March 21, 1961 P. L. PAULL 2,976,134

HYDROCARBON CONVERSION PROCESS

Filed Dec. 7, 1956 2 Sheets-Sheet 1

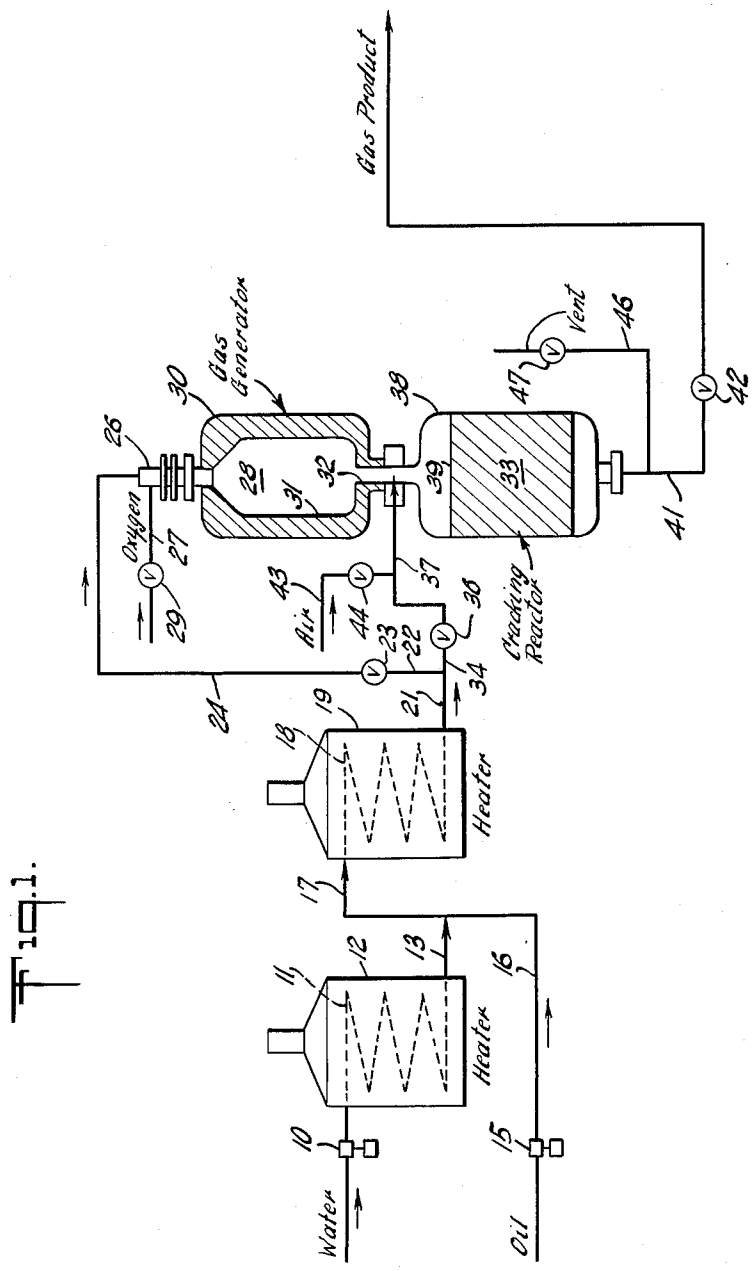


FIG. 1.

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Filed Dec. 7, 1956 2 Sheets-Sheet 2

