

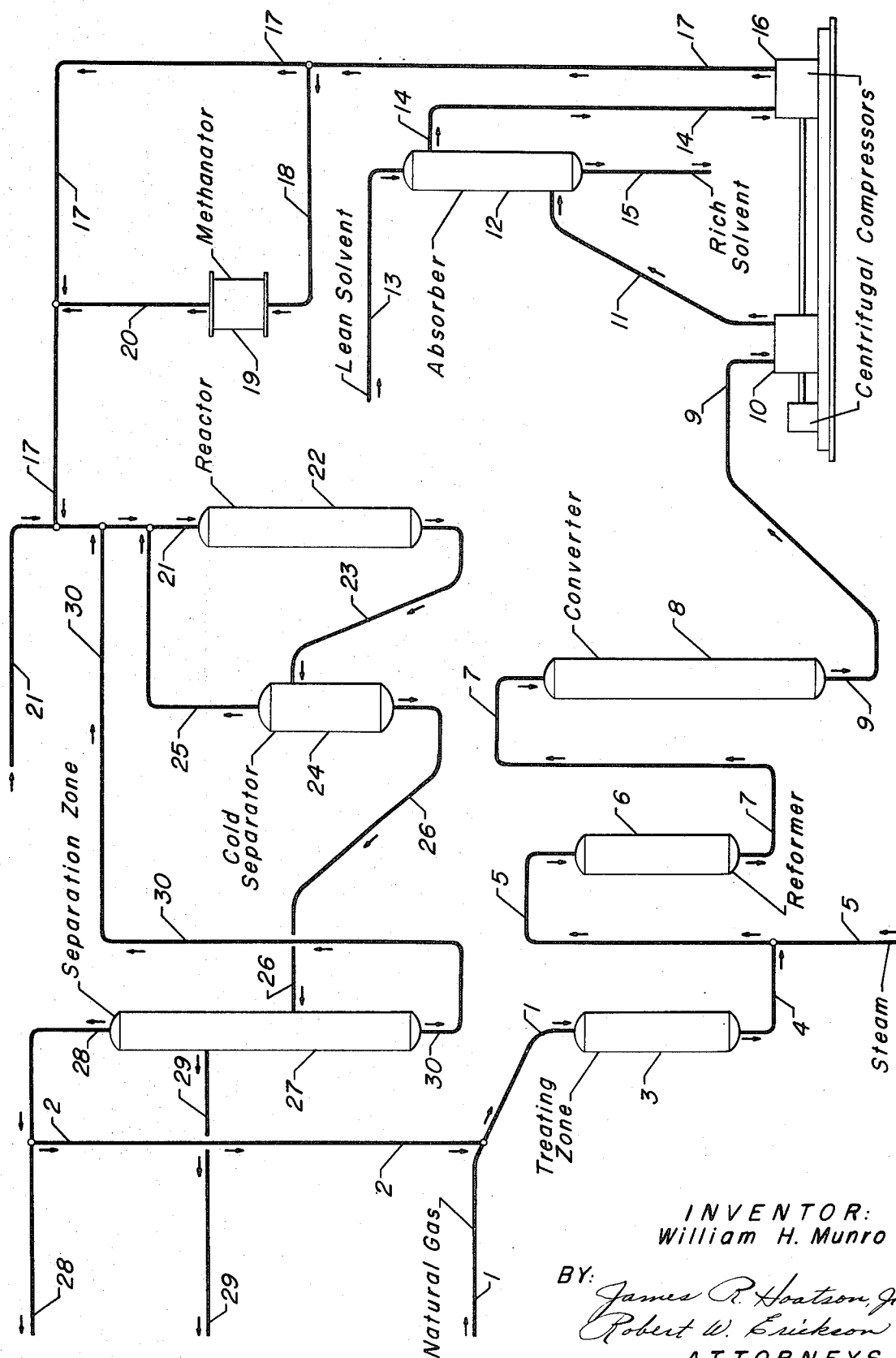
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HYDROPROCESSING OF HYDROCARBONS

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1

3,694,344

HYDROPROCESSING OF HYDROCARBONS

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5 Claims

ABSTRACT OF THE DISCLOSURE

A hydrocarbon hydroprocess wherein the chemical consumption of hydrogen is effected. A combination process in which a hydrocarbonaceous charge stock is reacted with steam to produce an effluent containing hydrogen and carbon oxides. The relatively low pressure effluent is compressed to an intermediate pressure level, at which pressure the hydrogen concentration is increased through the removal of the oxides of carbon. The purified hydrogen stream is then compressed to a higher pressure level and introduced into the hydroprocessing reaction zone. Specific hydroprocesses are directed toward the hydrogenation of aromatic nuclei, hydrocracking, the ring-opening of cyclic hydrocarbons for producing jet fuel components, desulfurization, denitrification and hydrogenation.

RELATED APPLICATIONS

The present application is a continuation-in-part of my copending application, Ser. No. 774,378, filed Nov. 8, 1968, now abandoned, all the teachings of which copending application are incorporated herein by specific reference thereto.

