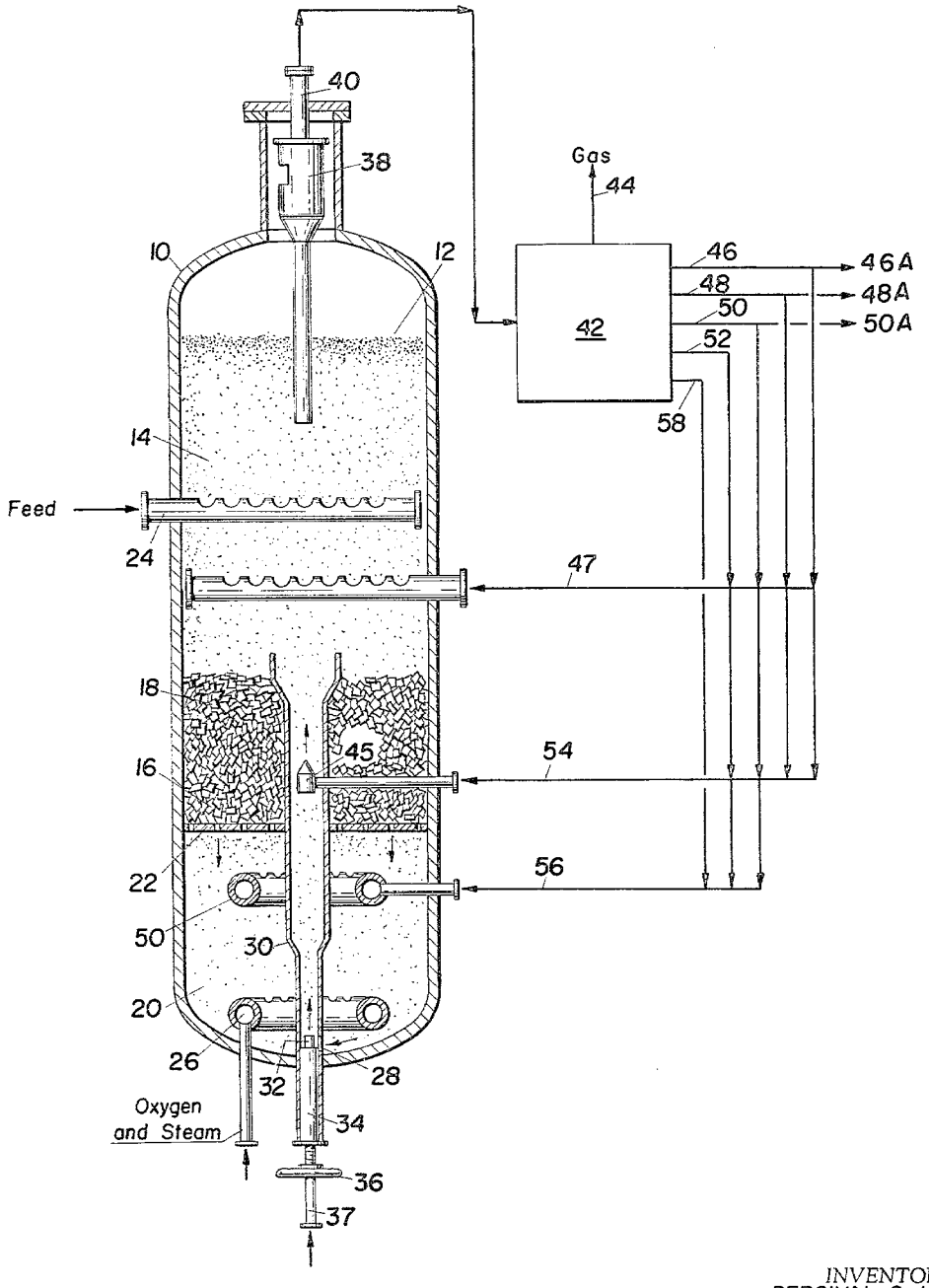
Aug. 24, 1965 P. C. KEITH ETAL 3,202,603