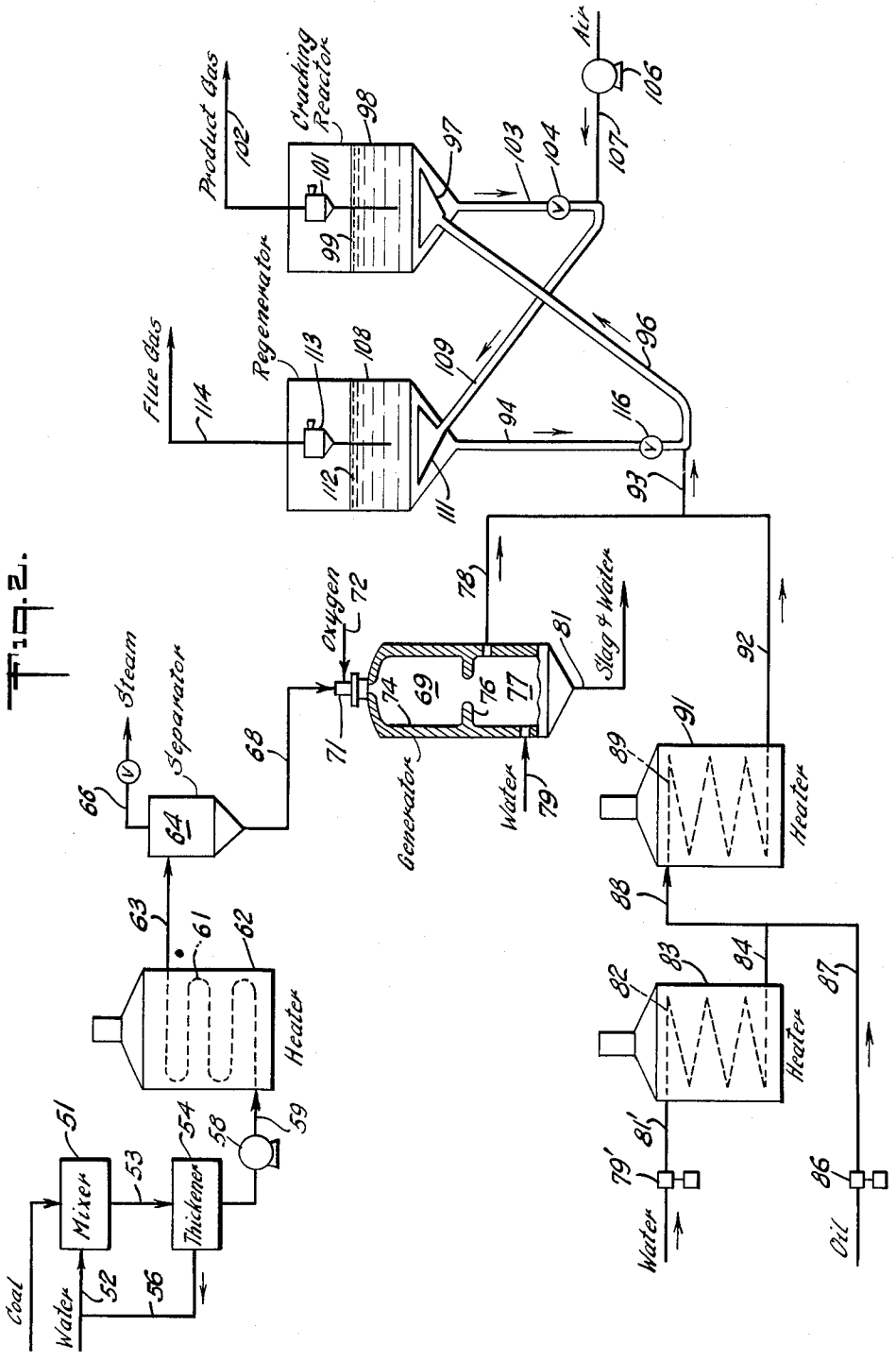


Fig. 2.

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2,976,134

HYDROCARBON CONVERSION PROCESS

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11 Claims. (Cl. 48—215)

This invention relates to a method and apparatus for the conversion of carbonaceous fuels to gases. In one of its more specific aspects, it is directed to a process for the continuous and complete conversion of heavy oils into fixed gases of high calorific value. By heavy oil is meant an oil which cannot be completely vaporized by heat alone without cracking and the formation of carbonaceous deposits under gasification pressure, for example, crude oil, reduced crude, cracking plant residual oil and coal tar.

In a preferred embodiment, the invention relates to the conversion of heavy oils to high B.t.u. gases by the following steps: A dispersion of heavy oil in steam is formed by subjecting a mixture of heavy oil and steam to highly turbulent flow conditions in a preheater. A synthesis gas comprising carbon monoxide and hydrogen is generated at elevated temperature and pressure by the partial combustion of a carbonaceous fuel with oxygen. The preheated steam-heavy oil dispersion and hot synthesis gas are combined and the combined stream is contacted with a cracking catalyst to effect cracking and generation of a gas of high B.t.u. content. The resultant product gas is suitable for distribution as fuel.