APPLICABILITY OF INVENTION

The present invention relates to a combination process for effecting hydrocarbon hydroprocessing. In particular, the invention is directed toward the catalytic hydrocracking of heavy hydrocarbonaceous material to produce lower-boiling hydrocarbon products. As utilized herein, the term "hydroprocessing" is intended to be synonymous with the term "hydrogenation," and involves the conversion of hydrocarbons at operating conditions which effect the chemical consumption of hydrogen. Processes intended to be encompassed by the term "hydroprocessing," include hydrocracking, aromatic hydrogenation, ring-opening, hydrorefining (for nitrogen removal and olefin saturation), desulfurization (often included in hydrorefining), hydrogenation, etc. One common attribute of these processes, and the reactions being effected therein, is that they are hydrogen-consuming and are, therefore, exothermic in nature. In employing the term "hydroprocessing," it is intended to allude to a hydrocarbon conversion process wherein there exists the chemical consumption of hydrogen. It is further intended to exclude those conversion processes in which the hydrogen consumption stems primarily from the saturation of light olefins, resulting from undesirable cracking of charge stock and/or product component, which produces light gaseous waste material, principally methane, ethane and propane. In the interest of brevity, the following discussion will be limited to that hydrogen-consuming process commonly referred to as catalytic hydrocracking.

Hydrocracking is primarily employed for the purpose of converting a relatively heavy hydrocarbonaceous charge stock into lower-boiling hydrocarbon products. For example, a heavy vacuum gas oil may be intended for conversion into lubricating oil, kerosene, gasoline boiling range naphthas, or a product slate comprising a

2

mixture thereof. Hydrocracking involves cracking of high molecular weight materials followed by hydrogenation of the cracked products in order to produce a substantially saturated product stream. A hydrogen atmosphere of relatively high purity is a requirement for effecting hydrogenation reactions, particularly hydrocracking, and there is a corresponding need to produce hydrogen of the requisite purity from various external sources. With respect to many of the hydrogen-consuming processes, a special unit is designed and constructed for the sole purpose of producing high purity hydrogen which is then introduced into the hydrocarbon hydroprocess.

External hydrogen, to be utilized in a hydrogen-consuming process, may be obtained, for example, from either a catalytic reforming process, or a hydrogen-producing unit, and either directly, or from storage at a relatively low pressure. Make-up hydrogen, to compensate for that chemically consumed within the hydroprocess, is compressed to the required pressure and introduced into the hydroprocessing reaction zone. Recently, however, hydroprocessing reactions, and, in particular, hydrocracking reactions, have been effected at exceedingly high pressures up to about 10,000 p.s.i.g. Hydrocracking reactions, for example, are effected at pressures in the range of about 1,000 to about 5,000 p.s.i.g., and preferably at pressures in the range of about 1,500 to about 3,000 p.s.i.g. For reasons well within the purview of those possessing expertise in the art, reciprocating or piston-type compressors have been employed to compress the hydrogen stream to the extent necessary to achieve the requisite reaction zone pressure. In general, as the size of the processing unit increases, resulting in increased flow rates, the single-train centrifugal compressor system is desirably installed. Those skilled in the art are also aware that reciprocating, or piston-type compressors have unusually high maintenance factors, are cumbersome and generally require close supervision for proper operation. Therefore, it is highly desirable to provide a process for the hydroprocessing of the make-up hydrogen stream in a relatively simple and economical manner.

With respect to a centrifugal compressor system, a major consideration in the determination of a practical installation is the inlet cubic feet per minute (c.f.m.) to the last impeller in the train. While some impellers have been furnished with capacities in the 350 to 450 c.f.m. range at peak efficiency, a more realistic capacity is 500 c.f.m., for a present-day centrifugal compressor, and driver speeds of 10,000 to 13,500 r.p.m. In an all centrifugal compressor unit, this results in a horsepower requirement in the 20,000 to 25,000 range for the feed gas and 5,000 to 7,500 for the recycle gas. Due to considerations of process and process stability, the recycle is incorporated in a separate casing, although it may be used alternatively as a combination feed gas booster and recycle unit. With the lower molecular weight gas, accompanied by the high pressure head required, the number of centrifugal compressor casings becomes a serious consideration. Notwithstanding advanced technology in turbo-machinery, centrifugal compressors have not been found suitable for this use due to the inability to design an acceptable machine at an economic cost to accomplish the desired result.

OBJECTS AND EMBODIMENTS

Accordingly, it is an object of my invention to provide a process for the conversion of hydrocarbons. A corollary objective is to afford a hydrocarbon hydroprocess wherein the chemical consumption of hydrogen is effected. Another object of this invention is to provide a method for effecting the hydrocracking of heavy hydrocarbonaceous material. A specific object is to afford an improved method for producing high purity hydrogen for use in a hydrocracking process.