HYDROCRACKING OF HIGH BOILING HYDROCARBON OILS TO PRODUCE AROMATICS AND FUEL GASES

Original Filed June 26, 1961



INVENTORS
PERCIVAL C. KEITH
EDWIN S. JOHANSON
SEYMOUR C. SCHUMAN

BY Nathaniel Ely

ATTORNEY

United States Patent Office 3,202,603 Patented Aug. 24, 1965

3,202,603

HYDROCRACKING OF HIGH BOILING HYDROCARBON OILS TO PRODUCE AROMATICS AND FUEL GASES

Percival C. Keith, Peapack, and Edwin S. Johanson and Seymour C. Schuman, Princeton, N.J., assignors to Hydrocarbon Research, Inc., New York, N.Y., a corporation of New Jersey

Continuation of application Ser. No. 119,640, June 26, 1961. This application Aug. 16, 1963, Ser. No. 302,580

8 Claims. (Cl. 208—107)

This invention relates to the high temperature hydrocracking of heavy hydrocarbons and is more particularly concerned with a process for the efficient production of valuable materials including aromatics such as benzene and naphthalene, with a minimum yield of other less valuable normally liquid materials together with a high yield of fuel gas which is substitutable with natural gas or for natural gas as conventionally transported in pipelines and ultimately used for heating, cooking and other applications. It is a continuation of our prior application, Serial No. 119,640, filed June 26, 1961, now abandoned.

Pyrolysis of heavy hydrocarbons under conditions that yield appreciable fractions of normally gaseous hydrocarbons as carried out normally at low pressures, yields a gaseous component of highly olefinic and diolefinic character, some light oil of relatively high aromatic content, appreciable quantities of heavy tarry liquids, and a coke deposit. The lack of control of the reactions depresses gas yields and lowers light oil yield because the yield of hydrogen rich gaseous components is limited by the combined hydrogen available in the charge and the diolefinic constituents formed in such pyrolysis react readily with aromatic compounds in condensation reactions to depress the recovery of benzene and naphthalene.

In accordance with our invention we provide a process and an apparatus in which the carbonaceous and tarry constituents unavoidably produced in high temperature cracking are reacted with steam and oxygen to form hydrogen, which, when introduced into the cracking zone, under sufficient pressure and temperature, will direct the cracking reactions by providing more hydrogen for the production of normally gaseous hydrocarbons, suppress the formation of diolefinic constituents so that an increased portion of the light aromatic products are preserved, while the hydrogen reacts rapidly with aliphatic liquids corresponding in boiling point to aromatics produced so that the normally gaseous product and light aromatics are improved both in yield and quality.

As the amount of carbonaceous materials formed in such pyrolysis is insufficient to provide sufficient hydrogen for the fully effective completion of the functions described above, the apparatus is so arranged that the tarry materials primarily produced are returned to proper portions of the device to increase the hydrogen availability for direction of the cracking reactions.

The value of benzene and naphthalene as basic petrochemical intermediates is well known (see for example, Kirk-Othmer, Encyclopedia of Chemical Technology, Interscience Publishers, Inc., vol. 2, page 420, 1948; vol. 9, page 216, 1952), and little comment is required relative to the unique aspects of an invention which will increase the yields and improve the quality of these materials. However, the unique character of our invention to produce a high value gaseous product is not as well understood and deserves further comment. Virtually all gas is combustible and commands a price as conventionally used to yield heat or produce steam for industrial and commercial purposes. Such industrial grades of gases need not be of any particular composition, heating value or density since most commercial burners can either burn

a broad range of gaseous compositions or be adjusted to burn such compositions. However, even in such low grade commercial gas, the content of olefins and doilefins is preferably reduced to very low values, since these contaminants in the gas cause plugging of burner nozzles and other critical orifices in the burner, due to polymerization. As stated above, these undesirable constituents are essentially eliminated in our invention by providing sufficient hydrogen in the cracking zone so that they are hydrogenated to the much more stable paraffinic derivatives. Thus our invention results in the production of a gaseous product of substantially greater value than normal fuel gas due to its low content of polymerizable constituents. However, our invention accomplishes considerably more, in providing a gas which is essentially substitutable with natural gas. The gas produced in accordance with this invention may be added to presently existing natural gas pipelines for transmission to natural gas consumers, either commercial or domestic. This possibility upgrades the value of the gas still further, since domestic users of natural gas pay at least $1/MM B.t.u. and as high as $3/MM B.t.u. for such gas. The value of such domestic gas is even greater at the end of the pipeline during peakload conditions (i.e., at the end of a severe winter freeze). At this time the natural gas supply may be so limited that service to commercial and industrial companies is actually interrupted, due to the possibility of ultimately having to discontinue supplying gas to domestic customers consequently causing considerable hardship to families who use gas for heat.