The usual method of manufacturing gas from heavy oils is to spray the heavy oil into a furnace containing a checkerwork of heated brick or other refractory material. The oil is thus subjected to severe cracking which converts the oil to gaseous products, which are withdrawn from the furnace, and a carbonaceous residue which deposits upon the checkerwork. The furnaces are heated by burning oil or gas therein and by burning the carbonaceous residue from the checkerwork by blasting the furnace with air. This process necessarily employs alternating heating and cracking cycles. It has not been possible to crack heavy oils completely to gas in tubular heaters since such severe cracking results in the formation of carbon and the plugging of heater tubes. Catalytic processes have been developed for reforming light hydrocarbons, for example, methane, with steam to generate hydrogen and carbon oxides but these processes have not been successfully employed with heavier hydrocarbons, such as fuel oils, because of rapid catalyst fouling by carbonaceous deposits.

I have now found that the tendency of heavy oils to form carbonaceous deposits in catalytic gasification reactions can be materially reduced by the process of my invention to make such catalytic gasification processes economical and practical. In accordance with the process of this invention, the heavy oil feed is injected into a stream of steam and the resulting mixture subjected to highly turbulent flow conditions. In a preferred embodiment, the mixture is passed into an elongated tubular zone under conditions of high velocity and highly turbulent flow. The high turbulence disperses the oil uniformly in the steam. The oil is generally substantially unvaporized or at most only partly vaporized. Apparently the highly turbulent flow disperses the liquid oil as very small particles uniformly in the stream forming

a substantially homogeneous dispersion having the appearance of a mist.

Preferably, the steam is superheated prior to injection of the oil to a temperature such that there is substantially no condensation of the steam in the resulting steam oil mixture. The oil may be preheated to a temperature up to about 700° F. or may be at ambient temperature when injected into the stream of preheated steam. The dispersion is preferably formed by passing the oil-steam mixture through a relatively long tubular conduit at a velocity in excess of about 20 feet per second, preferably in excess of 50 feet per second. Lower velocities permit partial segregation of the oil, probably along the walls of the conduit, resulting in uneven flow of the dispersion, and pressure and flow rate fluctuations, or slugging, of the fuel feed to the generator or gasification reactor. Preferably, the tubular section in which the dispersion of oil in steam is accomplished has a length at least 100 times the inside pipe diameter. Advantageously, the mixing tube has a length at least 500 times its inside diameter. To avoid slugging and to insure a uniform dispersion, sufficient vapor, i.e., steam and vapor from the oil, must be present so that at least 70 percent by volume of the feed is in vapor form. Preferably, at least 90 mol percent of the oil-steam feed is in vapor form. In a preferred embodiment, the tubular mixing zone is heated to a temperature above the temperature of the initial mixture of steam and oil so that the mixture is preheated during flow therethrough.

The relative proportions of steam and oil may vary over a wide range, for example, from about 0.2 to about 3 pounds of steam per pound of oil supplied to the reaction zone. The effectiveness of the degree of dispersion of the oil in steam varies little with the porportions of steam and oil within the above range. This is of particular advantage from the standpoint that the rate of steam fed to the reaction zone may be regulated exclusively on the basis of the operating requirements, and particularly the temperature which it is desired to maintain in the reaction zone.

A preheated dispersion of oil in steam prepared in the manner described above is admixed with the effluent from a partial combustion zone. The partial combustion zone, for example, is maintained at a temperature within the range of about 1800 to 3500° F. at a level where the reaction goes rapidly to completion. At temperatures above about 2400° F. the products of combustion comprise carbon monoxide and hydrogen substantially free from methane. At the lower temperatures, for example, in the range of 1800 to 2200° F. appreciable amounts of methane appear in the products along with hydrogen and carbon monoxide.

The amount and preheat temperature of the oil dispersion stream are adjusted such that the combined stream of oil dispersion and partial combustion products is at a temperature within the range of about 1000 to 1800° F. preferably within the range of about 1200 to 1600° F. The combined stream is contacted at said temperature with a cracking catalyst to effect cracking and reforming of the heavy oil components of the stream and production of a gas of high calorific value. The catalyst may be disposed as a fixed bed or may be in the form of pulverulent solids. Although substantially less carbon is formed in the process of this invention than is formed in other processes for the gasification of heavy oils, some carbonaceous deposits form on the catalyst. These deposits may be readily removed from fixed beds of catalyst by discontinuing processing, and burning off the carbonaceous deposits with oxygen or oxygen-containing gas streams, for example, air or air diluted with flue gas. When a fluidized solids catalyst is used, the catalyst may be readily separated from the product gases and a por-

tion continuously regenerated by passing to a fluidized bed regenerator where the carbonaceous deposits are burned with a stream of air.