3

Therefore, in accordance with one embodiment of this invention, there is provided a method for the hydrogenation of hydrocarbons which comprises:

(a) Introducing feed hydrocarbons to be hydrogenated into a first reaction zone maintained under hydrogenation conditions including the presence of hereinafter specified hydrogen gas and a pressure from 1,000 p.s.i.g. to 5,000 p.s.i.g.;

(b) Separating the effluent from said first reaction zone into a hydrogen stream suitable for recycle to said first zone, a normally gaseous hydrocarbon stream and a normally liquid hydrocarbon stream;

(c) Introducing added hydrocarbons to a second reaction zone maintained under conditions including a relatively low pressure from 100 to 400 p.s.i.g. and sufficient to convert said introduced gaseous hydrocarbons into a mixture of hydrogen and carbon oxides;

(d) Compressing said mixture of hydrogen and carbon oxide to a relatively high pressure from 1,000 p.s.i.g. to 5,000 p.s.i.g.;

(e) Passing said compressed mixture into a separation zone under conditions sufficient to produce a hydrogen product stream at a pressure from 1,000 p.s.i.g. to 5,000 p.s.i.g. and a carbon oxide product stream;

(f) Introducing said hydrogen product stream into said first reaction zone as the specified hydrogen gas; and,

(g) Recovering said normally liquid hydrocarbon stream.

In another embodiment, my invention involves a hydrocarbon hydroprocess which comprises the steps of:

(a) Reacting a first hydrocarbonaceous charge stock and hydrogen in a first reaction zone, at conditions selected to effect the chemical consumption of hydrogen including an elevated pressure from 1,000 to about 5,000 p.s.i.g.;

(b) Separating the resulting first zone effluent to provide a first hydrogen-rich principally vaporous phase and a first normally liquid phase;

(c) Separating said first liquid phase to provide a second principally vaporous phase and to recover a second normally liquid phase;

(d) Reacting a second hydrocarbonaceous charge stock and steam in a second reaction zone at a pressure of 100 to about 4000 p.s.i.g. and at a temperature selected to produce an effluent containing hydrogen and oxides of carbon;

(e) Centrifugally compressing at least a portion of the resulting second reaction zone effluent to a pressure from 500 to about 3,000 p.s.i.g.;

(f) Removing oxides of carbon from said compressed second reaction zone effluent to produce a purified hydrogen stream;

(g) Compressing said purified hydrogen stream to a pressure of 1,100 to about 5,100 p.s.i.g.; and

(h) Introducing the thus-compressed purified hydrogen stream into said first reaction zone.

In still another embodiment, this invention includes the method hereinabove described wherein said conditions are hydrocracking conditions and said high pressure is obtained by passing said mixture through a multiple-stage centrifugal compressor.

In essence, therefore, the present invention provides an improved method for the hydrogenation of hydrocarbons utilizing a specified hydrogen stream which is obtained from a specific hydrogen-producing plant. In a preferred embodiment, the hydrogen-producing plant is a steam reforming unit which utilizes centrifugal compression between conversion zones and the carbon dioxide adsorption zones of the unit.

Other embodiments, as hereinafter set forth in greater detail, are principally concerned with particularly preferred processing techniques and ranges of various process variables. These, as well as other objects relating to the present inventive concept, will become evident from the following additional description of the process. In one such other embodiment, the second hydrocarbonaceous

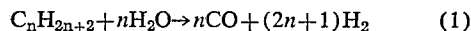
4

charge stock comprises at least a portion of said second vaporous phase.

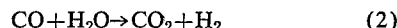
SUMMARY OF INVENTION

Various methods of producing hydrogen are well known to those skilled in the art. For example, U.S. Pat. No. 2,750,261, Ipatieff, et al., teaches a process for the production of hydrogen through the inter-action of an aliphatic hydrocarbon and steam at elevated temperatures, and in the presence of a catalytic material. As noted from the stoichiometry presented in this patent, hydrogen and carbon dioxide are the products from the steam cracking of a normally gaseous hydrocarbon. As currently practiced, hydrogen production in this manner involves the major processing steps of steam reforming, water-gas shift reaction and the removal of acid gases. It is known that various hydrocarbonaceous materials may be employed as feed streams to the steam reforming reaction zone. It is generally acknowledged that the ideal feed stream is rich in low molecular weight, normally gaseous paraffins including methane, ethane, and propane, with natural gases of relatively low nitrogen content being distinctly preferred.

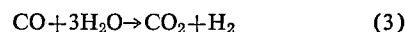
In the production of hydrogen, in accordance with the steam reforming process, preheated feed gases and superheated steam are introduced into catalyst-filled tubes in the furnace-type reforming zone at a temperature of about 1400° F. to about 1500° F., the hydrocarbons react with steam to form hydrogen and carbon oxides. The initial reaction may be represented by the following formula:



The carbon monoxide which is formed is then reacted with excess steam originally present in the feed mixture to form additional hydrogen via the following reaction:



This latter reaction is known as the water-gas shift reaction. Finally, the remaining impurities, such as carbon monoxide, are converted into a more desirable hydrocarbon by reaction with hydrogen. Typically, a methanator is employed to remove carbon monoxide to extremely low levels. This latter reaction is promoted by a nickel catalyst at a temperature of about 500° F. to about 800° F. in accordance with the following reaction:



Alternatively, a nitrogen washing column may be employed to remove methane and carbon monoxide, thereby producing a gas suitable for the synthesis of ammonia.