However, gas requirements for domestic use are even more severe than those indicated above for commercial and industrial purposes. Domestic burners are "set" in accordance with the characteristics of natural gas with respect to luminosity, carbon formation, flashback, and other properties. A gas which is substitutable with or for natural gas should preferably have properties which approach those of natural gas, or the gas company will be forced to "reset" the burners in every household before the new gas can be utilized. Obviously, this would require a considerable expense. The two properties which are of greatest importance with respect to substitutability are heating value and specific gravity, or molecular weight. As is well known, natural gas may have a heating value from about 900 to 1100 B.t.u./cu. ft. and a specific gravity of about 0.60 to about 0.70 relative to air and a molecular weight of about 17 to 20. Thus, it is the object of our invention to produce a fuel gas of properties as close as possible to those of natural gas, so as to be able to obtain the considerable premium in value of such gas.

Ordinary cracked gases contain higher hydrocarbons such as ethane and propane in addition to methane. Thus, such cracked gases are of greater unit heating value and specific gravity (or molecular weight) than natural gas. If such cracked gases are diluted with air or nitrogen to reduce their unit heating value, density (and molecular weight) are still too high. In general, then, a gas containing methane and higher hydrocarbons must have hydrogen which is the only component known to reduce both heating value and specific gravity (or molecular weight) to that which is required to become substitutable with and for natural gas.

In accordance with this invention, low grade heavy hydrocarbon oil of high Ramsbottom carbon residue and other sour crudes and petroleum residues which can not normally be treated by other means are subjected to treatment at elevated temperature (above 1100° F. and usually at temperatures in the range of 1300° F. to 1500° F.) in the presence of a particulate contact material or carrier and in a gaseous atmosphere. This atmosphere is produced by the reaction in a subjacent combustion zone of carbon with oxygen and steam at temperature above

about 1600° F. to produce in the reaction zone an amount of hydrogen which provides a hydrogen partial pressure of 35 to 2000 p.s.i. (pounds per square inch), preferably 75 to 150 p.s.i. The hydrocarbon oil, preferably preheated, is fed into the reaction zone, hereinafter designated as the cracking zone, containing the particulate solids carrier in fluidized condition. The cracking zone is preferably superposed on and in communication with a higher temperature zone of restrained fluidization, hereinafter designated as the secondary zone or stripping zone.

Fluidization of the particulate solids carrier is restrained in the secondary zone in the sense that the vertical movements of the fluidized particles are restricted to the extent that a temperature gradient is established along the vertical dimension of the secondary zone, ranging from the temperature of the cracking zone which is contiguous with the upper end of the secondary zone to the higher temperature of the combustion zone which is contiguous with the lower end of the secondary zone. Such restrained fluidization is obtained by filling the secondary zone with coarse packing bodies of the type of Raschig rings and Berl saddles.

In the cracking zone, a deposit of heavy hydrocarbons and carbon forms on the carrier particles and these particles under restrained fluidization, pass downwardly through the secondary zone countercurrently to a gaseous stream containing steam and the gaseous products of reacting carbon with oxygen and steam at a temperature above about 1600° F., the gaseous stream thus contacting the carrier particles in initimate thin film relationship. From the secondary zone, the particulate carrier then passes into a subjacent combustion zone wherein the carbonaceous matter on the carrier is reacted with steam and oxygen at a temperature in the range of 1600° F. to 2500° F. to produce the previously mentioned gaseous atmosphere required in both the cracking and the secondary zones. Besides hydrogen, this gaseous atmosphere contains carbon monoxide, carbon dioxide and steam. The "regenerated" particulate carrier is then returned to the cracking zone. The regeneration product gases, after passing upwardly through the secondary zone, enter the cracking zone to provide the atmosphere for the hydrocarbon conversion and are withdrawn together with the hydrocarbon conversion products from the top of the cracking zone.