Pressure in itself is not critical in the dispersion step. The temperature and pressure relationships relating to vaporization are well known. Steam and oil are passed through the dispersion coil at a pressure such that the steam-oil dispersion is discharged at a pressure at least as high as the subsequent gasification zones. A considerable pressure drop takes place in the dispersion coil due to resistance to flow which may be, for example, about 100 pounds per square inch.

In the generation of fuel gas it is desirable to operate the gas generation zone and cracking zone at a superatmospheric pressure, preferably within the range of about 150 to about 1500 pounds per square inch gage. By this means, gas is generated at a pressure high enough for distribution in pipe lines and mains without the necessity of compression. Pressure also exerts an effect on the partial oxidation reactions and the cracking reactions in that pressure favors formation of products of high calorific value.

Carbonaceous fuels generally may be employed in the partial combustion step of the process of this invention. For example, pulverized coal may be gasified by partial combustion with oxygen to provide a stream of carbon monoxide and hydrogen at temperatures in the range of about 1800 to 3500° F. In any event, the heavy oil dispersion prepared as described above is employed in the cracking step of the process of this invention.

An advantage of the process of this invention is that the tendency of heavy hydrocarbon oils to form carbonaceous deposits on the catalyst when employing these oils for catalytic gasification is substantially reduced. The uniform dispersion of oil in steam employed in this process avoids the formation of carbonaceous deposits caused by overcracking which occurs as a result of irregular wetting of catalyst by droplets of oil. The tendency of oil to form carbonaceous deposits during heating is avoided by my method of heating the oil dispersion since only a part of the heating is effected in tubular heaters and the final increase to cracking temperature is effected by injecting the dispersion into hot synthesis gas. Further, conducting the cracking reaction in the presence of a gas comprising carbon monoxide and hydrogen tends to suppress the formation of carbonaceous deposits.

Another advantage of this process is that steam-oil dispersions may be readily formed at superatmospheric pressures, for example about 100 to 1500 pounds per square inch. Dispersions formed in accordance with the method of this process permit the uniform distribution of charge components throughout a catalytic reactor equivalent to the distribution of completely vaporized charge oils. Accordingly this method provides an improved means to charge a heavy oil to a catalytic reactor under pressures at which the heavy oil could not be vaporized without cracking.

The accompanying Figure I diagrammatically illustrates one form of the process of this invention. Figure II illustrates another form of the process of this invention. Although the drawings illustrate arrangements of the apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or materials described.

Figure I illustrates a form of the process of this invention in which a dispersion of a heavy oil in steam is formed, a part of said dispersion is subjected to partial combustion and another part of said dispersion is admixed with the products of partial combustion and the combined stream contacted with cracking catalyst at cracking temperatures to produce a gas of high calorific value. Water is introduced into the system by pump **10** which feeds water to heating coil **11** in heater **12** where the water is converted to steam. The steam produced in coil **11** is discharged through line **13**. Heavy oil from an external source not shown is pumped at a controlled rate by pump **15** through line **16** and is combined with the stream from line **13** in line **17**. Pumps **10** and **15** for water and oil respectively permit accurate proportioning of the steam and oil. The mixture of oil and steam, which is at first rather crude, is developed into an intimate dispersion of oil particles in steam by passage through a long tubular zone at relatively high velocity, preferably in excess of 50 feet per second, so that the highly turbulent flow thoroughly and evenly disperses the oil droplets in the steam. In the form of the process illustrated in Fig. I, the steam-oil mixture passes through heating coil **18** in heater **19**. The oil is continuously injected into the stream of steam in desired proportions and subjected in heating coil **18** to a temperature within the range of about 300 to 1000° F. A part of the resulting steam-oil dispersion passes through lines **21** and **22**, flow control valve **23** and line **24** to burner **26** where it is mixed with oxygen from line **27** and discharged directly into gas generator **28**. Oxygen is introduced through line **27** into burner **26** at a rate controlled by regulator **29**. A suitable burner for the partial combustion of oil with oxygen is described in the copending application of Leon P. Gaucher, Serial Number 266,840, filed January 17, 1952, now Patent Number 2,810,433.

