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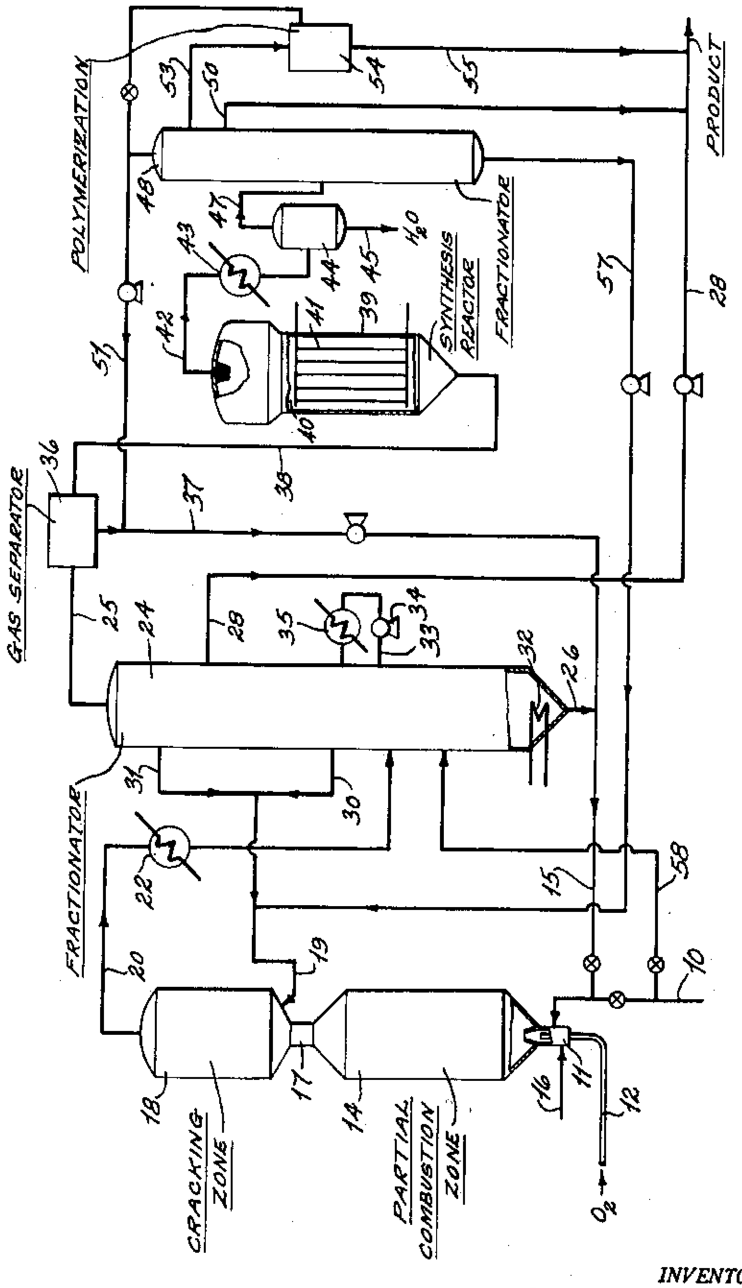

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# PREPARATION OF MOTOR GASOLINE FROM CARBONACEOUS FEED MATERIAL

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5 Claims. (Cl. 44—80)

The present invention relates to the preparation of high quality motor gasoline from carbonaceous feed materials, particularly undesired hydrocarbon stocks, and more specifically, is concerned with effecting the essentially complete conversion of the entire carbonaceous feed into desired proportions of olefinic and aromatic motor gasoline fractions.

In accordance with the copending application, United States Serial No. 188,693, filed October 6, 1950 (No. 32,863) in the name of Frank J. Jenny, undesired liquid hydrocarbons, particularly heavy residual stocks of relatively high carbon residue, which cannot be economically converted by conventional thermal or catalytic methods, are subjected to thermal cracking in a flowing stream of partial combustion products, composed of a mixture of hydrogen and carbon monoxide, issuing from a synthesis gas generator substantially at combustion temperatures at least about 2000° F. and up to 3000° F. and above, or higher. Pyrolytic decomposition of the injected liquid hydrocarbon takes place at a cracking temperature controlled by the relative rate of hydrocarbon feed injection, or otherwise, to yield a preferably highly aromatic cracked gasoline fraction.