While the utility of the foregoing invention has been demonstrated at low temperatures for the production of valuable gasoline boiling range hydrocarbons together with light and heavy gas oils it has been found that economic conditions justify the conversion of essentially all of the initially formed heavy gas oils and a substantial part of the light gas oils to produce gasoline, aromatic chemicals such as naphthalene and benzenes, benzene itself, and/or fuel gas of relatively high heating value. Generally, there are three preferred operating conditions designated as:

(a) The production of gasoline together with fuel gas of relatively high heating value.

(b) The production of benzene and naphthalene together with fuel gas of high heating value.

(c) The production of substantially only fuel gas of high heating value.

In accordance with our present invention as hereinafter described, we have found that by variation of the temperatures of the reactor zones, and particularly with a controlled production of hydrogen, and recycle of predetermined liquid fractions, we are able to obtain substantial yields of more valuable lighter products. Similarly, the production of relatively high yields of light hydrocarbon products is an unexpected result of the controlled hydrogen production, which is substantially above that normally required for the conversion reactions in the process.

Our invention thus relates to the gasification of a feedstock such as a heavy crude or residual oil, usually containing large quantities of impurities such as sulfur, nitrogen, and metallic compounds, wherein the gasification takes place in the presence of supplemental hydrogen to produce valuble light hydrocarbons.

An object of our invention is to provide an improved process for economically recovering valuable constituents from low grade crude or residual oils wherein the entire treatment may be accomplished in a single apparatus.

A further object of our invention is to produce fuel gas of a relatively high heating value, essentially substitutable for and with natural gas, together with such normally liquid products including gasoline, benzene, alkyl benzenes, and naphthalene, as may be dictated by the economic requirements of a particular application.

A particular object of our invention is to provide an improved process for economically producing a high value fuel gas which is substitutable for and with natural gas together with benzene and naphthalene.

Further objects and advantages of our invention will appear from the following disclosure of a preferred form of embodiment thereof when taken with the attached drawing illustrative thereof and in which the figure is a schematic view of a reactor and recovery system for production of normally gaseous hydrocarbons and aromatics.

In accordance with our invention we provide a multizone reactor of the type disclosed in the Finneran et al. Patent 2,861,943, and the Schuman Patent 2,875,150. The vessel 10 contains a fluidized carrier mass of particulate solids with a pseudo-liquid level 12. The upper portion of the fluidized mass provides a cracking zone 14, an intermediate portion containing packing bodies 16 like Raschig rings or Berl saddles provides a secondary zone 18 and the lower portion provides a combustion zone 20. The packing bodies 16 are supported on a perforated plate 22. The charge stock is supplied to zone 14 through inlet 24 while oxygen and steam for regeneration of the carrier particles are introduced through inlet 26.

The temperature of the cracking zone 14 is generally maintained substantially above 1100° F., preferably in the range of 1300° F. to 1500° F. as by supplying hot solids and gases as hereinafter described and such temperatures will crack and gasify the liquid feed. The fouled carrier in zone 14 coated with coke and carbon then moves down through packed zone 18 countercurrent to regeneration product gases rich in hydrogen and is subjected to stripping conditions at increasing temperatures as the carrier approaches zone 20. The carrier stripped of absorbed hydrocarbons then discharges from zone 18 through plate 22 into zone 20 where the carbonaceous residue on the carrier particles is gasified by reaction with oxygen and steam. This is carried out at temperatures of at least 1600° F. and not to exceed 2500° F. and usually in the range of 1800° F. to 2000° F.

Regenerated and reheated carrier then flows from zone 20 through opening 28 in up-transport conduit 30. The flow of carrier through opening 28 may be regulated by the position of valve body 32 mounted on tube 34 which is moved vertically by turning threaded handle 36. The carrier is conveyed upward through the conduit 30 into the cracking zone 14 by a suspending gas such as flue gas or recycle gas introduced through inlet 37 to tube 34.

The cracked hydrocarbons and the hydrogen-containing regeneration product gases emerge as reactor effluent from pseudo-liquid level 12, pass through cyclone separator 38 and flow through outlet 40 to a conventional recovery plant 42 to fractionate the liquid and separate various fractions from the gaseous products.

The recovery plant for the products is shown schematically because of the many different arrangements by which it can be designed. However, the lines shown issuing from the recovery plant illustrate schematically the various products and recycle streams which can be obtained in accordance with this invention.

The fuel gas product is removed at line 44 and is substitutable for and with natural gas after the treatment

which it has undergone in the recovery system. Such treatment may include:

(a) Shifting of carbon monoxide with steam to produce additional hydrogen and carbon dioxide.