The generator **28** comprises a pressure vessel **30** provided with a suitable refractory and heat insulating lining **31** enclosing a compact, unpacked reaction chamber. Products of reaction flow through outlet **32** which communicate with cracking reactor **33**. Another part of the steam-oil dispersion in line **21** passes through line **34**, regulator **36** and line **37** and is continuously injected into gas generator outlet **32**. The hot product gases leaving generator **28** at substantially the temperature of the generator, in the range of about 1800 to 3500° F., are continuously contacted with steam-oil dispersion from line **37** to form a combined stream at a temperature within the range of about 1000 to 1600° F. and the combined stream passes into cracking reactor **33**.

Cracking reactor **33** comprises a pressure vessel **38** in which one or more beds of cracking catalyst **39** are disposed. Any of the well-known cracking catalysts may be used in the process of this invention. Iron group metal catalysts and bauxite, for example, are suitable; nickel catalysts or catalysts containing nickel and chromium are preferred. Cracking of the heavy oil and reaction of the synthesis gas in the combined stream to produce a high B.t.u. gas is effected at a temperature within the range of about 1000 to 1600° F. and at a pressure within the range of about 100 to 1500 pounds per square inch. Products are withdrawn from reactor **33** as the product gas of this process and are dicsharged for distribution or use not shown.

Although the use of the steam-oil dispersion of this process materially reduces the amount of carbonaceous deposits formed on the catalyst, it is necessary to periodically discontinue processing and remove said carbonaceous deposits. Processing is discontinued by closing regulators **23**, **29**, **36** and **42**. Air, from an external source not shown, is then introduced through line **43** and regulator **44** to line **37**. Air then passes through reactor **33** and burns the carbonaceous deposit off of the catalyst in bed **39**. Flue gas is withdrawn through vent line **46** and regulator **47**. After regeneration of the catalyst, regulators **44** and **47** are closed, and processing resumed by opening regulators **23**, **29**, **36** and **42**.

Figure II illustrates a form of the process of this invention in which coal is gasified by partial combustion with oxygen to form a gas comprising carbon monoxide and hydrogen, a steam-oil dispersion is formed as described heretofore, the partial combustion products and steam-oil dispersion are admixed and the combined stream is cracked in the presence of a fluidized solids catalyst to form heating gas of high calorific value.

Crushed coal from an external source not shown is fed into mixer 51 operated at atmospheric pressure wherein it is admixed with sufficient water from line 52 to form a fluid slurry. From the mixer 51 the slurry is passed through line 53 into a thickener 54. Excess water is eliminated from the slurry in thickener 54 and recycled to the mixer in line 56. Resulting slurry containing only sufficient water to render it fluid is withdrawn from thickener 54 through line 57 and charged at elevated pressure by means of pump 58 through line 59 to heating coil 61 in heater 62.

The water is vaporized in the heater dispersing the powdered coal in steam. The dispersion is passed through line 63 into separator 64 where excess steam is withdrawn for heating or other uses not shown through line 66 and regulator 67. Steam-coal dispersion is withdrawn from separator 64 through line 68 and is discharged into generator 69 through a suitable burner 71. Oxygen is admitted to burner 71 through line 72 to maintain the temperature in the generator within the range of 2200 to 3500° F., preferably in the range of about 2200 to 2800° F. Generator 69 may comprise a steel shell 73 designed to withstand the internal operating pressure which may be within the range of about 100 to 1500 pounds per square inch. The gas generator section is lined with a suitable refractory 74 to withstand the high temperatures generated within the gas generation zone and to protect the shell from overheating. A partition 76 divides the vessel into two separate zones, the gas generation zone 69 and a slag separator or slag pot 77. Product gases from the gas generator pass into the slag pot where hot gases are separated and withdrawn through line 78 and the slag falls to the bottom of the slag pot and is quenched by water introduced through line 79. Solidified slag and water are withdrawn for disposal through line 81.