Operating conditions for the production of hydrogen include a steam to carbon ratio from about 1.1:6.0, relatively low pressures from 100 p.s.i.g. to about 400 p.s.i.g. and a catalytic composite comprising nickel. Temperatures, as previously mentioned, will generally be within the range from 1400° F. to 1500° F. Space velocities are based on methane equivalents per hour per volume of catalyst, and will typically range between 50 and 1,000.

Generally, the stream produced from the steam reforming operations will contain from 80.0% to 98.0%, on a mole basis, of hydrogen. Purities above or below these limits can be produced by those skilled in the art according to the needs of the process where the hydrogen is to be utilized. In some cases it is possible to produce hydrogen in a purity exceeding 98.0%, but rarely will this be a requirement for a hydrogen-consuming process. In the practice of the present invention, it is preferred that the hydrogen produced be at least 80.0% pure.

Therefore, according to the description of the present invention thus far presented, a steam reformer, water-gas shift converter and in a acid-gas removal system are combined in an economical manner utilizing compression between the water-gas shift converter and the acid-gas removal system to produce relatively high purity hydrogen for use in a hydrogen-consuming process. The acid-gas

removal system referred to herein may comprise conventional methods for carbon dioxide removal including mono-ethanolamine (MEA) adsorption, hot potassium component adsorption, methanol wash, etc. In a preferred embodiment of this invention, the CO₂ adsorption system will utilize the conventional amine adsorber including conventional solvent regeneration facilities. Furthermore, the hydrogen effluent gas from the CO₂ adsorption system may be passed directly into the hydrogenation reaction zone, or may be passed into a methanation reaction zone, as previously described, and then into the hydrogenation reaction zone. The present invention is intended to encompass the methanation reaction as an integral part in the overall process; however, it is understood, if desired, that methanation can be omitted without departing from the spirit and intent of the inventive concepts set forth herein.

The centrifugal compressors referred to herein are conventional, and may be obtained from any number of manufacturers including Clark, Elliot, Ingersol-Rand, etc. These machines are multi-stage in employing a succession of pressure increasing impellers as well as in accommodating impeller series in each of the successive case stages and are customarily connected in tandem to a common drive shaft which is connected to a common driver and gear speed changer if required. The present invention is specifically directed to the use of multiple-case stage centrifugal compressors which significantly increase the pressure of the produced hydrogen stream containing from 10.0% to 30.0% carbon dioxide, at a point prior to the conventional carbon dioxide adsorption zone in a hydrogen-producing plant. As hereinafter set forth in greater detail, one scheme involves increasing the pressure of the CO₂-containing hydrogen stream, followed by CO₂ removal which, in turn, is followed by additional compression to the level required in the hydroprocessing reaction zone.

As hereinbefore set forth, the present invention is specifically applicable to a hydrocracking process, although it is not intended that this invention be unduly limited thereto. It is known in the art that hydrocracking, or destructive hydrogenation, effects definite molecular changes in the structure of hydrocarbons. Such a reaction produces relatively light, or lower molecular weight hydrocarbon products from a relatively heavy hydrocarbon feed stock, and is particularly applicable to producing products within the gasoline boiling range. For example, a hydrocracking process can convert a petroleum feed stock, such as a gas oil, virtually, completely into gasoline boiling range products. In effect, the reaction zone effluent contains unreacted hydrogen, normally gaseous hydrocarbons and normally liquid hydrocarbons. The normally liquid hydrocarbons are generally recovered by fractionation into various boiling range cuts according to the desired product slate. Therefore, hydrocracking may be designated as a conversion process wherein lower molecular weight products are produced, which products are substantially more saturated than when hydrogen, or a hydrogen-donor material is not present.

Although many of the prior art processes are conducted on a strictly thermal basis, the preferred processing technique of the present invention involves the utilization of a catalytic composite employed in a fixed-bed system. Through the judicious selection of catalyst, the hydrocracking reaction can selectively convert a wide variety of feed stocks into lower-boiling distillates with significantly less coke and light gas yield than is usually produced by conventional catalytic cracking processes conducted in the substantial absence of hydrogen. As used herein, the term "hydrogenation" is intended to allude broadly to the addition of hydrogen to unsaturated bonds between two atoms. Therefore, the process to which invention is applicable is suitable for any process involving the contacting of hydrogen and normally liquid hydrocarbons at reaction conditions selected to effect the chemical con-

sumption of hydrogen. The particular operating conditions for the various hydrogen-consuming reaction and processes are well known to those skilled in the art. For example, the desulfurization of lubricating oils boiling between about 400° F. and 800° F., is effected at temperatures ranging from 500° F. to about 1,000° F. and pressures up to about 10,000 p.s.i.g. Liquid hourly space velocities may be varied from 0.1 to about 20.0. Those skilled in the art are familiar with these operating conditions and are capable of selecting the proper conditions in accordance with the characteristics of the particular system in question.