In the flowing stream of partial combustion gas, the solid carbonaceous residues of cracking are liberated in the form of particles of dry and fluffy appearance which remain entrained in the gas stream and are carried out of the reaction zone with the gasiform product effluent. In this way, coke or carbon deposition in the reactor is avoided.

The effluent products of reaction pass into a fractionation tower, where the desired fractions are separated, while the upflowing gases are continuously scrubbed by the downflow oil reflux, which continuously delivers the carbon particles to the bottom of the tower as a slurry in the heavy hydrocarbon residuum. This slurry of fine particle coke in the heavy bottom fraction is continuously withdrawn and subjected to partial combustion with regulated quantities of essentially pure oxygen to continuously supply the aforementioned stream of partial combustion gas which feeds the cracking zone.

Thus, the fractionator residuum, with the coke particle residue of the thermal cracking slurried therein, is continuously consumed in the generation of the high temperature partial combustion gas which, in turn, supports continuous thermal conversion of the cracking fraction, so that the entire hydrocarbon feed is continuously consumed to extinction in the formation of desired liquid and gaseous fractions.

In accordance with the present invention, the normally gaseous fraction of the product effluent from the cracking zone, and including the stream of hydrogen and carbon monoxide from the partial combustion step, is continuously recovered from the fractionator. The separated fraction, rich in hydrogen and carbon monoxide, after further treatment, if desired, to separate light gaseous hydrocarbons and the like, is continuously contacted with an iron hydrocarbon-synthesis catalyst to form liquid, predominantly olefinic hydrocarbons in the motor gasoline boiling range. The desired olefinic gasoline fractions are separated from this synthesis effluent, residual hydrocarbons passing continuously as the cracking stock to the aforementioned pyrolytic conversion or cracking step. Preferably, the cracking step is operated as above to yield highly aromatic liquid fractions. Accordingly, the undesired residual fractions of the synthetic olefinic hydrocarbons are continuously converted into valuable aromatic gasoline fractions, while the heavy residues of cracking, including the solid carbonaceous particles formed therein, are continuously disposed of in forming a synthesis gas mixture of hydrogen and carbon monoxide, which is continuously converted in the catalytic synthesis step to form the olefinic motor gasoline fraction and the cracking stock.

Aside from the benefits of complete consumption of the feed materials in the continuous formation of desired motor gasoline fractions with elimination of the objectionable coking problem, the present invention has numerous additional advantages. More specifically, the simultaneous production of synthetic olefinic fractions and thermally cracked aromatic fractions in the motor gasoline boiling range enables continuous production of a blend which is ideal from the standpoint of motor fuel requirements.

Unfortunately, the motor gasoline boiling fractions formed by catalytic synthesis from hydrogen and carbon monoxide alone, fail to meet these requirements. With synthesis catalysts such as cobalt, the product is exclusively paraffinic, whereas the synthesis product of an iron type catalyst is predominantly olefinic throughout its entire range.

Actually, a preferred motor gasoline is one that is predominantly olefinic in the lower boiling portion of the range, as for example, up to about 220° F. and predominantly aromatic above. The present invention makes it possible to selectively realize this result by withdrawing as product the aromatic fractions boiling in the upper portion of the motor gasoline range and the olefinic products in the lower portion of this range, and continuously recycling remaining fractions to the cracking zone.

The conditions of thermal cracking conducive to maximum formation of motor gasoline boiling aromatics include relatively high temperatures of 1100–1500° F. and a contact time of 1 to 10 seconds.

As above intimated, the carbonaceous feed to the partial combustion or synthesis gas generation zone may include, in addition to the slurry of suspended coking particles in heavy liquid residuum, additional hydrocarbons, such as all or any desired portion of the primary feed stream of carbonaceous material. While this primary feed may be any desired liquid hydrocarbon fraction, practical considerations dictate use of some relatively low value fraction such as heavy residual fractions of relatively high carbon residue and low value for conventional cracking purposes. However, gaseous hydrocarbons may also constitute the feed to the gas generation step, and therefore, the primary feed to the process may comprise, or else consist exclusive of hydrocarbon gases, such as methane, natural gas and waste refinery gases. So also, generation of the synthesis gas mixture of hydrogen and carbon monoxide may be effected by the partial combustion of essentially solid carbonaceous materials containing hydrogen, as for example, coal, lignite, peat, etc. In general, feeds suitable for cracking go first to the cracking step, the others passing directly to the partial combustion step.