(b) Scrubbing of carbon dioxide partially or completely from the fuel gas.

(c) Reaction of hydrogen and carbon monoxide to produce methane and water (methanation), and

(d) Removal of sulfur compounds.

As will be shown in the detailed examples which follow, shifting, carbon dioxide scrubbing, and methanation may or may not be practiced, whereas removal of sulfur compounds is generally practiced because of the very low quantities of these impurities desired in fuel gas used for domestic requirements.

A benzene fraction boiling about 176° F. is removed as a product at line 46A in a preferred embodiment of this invention. However, when it is desired to produce fuel gas by itself, with no normally liquid by-products, this fraction may be completely recycled back to the reactor through lines 47 and/or 54.

Liquids boiling above the benzene fraction, consisting primarily of alkyl benzenes having a boiling range from about 230° F. to 400° F. are removed from the separation system at 48 and these may also be either all or partly removed at 48A as products or all or partly recycled through lines 47 and/or 54 back into the reactor.

A naphthalene fraction boiling about 424° F. is removed from the separation system at line 50 and all or part removed as product at 50A. In a preferred embodiment of this invention all of the naphthalene is removed at 50A. However, in other embodiments, this fraction may be recycled entering the reactor through lines 47, 54 or 56.

Liquids boiling immediately above the naphthalene fraction, consisting primarily of alkyl naphthalenes in the 450° F.–650° F. boiling range removed at 52, are preferably all recycled either through lines 47, 54 or 56.

The heavy ends (boiling above 650° F.) removed in line 58 are recycled through line 56 to the distributor 59 in the combustion zone 26.

As mentioned above, the amount and composition of recycle stocks fed back to the various zones of the apparatus vary considerably with the quality of the feedstock and the particular application which is economically desirable. In general, however, very heavy, low hydrogen-containing recycle components are fed into the combustion zone through line 56, alkyl aromatics with short alkyl chains into the high temperature cracking zone through line 54, whereas paraffins or aromatics with longer alkyl chains are fed into the lower temperature cracking zone through line 47. It may often be necessary to make compromises with respect to these recycle streams, since the ideal method for separating them and recycling them back to the apparatus may involve too much of an expenditure for the separation equipment shown diagrammatically in box 42. However, in all cases, some recycle will be provided through line 56 in order to produce additional hydrogen over that normally furnished by gasification of the coke formed in the reactions. When the charge stock is a relatively light material or does not form coke in large amounts, the streams of recycle material passing back into the reactor through line 56 may be as much as 20 v. percent to 40 v. percent on feed.

As described in the prior patent to Schuman, 2,875,150, the recycle of the fraction boiling above 700° F. into the upflow conduit and particularly where the carrier gas in the conduit 30 contains sufficient hydrogen to provide a hydrogen partial pressure in the range of 35 to 400 p.s.i., tends to convert the relatively heavy ends to useful normally gaseous products and light aromatics, while leaving a carbonaceous residue on the upflowing carrier which is useful to supply additional hydrogen for the cracking zone. The temperature in the upflow conduit 30 is usually in the range of about 1700° F. to about 1800° F.

and the contact time is limited to about one to five seconds. The effluent is then sharply quenched by the fluidized carrier in cracking zone 14.

As the temperature of the primary cracking zone is increased, the scission rate of aliphatic carbon-carbon bonds becomes more rapid. Aromatization of olefins also occurs. Thus, the effect of increasing cracking zone temperature above 1100° F., and particularly in the order of 1300° F. to 500° F., is to increase the aromatics content of the liquid product, and the proportion of the thermal energy of the feed recovered as gaseous fuel increases significantly.

As the cracking zone temperatures are increased to the range of 1300° F. to 1450° F., paraffins, olefins, and naphthenes are essentially completely gasified so that the only liquid products recovered are aromatics containing only methyl and ethyl side-chains. Thus, in this temperature range, gasification produces benzene, toluene, xylene, and ethyl benzene, together with naphthalene if desired; yields of liquid products are in the range of 15–25 v. percent. On recycling the alkylated benzenes, benzene and naphthalene are produced together with gas. In this case, about 78% of the thermal energy present in the feed is ultimately recovered as fuel gas; although the yield of liquid products is relatively small, they represent a large part of overall plant revenue.

