tubular reaction zone.

6. The process of claim **4** in which the liquid stream is contacted with said first effluent from the first reaction zone and then is contacted with a portion of the gas rich in hydrogen.

7. The process of claim **4** in which at least a portion of the gas rich in hydrogen is subjected to partial combustion and the partial combustion products are scrubbed for the removal of CO_2 and shift converted to produce substantially pure hydrogen a portion of which is introduced into at least one tubular reaction zone.

8. The process of claim **4** in which the gas rich in hydrogen is contacted with a molecular sieve thereby removing hydrocarbons from said gas rich in hydrogen.

9. The process of claim **4** in which a portion of the liquid rich in hydrocarbons is recycled to the high pressure separation zone.

10. The process of claim **4** in which the liquid rich in hydrocarbons is cooled by rapid expansion and the cooled expanded material is passed into indirect heat exchange with the effluent from the catalytic reaction zone.

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