Referring now to the attached flow sheet, wherein one embodiment of the present invention is disclosed, a carbonaceous feed stock, such as natural gas, enters from any suitable source not shown, through pipe **10** leading into mixing burner **11**. Pipe **10** also receives from branch pipe **15** a heavy, high carbon residue slurry containing suspended solid residues of coking, as will be hereinafter described in greater detail.

At the burner **11**, the hydrocarbons meet a stream of substantially pure oxygen, of at least 90 percent and preferably 95 percent purity, or higher, which is introduced from a suitable source, not shown, through pipe **12**.

As indicated, the burner discharges into a refractory-lined combustion chamber **14** where the reactants undergo partial combustion to form a product gas composed essentially of hydrogen and carbon monoxide.

To effect this result, the feed streams to the burner are carefully regulated to maintain the atomic O/C ratio of the entering feed materials less than about 2:1, and preferably in the vicinity of about 1:1 to about 1.5:1, since it is in this range that maximum yield of a high purity mixture of hydrogen and carbon monoxide results. As previously stated, combustion is effected at a high temperature, as high as 3000° F. and above, and in any event, not substantially below about 2000° F. When the hydrocarbon fed to burner **11** is natural gas, it is advantageous to preheat the gas in order to maintain such temperatures. On the other hand, means are provided in the form of an inlet pipe **16** for injecting into the mixing burner regulated quantities of steam to moderate excessive combustion temperatures which would attack the chamber **14**. Steam injection is particularly advantageous with a feed comprising or composed of heavy residual stocks which burn with a high rate of heat release.

While the combustion zone **14** is operable at atmospheric pressure, it is advantageous in most cases to maintain therein substantially superatmospheric pressures, as for example, from 100 to 600 p. s. i. g. and preferably from 200 to 500 p. s. i. g.

The substantial stream of synthesis gas from the combustion zone **14** passes, without substantial cooling, through constriction **17** into cracking zone **18** at substantially the combustion temperature. Into cracking chamber **18**, there is also injected, through pipe **19**, the aforementioned heavier, synthetic hydrocarbon fractions, the origin of which is to be hereinafter described in greater detail.

The rate of oil injection through line **19** is such as to continuously maintain in the chamber a cracking temperature of, for example, 1100 to 1500° F. Cracking takes place, therefore, in a substantial carrier stream of partial combustion gases. Residence time in the cracking zone is from about 1 to 10 seconds, preferably above about 2 seconds, such that predominantly aromatic, pyrolytic conversion products in the gasoline boiling range are produced.

As indicated in the drawing, the cracking or pyrolytic conversion chamber **14** is preferably free, refractory-walled space, completely free from packing, partitions, checkerwork or any other internal obstructions.

As a result of this free and open internal space, the low area of confining wall surface, and the substantial flow rate of combustion gas through chamber **14**, solid carbon or coke resulting from cracking occurs in the form of fine dry, and somewhat fluffy appearing particles which, instead of being deposited within or upon the walls of chamber **18**, remain entrained in the effluent gasiform stream of cracking products and carrier gas.

The entire product effluent continuously passes through transfer pipe **20**, through cooling exchanger **22** where its temperature range is reduced below about 650° F., and thereafter is injected into the lower portion of the fractionator **24**.

The normally gaseous fractions of this effluent pass upwardly through fractionation column **24**, countercurrent to the constant downflow of oil reflux in the tower. Therefore, the gaseous stream is effectively scrubbed of the entrained solid particle carbonaceous materials, and issues overhead through pipe **25** free of solid particles.

As a further result of this scrubbing action, all the solid pyrolytic residue ultimately descends to form a slurry with the tower bottoms. Accordingly, the tower bottoms, withdrawn through pipe **26**, contain substantially all the coking residue of solid carbon particles slurried in the bottoms, tar and other heavy residuum. This passes, as indicated, into the aforementioned pipe **15**, which merges with the first mentioned pipe **10**, feeding the burner **11**. Advantageously, therefore, the withdrawn bottoms fraction is restricted to high carbon residue fractions which are particularly disadvantageous for thermal cracking, and, therefore, an indicated feed for partial combustion.

The desired, highly aromatic motor gasoline fraction is continuously drawn off as a side stream from tower **24** through pipe **28** for blending into a final product gasoline, as will hereinafter more fully appear. For example, the withdrawn side stream may be approximately a 220–400° F. cut, of predominantly aromatic product.