As hereinbefore stated, with respect to the hydrocracking process, relatively heavy hydrocarbonaceous material is converted into lower-boiling hydrocarbon products. The normally liquid hydrocarbon stream, separated from the effluent emanating from the hydrocracking reaction zone, can further be separated into desired fractions such as a gasoline fraction containing butanes and other hydrocarbons boiling up to about 400° F., a middle-distillate oil containing hydrocarbons boiling from about 400° F. to about 650° F., a heavy hydrocarbon fraction boiling from about 650° F. to about 950° F., and or a recycle oil containing those hydrocarbons boiling above a temperature of about 950° F. Other fractions can, of course, be separated as desired. As hereinafter more fully discussed, at least a portion of the separated light hydrocarbons, including normally gaseous hydrocarbons, may be introduced as a part of the feed mixture to the steam reforming zone for the production of hydrogen. In some instances, that portion of the normally liquid product effluent boiling above the end point of the ultimately desired product, will be recycled to combine with the charge stock to the hydrocracking reaction zone. In such situations, the combined liquid feed ratio to the hydrocracking reaction zone will be in the range of about 1.1 to about 6.0.

In the hydrocracking process, the hydrocarbons to be converted into lower-boiling material are contacted with a suitable catalyst at a temperature from 450° F. to about 900° F. and under an imposed pressure within the range of 1000 p.s.i.g. to about 5000 p.s.i.g., a liquid hourly space velocity from 0.1 to about 10.0 and in the presence of hydrogen in amount of about 1,000 to about 30,000 s.c.f./bbl. The hydrocracking conditions are chosen to produce an effluent stream containing unreacted hydrogen, normally gaseous hydrocarbons and normally liquid hydrocarbons.

It is distinctly preferred that the pressure imposed upon the hydrocracking reaction zone be at least 1,000 p.s.i.g., and still more preferable for the pressure to be within the range of about 1,500 to about 3,000 p.s.i.g. i.e. 2,000 to 2,500 p.s.i.g. At pressures below about 1,500 p.s.i.g., the recycle oil obtained from the hydrocracking reaction is dehydrogenated as evidenced by an increased Ramsbottom residue as compared to the charge, whereas pressures above 1,000 p.s.i.g., preferably above 1,500 p.s.i.g., the recycle oil from the hydrocracking operation has a reduced Ramsbottom carbon, and, therefore, can be effectively recycled to extinction.

The feed stocks which may be satisfactorily converted in the present invention have a wide range of compositions, and may contain large concentrations of saturates and aromatic hydrocarbons. In the hydrocracking reaction, saturates are cracked to gasoline boiling range paraffinic hydrocarbons containing a greater than equilibrium concentration of isoparaffins in the product effluent. In the case of poly-nuclear aromatics, these are partially hydrogenated with the hydrogenated ring portion being cracked to afford alkyl-substituted benzene and an isoparaffin. Most generally, for the hydrocracking reaction, the charge stock will range from naphtha and kerosene through the light and heavy gas oils. A particularly suitable feed stock will be one containing paraffinic hydrocarbons of at least 5 carbon atoms per molecule and having an upper boiling point in the range of from 600° F. to about 1100° F.

7

Product yields from the process of the present invention are dependent upon the nature of the charge stock, process conditions, availability of hydrogen and the catalytic composite employed. It should be noted, however, that the operating conditions and the specific catalyst employed form no essential part of the present invention except within the concepts described herein. The catalyst employed may be selected from the various well known hydrocracking catalysts which generally comprise a metallic hydrogenation component and a solid acidic hydrocracking component. Preferably, the hydrocracking catalyst further comprises a minor amount of an activity-controlling material which effectively provides a balance in the catalyst-hydrogenation activity relatively to the acidity during the overall conversion reaction. The catalyst so constituted serves a dual function; that is, it is non-sensitive to the presence of substantial quantities of nitrogenous and sulfurous compounds, while at the same time is capable of effecting the destructive removal thereof, and also of converting at least a portion of those hydrocarbons boiling in the upper range of the feedstock; in excess of about 600° F. to about 700° F.