The reactor may also be operated to produce all gaseous fuel. Fuel gas is produced in two zones. The gas produced in the cracking zone is of high unit heating value and consists of the paraffins and olefins of carbon numbers 1 to 4. The gas produced in the combustion zone where coke (together with oil in most cases) is gasified with oxygen and steam, is of low heating value and essentially consists of carbon monoxide, carbon dioxide, and hydrogen. By control of the quantities and feeds to the zones and the conditions extant in the zones, the unit heating value and specific gravity of the overall fuel gas product can be varied over wide limits. The substantial recycle of heavy ends to the combustion zone is particularly economical in the cost of production of adequate hydrogen not only to reduce the yield of coke but especially to supply the needed hydrogenation for the chemical reactions that take place in the cracking zone.

The production of hydrogen in the combustion zone from the recycled heavy ends as well as by the conversion of the carbonaceous deposit on the carrier is of significant importance in that it supplies a hydrogen partial pressure of from 35 p.s.i. to 200 p.s.i. in the high temperature cracking section and in the upflow conduit. It is found that the requirements for oxygen and steam are markedly reduced over that customarily required for partial oxidation.

Ordinarily the recycle of the liquid stream is sufficient to produce the desired amount of hydrogen by which the reactions desired in the apparatus can be carried out efficiently and at the same time producing a fuel gas of a quality substitutable with and for natural gas. However, it is also to be appreciated that part or all of the gas stream normally obtained at line 44 could also be recycled back to the apparatus through line 56, to assist in the formation of the desired hydrogen atmosphere.

It will also be appreciated that in some cases it may be desirable to produce, in addition to normally liquid products and fuel gas, a considerable quantity of gas of high hydrogen content as for use in the steel, chemical and petroleum industries where hydrogen of 70–90% purity is particularly in demand. Here again, part of the normally obtained fuel gas might be recycled through line 56 to increase the hydrogen content of the gas which is produced.

The following examples further illustrate the invention without, however, being intended as limitations thereof:

EXAMPLE I

An apparatus as illustrated is charged with bauxite

averaging 160 mesh size. At an operating gauge pressure of 400 p.s.i., the unit treats 100 barrels per day of Boscan crude oil having the following characteristics:

Gravity, ° API	10.7
Ramsbottom carbon, w. percent	10.4
Sulfur, w. percent	5.47

The charge stock preheated to about 700° F. is injected into the distributor **24**. At the point of oil injection the fluidized bed is maintained at a temperature of 1400° F. The volume of the fluidized cracking zone is such that the gasiform materials remain in the zone for 15–20 seconds. Fifty barrels per day of alkylated benzenes and naphthalenes boiling below 700° F. are recycled from separator through line **47** into zone **14**. Five barrels per day of recycle oil boiling above 700° F. are recycled through line **54** to conduit **30**, and ten barrels per day of recycle oil boiling above 700° F. are recycled through line **56** to distributor **50**.

About 163,000 s.c.f.d. of oxygen (96% by volume purity and 500,000 s.c.f.d. of steam, respectively preheated to 300° F. and 1000° F., enter through distributor **25** to regenerate fouled bauxite at a temperature of about 1800° F. An additional 168,000 s.c.f.d. of gasiform product from separator **42** preheated to 1000° F. is supplied through tap **37** to lift 430,000 pounds per day of bauxite from zone **20** to zone **14** through conduit **30**.

The solid lifted from zone **20** at 1800° F. heats the heavy recycle oil from line **54** to 1750° F. for 2 to 5 seconds, and then heats the crude oil feed and light recycle oil in zone **14** to 1400° F.

The results for Example I are as follows:

Transport gas	containing H_2
Regenerating gas	O_2 and H_2O
Yields (net from separator):	
Benzene, bbls./day	8.8
Naphthalene, lbs./day	770
Fuel gas, MM s.c.f.d.	0.64
Fuel gas properties (sulfur free):	
Gross heating value, b.t.u./s.c.f.d.	802
Gravity (air=1.0)	0.98

EXAMPLE II

The basic gas produced from Example I by the simple recovery system provided is somewhat low in gross heating value and high in specific gravity as compared with natural gas. This gas could be blended in with a substantially larger quantity of natural gas, but would not be substitutable for natural gas by itself. However, it can readily be converted to a more satisfactory gaseous fuel by addition of shifting and scrubbing facilities to recovery system **42**. The first column of Table I provides an analysis and properties of the basic gas as produced in Example I. The second column of Table I provides an analysis of the gas produced when the basic gas is partially shifted and scrubbed to complete elimination of carbon dioxide. The third column of Table I illustrates the case where the basic gas is partially shifted with carbon dioxide then only partially removed. The fuel gases as shown in the second and third columns of Table I are substitutable for natural gas with no difficulty.