A second side stream, preferably a 400–700° F. cut gas oil withdrawn from tower **24** by pipe **30**, passes into aforementioned pipe **19** feeding the thermal cracking zone **18**. To this may be added a second side stream withdrawn from the upper portion of tower **24** through pipe **31** corresponding to the lower end fraction of the motor gasoline range; for example, up to about 220° F.

To effect the foregoing results, reboiler **32** is advantageously provided in the bottom of the tower, and additional refluxing is provided by withdrawing a side stream from the tower through line **33**, pump **34** and cooling exchanger **35**, and returning it at a higher point in the tower. Accordingly, therefore, the fractionator **24** continuously functions to deliver a desired product gasoline fraction, and to segregate the remainder into a normally gaseous overhead, relatively low carbon residue recycle fractions and an ultimate bottoms slurry, containing substantially all the coking residue of thermal cracking.

The overhead, normally gaseous fraction is withdrawn through pipe **25** and preferably treated for removal of light gaseous hydrocarbons, methane, ethane, ethylene and the like, leaving a high grade, relatively pure stream of synthesis gas. Gas separation plant **36** is provided for this purpose. Separation may be effected, for instance, by absorption of light hydrocarbons in a suitable oil fraction, or even in an activated, absorbent material, the details of which, per se, form no part of the present invention. The separated hydrocarbon stream may pass continuously through pipe **37** to supplement the hydrocarbon feed to mixing burner **11**.

The resulting synthesis gas mixture of hydrogen and carbon monoxide flows through pipe **38** into reactor **39**, where it passes in contact with a hydrocarbon synthesis catalyst. As indicated, the synthesis reactor **38** comprises an upstanding chamber containing a preferably fluidized mass of solid particle catalyst **40**. A heat exchanger bundle **41**, immersed in the fluidized mass of catalyst, is internally supplied with coolant to control reaction temperature.

The catalyst **40**, preferably comprises an iron type, hydrocarbon synthesis catalyst which characteristically converts hydrogen and carbon monoxide into desired, predominantly olefinic products. For this purpose, the operating temperature is held in a critical, narrow range which may vary with the specific catalyst employed, but which is usually between 550 and 700° F., typically about 650° F. Operating pressures are in the range of about 150 to 600 p. s. i. g., usually 200 to 400 p. s. i. g. The effluent gasiform products of reaction disengage from the upper surface of the catalyst and pass outwardly through transfer line **42**, and cooling exchanger **43**, into condenser **44**, from which aqueous condensate is drained via line **45**.

The resulting oil condensate, as well as the normally gaseous effluent, pass through pipe **47** into fractionator **48**, operating to deliver through pipe **50** a lower end motor gasoline cut, with an end point, for example, of about 220° F. This fraction blended, as indicated, with the aromatic, 220–400° F. motor gasoline boiling cut in pipe **28**, yields valuable motor gasoline, predominantly aromatic in the higher boiling range and predominantly olefinic in the lower boiling range.

Referring now to the other product fractions separated in column **48**, an overhead of light gaseous hydrocarbons, together with some byproduct carbon dioxide from the hydrocarbon synthesis step, passes through line **51** into line **37**, feeding the mixing burner **11** of the partial combustion chamber **14**. The $C_3$–$C_4$ olefin fractions are withdrawn through pipe **53** to polymerization plant **54**, yielding additional quantities of desirable polymer gasoline fractions which flow into the product blend through pipe **55**. Undesired residues from the polymerization plant **54** pass through line **56** into pipe **51**.

The residual fractions boiling above 220° F. accordingly comprise the tower bottoms withdrawn through line **57** and these, as indicated, continually cycle into pipe **19**, as the previously mentioned feed to the cracking zone **18**.

Accordingly, the present process functions continuously to convert hydrocarbon fractions, unsuitable for cracking by ordinary means, into a partial combustion gas which is, in turn, converted into a synthetic, olefinic motor gasoline and thermal cracking stock. The synthetic thermal cracking stock is continuously subjected to pyrolytic conversion to form valuable aromatic fractions by continuous injection into the hot stream of partial combustion gas. The solid residue of coking which accompanies the pyrolytic conversion, therefore, occurs in the form of solid particles which pass off with the cracking products and are recovered as a slurry in the residual hydrocarbon fractions thereof. These high carbon residue materials, as well as otherwise waste gaseous product streams, are continuously consumed to extinction in the formation of the high temperature partial combustion or synthesis gas while the relatively low carbon residue hydrocarbon liquids outside the desired boiling range are continuously supplied as thermal cracking feed.