Suitable catalytic composites comprise at least one metallic component selected from the metals of Groups VI-B and VIII of the Periodic Table combined with a suitable refractory inorganic oxide such as alumina, silica, and mixtures thereof. It is preferred that the catalyst comprise at least two refractory inorganic oxides, and preferably alumina and silica. When employed in such a combination, the silica will be present in an amount within the range of about 10.0% to about 90.0% by weight. The alumina-carrier material may be amorphous or zeolitic in nature, the latter often being referred to as crystalline aluminosilicate. The total quantity of metallic components within the catalytic composite disposed within the hydrocracking reaction zone is generally within the range of from about 0.1% to about 20.0% by weight. The Group VI-B metal, such as chromium, molybdenum or tungsten, is usually present in an amount of from about 0.5% to about 10.0% by weight. The group VIII metals, which may be divided into two sub-groups, are present in an amount of from about 0.1% to about 10.0% by weight. When an iron group metal such as iron, cobalt or nickel is employed, it is present in an amount from about 0.2% to about 10.0% by weight. While, if a noble metal, such as platinum, palladium, iridium, osmium, ruthenium, or rhodium, is employed, it is present within an amount within the range of about 0.1% to about 4.0% by weight. A preferred catalytic composite, for utilization in the present process, comprises nickel in an amount from about 0.5% to about 10.0% by weight, composited with an alumina-silica carrier material. A preferred carrier material constitutes faujasite, a form of crystalline aluminosilicate, which carrier material is at least about 90.0% by weight zeolitic. The catalytic composite may be manufactured in any suitable manner known to those skilled in the art. Thus, where the catalyst contains nickel, the method of preparation generally involves first forming an aqueous solution of a water-soluble compound such as nickel nitrate hexahydrate. The alumina particles serving as a carrier material are commingled with the aforementioned aqueous solution and subsequently dried at a temperature of about 200° F. The dried composite is then oxidized in an oxidizing atmosphere such as air, at an elevated temperature from 1100° F. to about 1700° F., and for a period of from 2 to about 8 hours. The exact manner of formulating the catalytic composite is not critical, and is well known to those skilled in the art, and only general reference thereto need be made herein.

Since hydrogen is consumed within the hydrocracking reaction zone, it is necessary to maintain an excess of hydrogen therein. The present invention utilizes a steam reforming reaction zone in order to obtain the hydrogen necessary to supplant that chemically consumed within

8

the process. For the production of hydrogen in accordance with this invention, various feed stocks may be satisfactorily used. It is distinctly preferred, however, that at least one of the feed stocks encompass normally gaseous hydrocarbons of the type found in conventional natural gas streams. It is further preferred that the feed stock have a relatively low nitrogen content. In one embodiment of the present invention, the normally gaseous hydrocarbons separated from the effluent of the hydrocracking reaction zone, are introduced into the steam reforming reaction zone, and may be so introduced in admixture with the feed stream from a suitable external source. Other feed stocks may be used in and of themselves, or combination with each of the above-mentioned feed stocks, or in combination only with the natural gas feed stock. Such other hydrocarbons may be ethylene, ethane, propane, propylene, hexene, hexane, normal heptene, etc., mixtures thereof including various petroleum derived fractions, such as light naphtha, heavy naphtha, gas oil, as well as mineral oils, crude petroleum, topped residual oil, refinery and coke oven gases. A light naphtha generally has a boiling range from about 100° F. to about 250° F., while a heavy naphtha boils from about 200° F. to about 400° F., and a gas oil indicates a boiling range from about 400° F. to about 700° F. As utilized herein, the term "added hydrocarbons," or words of similar import, is intended to allude to the fact that the charge stock to the steam reforming reaction zone may be obtained from an additional, or extraneous source other than the process encompassed by the series of interrelated and inter-dependent steps making up the present invention.

In view of the fact that high purity hydrogen has a relatively low molecular weight, centrifugal compressors have not been considered feasible or economical in compressing the hydrogen to the required high pressure level. The carbon dioxide-containing hydrogen stream has a higher molecular weight and can, therefore, be centrifugally compressed to the elevated pressured level. The corresponding increase in power requirements when compressing the carbon dioxide-containing hydrogen stream, presents a problem with respect to the economics of the process. On one hand there exists the desirability of using centrifugal compressors, and the other an increase in utility costs. By optimizing the degree to which the pressure of the carbon dioxide/hydrogen stream is raised, followed by carbon dioxide removal and further compression to the desired pressure level, the overall economics can be improved. Thus, where the pressure is in the range of 1,500 to about 3,000 p.s.i.g., the carbon dioxide-containing hydrogen stream is centrifugally compressed to a pressure level from about 1,200 to about 2,000 p.s.i.g., and the purified hydrogen stream, after carbon dioxide removal is further compressed to a pressure from 1,600 to about 3,100 p.s.i.g. This permits the second compression to be effected either with a centrifugal compressor, or a reciprocating compressor. This particular embodiment of my invention is that which is illustrated in the accompanying drawing.

DESCRIPTION OF DRAWING

The present invention may be more clearly understood upon reference to the accompanying drawing, wherein one embodiment is illustrated. In the drawing, various heaters, coolers, control valves, start-up lines, instrumentation and other miscellaneous appurtenances have been reduced in number, or eliminated entirely, as not being necessary for the purpose of illustration. Such modifications are well within the purview of those possessing ordinary skill in the art.