EXAMPLE III

This example illustrates another possible method of adjusting the basic gas produced in Example I to the desired quality characteristics. In this case, an absorption system is placed into the purification train indicated in **42**, remove 85% of the butanes and 55% of the propanes present in the basic gas. After the higher hydrocarbons are removed, the basic gas is partially shifted and completely scrubbed of carbon dioxide as previously. The fourth column of Table I illustrates the resultant product gas.

From Examples I, II, and III, it is obvious that the basic gas produced in accordance with this invention may be treated by various procedures in recovery system **42** to produce fuel gas substitutable for natural gas if enough hydrogen and carbon monoxide are produced in the basic gas to ultimately provide low density, low heating value components sufficient to balance the high density, high heating components provided by the higher hydrocarbons.

EXAMPLE IV

Operating at a gauge pressure of 400 p.s.i. a unit treats 10,000 barrels per day of West Texas-New Mexico residuum having the following characteristics:

Gravity, ° API	10.2
Ramsbottom carbon residue, wt. percent	13.7
Sulfur, wt. percent	3.5

The charge stock is preheated to about 700° F., is injected into the inlet **24**, at a point where the fluidized bed is at a temperature of 1400° F., and the gasiform materials flowing upwards will remain in the cracking zone for 20–30 seconds. 2,500 barrels per day of alkylated monocyclic aromatics boiling from 230° F. to 400° F. from separator are recycled into cracking zone **14**. 1,000 barrels per day of recycle alkylated naphthalene boiling above 450° F. are recycled also to the cracking zone, and 500 barrels per day of the same oil are recycled to the distributor **50** in combustion zone **20**.

About 15,500,000 s.c.f.d. of oxygen (96% by volume purity) and 46,500,000 s.c.f.d. of steam respectively preheated to 300° F. and 1000° F. enter through distributor **25** to regenerate fouled bauxite at a temperature of about 1850° F. An additional 15,700,000 s.c.f.d. of gasiform product from separator **42** preheated to 1000° F. is supplied through tap **37** to lift 4,700,000 pounds per day of bauxite from zone **20** to zone **14** through conduit **30**. The solids at 1800° F. heat the heavy oil from line **54** to 1700° F. for 3 to 6 seconds, and then crude oil and light recycle oil in zone 14 to 1400° F.

The results for Examples IV are as follows:

Transport gas	containing H_2
Regenerating gas	O_2 and H_2O
Yields (net from separator):	
Benzene, bbls./day	950
Naphthalene, lbs./day	210,000
Fuel gas, MM c.f.d.	64.0
Fuel gas properties (sulfur free):	
Gross heating value, B.t.u. s.c.f.	780
Gravity (air=1.0)	1.00

As illustrated in Examples II and III the basic fuel gas produced can be converted to a gas substitutable with and for natural gas by routine procedures, usually involving shifting and carbon dioxide and hydrogen sulfide removal, and possibly involving absorption, low temperature condensation or the like.

EXAMPLE V

An alternative to Example IV, where naphthalene is not desired, is that 1,000 b./d. of the naphthalenic primary products are also introduced through line **54** to conduit **30**, which will then be at a temperature of 1600° F., so that naphthalenic compounds will be converted to benzene, with the following results:

Yields (net from separator):	
Benzene, bbls./day	1,250
Fuel gas, MM c.f.d.	65.6
Fuel gas properties:	
Gas heating value, B.t.u./s.c.f.	795
Gravity (air=1.0)	0.99

As illustrated in Examples II and III the basic fuel gas produced can be converted to a gas substitutable with and for natural gas by routine process steps.