It is apparent from the foregoing that the invention is not limited to the recovery of the specific final product fractions above mentioned for purposes of illustration, since various other product requirements may also be met. For example, according to one aspect of the invention, it is contemplated recovering as final product the entire motor gasoline boiling fractions from both the cracking and the hydrocarbon synthesis effluents. In any event, however, the residual, relatively low carbon residue liquids form the pyrolytic conversion feed, while the excessively high carbon residue products are consumed to extinction in the formation of high temperature synthesis gas cracking medium.

As above indicated, the fresh feed of natural gas mentioned in the illustrative embodiment may be substituted in part or in its entirety by any suitable liquid or even solid fraction, such as a residual fuel oil or the like. Advantageously, with a liquid hydrocarbon feed, a portion, at least, thereof, is diverted through branch pipe **58** into the fractionating tower **24** to provide additional reflux and increase the volume of liquid bottoms sufficiently to maintain desirable fluidity of the slurry. This procedure is particularly advantageous where the feed introduced through pipe **10** contains appreciable low carbon residue constituents recoverable through pipe **30** and/or **31** as a desirable feed to the cracking zone.

It is particularly desirable, in order to prevent carbon deposition in the cracking chamber **18**, that the linear velocity of the carrier gas flow be held at a substantial level, as for instance, ½ to 10 feet per second, preferably 1 to 6 feet per second.

The term "high carbon residue," as used herein, refers to stocks which are relatively unsuitable for cracking and are therefore, more advantageously consumed in the gas generation zone. The "low carbon residue" stocks referred to are those having a relatively lower carbon residue value, which yield substantial proportions of cracked motor gasoline fractions by the pyrolytic steps disclosed herein. In general, streams with a Conradson number below about 5 fall within the latter category, while those with a Conradson number materially above 5 are generally considered to be high carbon residue materials.

Reference is made to the aforementioned application, Serial No. 188,693, as regards the specific conditions of partial combustion, thermal cracking and the recovery and disposition of the solid products of coking.

Obviously, many modifications and variations of the invention as above 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 production of a motor gasoline which comprises subjecting a hydrocarbon to reaction with oxygen at a temperature above about 2,000° F. in a synthesis gas generation zone to produce a stream of synthesis gas consisting essentially of hydrogen and carbon monoxide, injecting a hydrocarbon liquid cracking stock into said stream of synthesis gas at substantially said reaction temperature in a cracking zone to form a resulting mixture having a temperature in the range of from about 1,100 to about 1,500° F. effecting substantial thermal cracking of said stock with the formation of a cracked product comprising an aromatic fraction boiling within the motor gasoline boiling range, separating said aromatic fraction from the resulting product of said cracking, passing carbon monoxide and hydrogen from said cracking zone to a hydrocarbon-synthesis reaction zone, converting said carbon monoxide and hydrogen in the presence of an iron-type hydrocarbon synthesis catalyst into synthetic hydrocarbons comprising an olefinic fraction boiling within the motor gasoline boiling range and a higher boiling fraction, separating said higher boiling fraction from the resulting products of said synthesis reaction, supplying said higher boiling fraction to said cracking zone as cracking stock, separating said olefinic fraction from the products of said synthesis reaction, blending said olefinic fraction with said aromatic fraction to produce a motor gasoline fraction.

2. A process as defined in claim 1 wherein a contact time within the range of 1 to 10 seconds is maintained in said cracking zone.

3. A process as defined in claim 1 wherein said aromatic fraction has a boiling range of from about 220 to about 400° F. and said olefinic fraction has a boiling range below about 220° F.

4. A process as defined in claim 1 wherein said hydrocarbon-synthesis is effected at a superatmospheric pressure and at a temperature in the range of 550 to 700° F.

5. A process as defined in claim 1 wherein liquid hydrocarbons from said cracking zone boiling outside said gasoline boiling range fraction and below about 700° F. are supplied to said cracking zone as part of said cracking feed, and residue from said cracking zone boiling above about 700° F. is supplied to said synthesis gas generation zone to produce carbon monoxide and hydrogen.

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