Referring now to the drawing, a heavy hydrocarbonaceous charge stock, boiling between 400° F. to about 1,000° F., is introduced into the process by way of line 21 wherein it is admixed with a purified hydrogen stream in line 17 and a recycle hydrogen stream from line 25.

In many instances, the hydrocarbonaceous charge stock will also be admixed with a heavy hydrocarbon recycle stream from line 30. The mixture continues through line 21 into reactor 22 which constitutes a catalytic hydrocracking reaction zone. Illustratively, the operating conditions maintained in reactor 22 include a temperature of about 700° F., a liquid hourly space velocity of about 0.75 and a pressure of about 2,000 p.s.i.g. These conditions are sufficient to produce an effluent stream containing normally liquid hydrocracked products; that is, a liquid product stream being lower boiling than the fresh feed charge stock, a hydrogen-containing stream and a normally gaseous hydrocarbon fraction comprising low molecular weight paraffinic hydrocarbons including methane, ethane and propane. The effluent from reactor 22 is withdrawn through line 23 into cold separator 24 which functions at substantially the same pressure but at a temperature in the range of about 60° F. to about 140° F. Hydrogen gas of relatively high purity is separated from the effluent in separator 24 and recycled via line 25 to reactor 22. The remainder of the hydrocracked product effluent is withdrawn through line 26, and introduced thereby into separation zone 27. Suitable distillation conditions are maintained in separation zone 27 in order to produce an overhead fraction comprising light hydrocarbons, which are withdrawn via line 28, and a distillate fraction, for example, boiling within the gasoline boiling range which is removed via line 29. Also, as hereinabove set forth, a residue stream comprising heavier hydrocarbons is withdrawn via line 30 and preferably recycled therethrough to hydrocracking reaction zone 22.

Referring now to the hydrogen-producing section of the present process, a natural gas stream is introduced into the process by way of line 1. The natural gas stream has the composition indicated in the following Table I:

TABLE I

Natural gas composition	
Component:	Vol. percent
Nitrogen	0.25
Hydrogen	40.03
Methane	23.28
Ethane	15.07
Propane	19.12
Butanes	0.95
Pentanes	0.74
Hexanes-plus	0.56
Total	100.00

In the illustrated embodiment, a portion of the light paraffinic hydrocarbons from line 28 is diverted by way of line 2 being admixed with the natural gas in line 1. This feed mixture is introduced into treating zone 3 which comprises a series of zinc oxide catalyst beds for the purpose of removing sulfur from the gaseous feed streams. The treater functions at a temperature of about 750° F. in accordance with practices well known to those skilled in the art. If two catalytic vessels are employed in series for treating zone 3, when sulfur "breaks down" in the first vessel it is taken out of service and recharged with fresh zinc oxide. The freshly charged vessel is then preferably placed in service in the downstream position. Treater 3 is operated under conditions sufficient to reduce the total sulfur content of the feed gas to less than about 0.5 p.p.m. The treated gas passes out of treating zone 3 through line 4, is admixed with steam in line 5 and passes therethrough into reforming zone 6.

Reforming zone 6 contains a series of vertical tubes filled with a nickel catalyst, and the gas stream mixture reaches reformer 6 at a temperature of 1541° F. and a pressure of about 250 p.s.i.g. The effluent gas in line 7 has the following composition on a dry basis: 1.81 vol. percent methane, 11.20 vol. percent carbon dioxide, 11.64 vol. percent carbon monoxide, 75.30 vol. percent hydrogen, and about 0.05 vol. percent nitrogen.

The carbon monoxide contained in the reforming furnace effluent in line 7 is converted into carbon dioxide and additional hydrogen in converter 8 which comprises two shift converters. The first shift converter operates with an inlet temperature of 275° F. and an outlet temperature of about 772° F. The second shift converter functions with an inlet temperature of about 394° F. and an outlet temperature of 425° F. The gas is cooled between the two shift converters by heat-exchange means, not illustrated, generally with boiler feed water employed in the production of steam.

The composition of the gas stream after each of the two shift converters in converter zone 8, on a dry basis, is presented in the following Table II:

TABLE II.—SHIFT CONVERTER STREAM COMPOSITIONS

	Volume percent	
	High temperature shift	Low temperature shift
Methane.....	1.66	1.63
Carbon dioxide.....	18.32	20.24
Carbon monoxide.....	2.69	0.28
Hydrogen.....	77.28	77.80
Nitrogen.....	0.05	0.05

The effluent stream, containing about 20.0 vol. percent carbon dioxide, is withdrawn via line 9 and passed into centrifugal compression zone 10, which, as previously indicated, comprises a series of case stages individually containing their respective impeller series. In passing through compressor 10, the hydrogen/carbon dioxide is progressively increased in pressure to a level of about 1,600 p.s.i.g. The compressor discharges by way of line 11 into a conventional carbon dioxide adsorber 12 of the mono-ethanolamine type. Adsorber 12 is operated in accordance with conventional techniques involving the introduction of the compressed gas into the lower end of the adsorbent column, which gas then flows upwardly through the suitable liquid contact devices against down-flowing liquid mono-ethanolamine being introduced by way of line 13. The rich mono-ethanolamine, having a high carbon dioxide content, is withdrawn by way of line 15 and passed into a conventional stripping regeneration system for the recovery and reuse of the mono-ethanolamine solvent.