Table I.—Compositions of fuel gas from Examples I, II, and III

Example	1	2	2	3
Fuel gas composition, percent:				
Hydrogen	13.4	38.1	35.4	41.6
Carbon monoxide	19.0	7.4	6.9	7.6
Carbon dioxide	28.8	0.0	6.9	0.0
Methane	12.8	18.0	16.8	19.6
Ethylene	1.7	2.4	2.2	2.6
Ethane	13.9	19.5	18.2	21.1
Propylene	0.7	1.0	0.9	0.5
Propane	5.5	7.8	7.2	4.7
Butanes	3.1	4.2	3.9	0.6
Nitrogen	1.1	1.6	1.5	1.7
Unit heating value, gross	802	1,102	1,011	941
Specific gravity (air = 1)	0.98	0.65	0.71	0.58

Under the usual economic conditions, it is considered that the recycle of liquid to supply the desired hydrogen atmosphere is preferable. However, it is within the scope of the invention to substitute petroleum coke or coal if it is found that conservation of liquid is beneficial, i.e., that the liquid fractions have a higher value as products rather than as the hydrogen source. In such case, as an example, coal which is preferably bituminous or sub-bituminous or lignite where enonomics indicate its favorable use, is added to the combustion chamber in the order of 5 to 20 wt. percent, preferably under 10 wt. percent based on the liquid feed at 24. In such case, the solid carbon particles would be of a fineness to all pass 20 mesh (Tyler) and usually not more than 25 percent passing 325 mesh.

While we have shown and described preferred forms of embodiment of our invention we recognize that modifications may be made thereto without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the high temperature hydrocracking of heavy liquid hydrocarbons to produce normally gaseous materials together with a light aromatic liquid fraction with a minimum yield of other normally liquid materials, which comprises injecting a hydrocarbon oil having a Ramsbottom carbon value of at least about 8 into a cracking zone containing particulate solids at a temperature substantially above 1100° F. and under a pressure of at least 200 p.s.i.g. with a hydrogen partial pressure of at least 35 p.s.i. thereby producing a gaseous overhead and depositing carbonaceous material on the solids, passing said solids from the cracking zone to a combustion zone, contacting said solids in the combustion zone with an oxygen containing gas and steam to produce a temperature of at least 1600° F. thereby removing the carbonaceous deposit from the solids and reheating the solids to a predetermined temperature, returning the reheated solids to the cracking zone, separating the effluent from the reactor into a gaseous fraction, a light normally liquid aromatic fraction, and a heavy normally liquid fraction, recycling to the combustion zone said heavy normally liquid fraction in an amount corresponding to at least 5% by volume of the fresh feed in order to establish the desired hydrogen partial pressure in the cracking zone, and producing from the process a major quantity of fuel gas having a unit heating value of 900–1100 B.t.u. per cubic foot; a specific gravity of 0.6 to 0.7, and a molecular weight of 17 to 20 which is substitutable with and for natural gas.

2. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1, wherein all of the normally liquid products obtained from the reactor are recycled to completion so that the net product from the process is a fuel gas essentially substitutable with and for natural gas.

3. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1 wherein the primary effluent from the reactor is fractionated to produce naphthalene and recycling said naphthalene to the solids returning to the cracking zone to produce major yields of benzene and a fuel gas which is substitutable with and for natural gas.

4. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1 wherein the liquid fraction recycled to the cracking zone has a boiling range of between about 230° F. to about 400° F. and is essentially alkyl benzenes.

5. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1 wherein the portion of the effluent returned to the cracking zone has a boiling range of from about 450° F. to about 650° F. and is essentially alkyl naphthalenes.

6. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1 wherein the liquid recycled to the cracking zone is of the class of alkyl benzenes and alkyl naphthalenes and wherein all materials boiling in the range of 450° F. to about 650° F. and all materials boiling in the range of 230° F. to about 400° F. are recycled to extinction.

7. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1 wherein coal is added to the heavy normally liquid fraction which is recycled to the combustion zone to establish the desired hydrogen partial pressure in the cracking zone.

8. A process for the high temperature hydrocracking of heavy liquid hydrocarbons as claimed in claim 1 wherein a part of the primarily obtained gaseous product is recycled back to the combustion zone along with a heavy normally liquid fraction.

References Cited by the Examiner

UNITED STATES PATENTS

2,875,147	2/59	Engle	208—164
2,976,134	3/61	Paull	48—215

ALPHONSO D. SULLIVAN, *Primary Examiner.*