The carbon dioxide content of the gas is reduced from 20.24 vol. percent to less than 180 p.p.m. The gas, in line 14, is then generally scrubbed with a small amount of process condensate, not illustrated, in order to remove the last traces of mono-ethanolamine. However, since the washing condensate is also saturated with carbon dioxide in some cases, the carbon dioxide content of the gas in line 14 increases to 242 p.p.m.; the gas has the composition indicated in Table III:

TABLE III

Purified hydrogen stream

	Vol. percent
Methane	2.04
Carbon dioxide	0.024
Carbon monoxide	0.35
Hydrogen	97.53
Nitrogen	0.06

The purified hydrogen stream emanates from adsorber 12 at a pressure of about 1,550 p.s.i.g., and is introduced by way of line 14 into centrifugal compressor 16 wherein the pressure is increased to a level of about 2,100 p.s.i.g. In a preferred embodiment of this invention, the purified hydrogen gas in line 17 is now preheated by means not shown, and passed via line 18 into methanator 19. Methanator 19 contains a nickel catalyst and converts residual carbon monoxide and carbon dioxide to methane. The gas reaches methanator 19 at a temperature of about 700° F. and a pressure of about 2,050 p.s.i.g., and has the following composition: 2.44 vol. percent methane, 97.50 vol. percent hydrogen, 0.06 vol. percent nitrogen and

11

less than about 10 p.p.m. carbon oxides. The gas stream emanating from methanator 19 passes through line 20 into line 17. If desired, a selected amount or, in fact, all of the gas in line 17 may be introduced into the hydrocracking reaction system. The purified gas in line 17 is now passed at a pressure of about 2,000 p.s.i.g., in admixture with the fresh feed charge stock in line 21, into reactor 22.

It can be seen that the present invention provides a method for hydrogenating hydrocarbons in the presence of relatively high purity hydrogen, wherein the hydrogen employed in the hydrogenation reaction is produced at the required pressure by centrifugal compression in a steam reforming operation. This interrelated and interdependent series of processing steps accomplishes a hydrogenation reaction, and, in particular, a hydrocracking reaction in a facile and economical manner.

I claim as my invention:

1. A hydrocracking process which comprises the steps of:

- (a) reacting a first hydrocarbonaceous charge stock and hydrogen, in a first reaction zone, at conditions selected to effect the chemical consumption of hydrogen, including an elevated pressure from 1,500 to about 3,000 p.s.i.g.;
- (b) separating the resulting first zone effluent to provide a first hydrogen-rich principally vaporous phase and a first normally liquid phase;
- (c) separating said first liquid phase to provide a second principally vaporous phase and to recover a second normally liquid phase;
- (d) reacting a second hydrocarbonaceous charge stock comprising at least a portion of said second vaporous phase and steam, in a second reaction zone, at a pressure of 100 to about 400 p.s.i.g. and at a temperature selected to produce an effluent containing hydrogen and oxides of carbon;
- (e) centrifugally compressing at least a portion of the resulting second reaction zone effluent to a pressure from 1,200 to about 2,000 p.s.i.g.;

12

(f) removing oxides of carbon from said compressed second reaction zone effluent to produce a hydrogen stream;

(g) compressing gas consisting essentially of said purified hydrogen stream to a pressure of 1,600 to about 3,100 p.s.i.g.; and,

(h) introducing the thus-compressed purified hydrogen stream into said first reaction zone.

2. The process of claim 1 further characterized in that said purified hydrogen stream is centrifugally compressed.

3. The process of claim 1 further characterized in that a reciprocating compressor raises the pressure of said purified hydrogen stream.

4. The process of claim 1 further characterized in that said second hydrocarbonaceous charge stock comprises a mixture of natural gas and at least a portion of said second vaporous phase.

5. The process of claim 1 further characterized in that said hydroprocess is catalytic hydrocracking, and said conditions include a temperature of 400° F. to about 900° F., a liquid hourly space velocity from 0.1 to 10.0 and hydrogen circulation of 1,000 to about 30,000 s.c.f./bbl.

References Cited

UNITED STATES PATENTS

3,551,106	12/1970	Smith et al.	23—212
3,567,381	3/1971	Beavon et al.	23—212
3,401,111	9/1968	Jackson	208—108
2,750,261	6/1956	Ipatieff et al.	23—212
3,532,467	10/1970	Smith et al.	23—210
3,044,951	7/1962	Schlinger et al.	208—58
3,251,652	5/1966	Pfefferle	23—213

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