Water is introduced through pump 79' and line 81' into heating coil 82 in heater 83 to generate steam. Steam from heating coil 82 discharges through line 84. Heavy oil from an external source not shown is pumped by pump 86 through line 87 and combined with the steam in line 84. The mixture of steam and oil is passed through line 88 to heating coil 89 in heater 91. The intimate dispersion of oil in steam formed by passage through heating coil 89 discharges through line 92 and is combined with the hot gases in line 78 to form a combined stream in line 93 at a temperature within the range of about 1000 to 1600° F. The combined stream in line 93 is contacted with regenerated catalyst from line 94 and is passed through line 96 and inlet cone 97 to cracking reactor 98. A fluidized bed of bauxite cracking catalyst 99 is maintained in reactor 98. The combined stream of oil-steam dispersion and partial combustion products is cracked in reactor 98 at 1400° F. and 300 pounds per square inch pressure to form high B.t.u. gas which passes through cyclone separator 101 and outlet line 102 for external use not shown. In the course of the cracking reaction a carbonaceous deposit forms on the catalyst. This carbonaceous deposit is continuously removed by withdrawing a portion of the catalyst from cracking reactor 98 through sandpipe 103 and regulator 104 for regeneration. Air from compressor 106 is discharged through line 107 to entrain catalyst from standpipe 103 and transfer it to regenerator 108 through transfer line 109 and regenerator inlet cone 111. A fluidized bed of catalyst 112 is maintained in regenerator 108 and the carbonaceous deposit on the catalyst is removed by combustion. Flue gas passes through cyclone separator 113 and is discharged through line 114 to the atmosphere. Regenerated catalyst is withdrawn from regenerator 108 through standpipe 94 and regulator 116 for recycle to the cracking reactor.

Example

A reduced crude oil characterized by a gravity of 14.4° API, a furol viscosity of 200 seconds at 122° F., an ash content of 0.1 weight percent and an ultimate analysis of 85.1 weight percent carbon, 11.0 weight percent hydrogen and 3.9 weight percent sulfur is converted to a high B.t.u. fuel gas by the process of this invention. Steam is generated at a rate of 12,668 pounds per hour and is admixed with 25,852 pounds per hour of the aforesaid oil preheated to a temperature of 220° F. The mixture at a pressure of 1000 pounds per square inch is passed through a heating coil at a velocity of 55 feet per second wherein the temperature is raised to 750° F. thereby generating a mist-like dispersion of oil in steam. Eighteen thousand two hundred and fifty-six pounds per hour of said dispersion comprising 12,252 pounds per hour of oil and 6,004 pounds per hour of steam are subjected to partial combustion with 13,700 pounds per hour of 95 percent oxygen at a temperature of 2500° F. and at a pressure of 475 pounds per square inch to form 618,000 cubic feet per hour of a gas having a heating value of 302 B.t.u. per cubic foot (dry basis).

Gas from the partial combustion zone at substantially the temperature of the partial combustion zone is admixed with 20,264 pounds per hour of the steam oil dispersion prepared above. The resulting mixture at a temperature of 1,580° F. and at substantially the pressure of the partial combustion zone is passed through a fixed bed of 15.9 cubic feet of a nickel cracking catalyst. Eight hundred sixty eight thousand cubic feet per hour of a fuel gas having a heating value of 575 B.t.u. per cubic foot (dry basis) are produced.

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

I claim:

1. A process for the generation of a fuel gas of high calorific value which comprises subjecting a carbonaceous fuel to partial combustion to form a gas comprising carbon monoxide and hydrogen at a temperature within the range of about 1800 to 3500° F., mixing said gas with a dispersion of heavy oil in steam to form a combined stream at a temperature within the range of about 1000 to 1600° F., said dispersion of heavy oil in steam being formed by introducing a heavy oil into a stream of steam and subjecting the resulting mixture of oil and steam to high turbulence effecting dispersion of the oil in the steam while maintaining a portion of the oil in the liquid phase, contacting said combined stream with a cracking catalyst under cracking conditions including a temperature within said range of 1000 to 1600° F., and recovering a composite gas of relatively high heating value as a product of the process.

2. A process for the conversion of a heavy oil to fuel gas of high calorific value which comprises introducing a heavy oil into a stream of steam, subjecting the resulting mixture of oil and steam to high turbulence effecting dispersion of said oil in steam while maintaining at least a portion of said oil in a liquid phase, introducing a part of said dispersion in admixture with oxygen into a partial combustion zone, effecting partial combustion of said oil to form a gas comprising carbon monoxide and hydrogen at a temperature within the range of about 1800 to 3500° F., admixing with said hot gas a part of said dispersion to form a combined stream at a temperature within the range of about 1000 to 1600° F., contacting said combined stream at said temperature with a cracking catalyst, and recovering a composite gas of relatively high heating value as a product of the process.

3. The process of claim 1 wherein the amount of steam employed to form said dispersion is within the range of about 20 to about 300 percent by weight of the weight of the oil.

4. The process of claim 2 wherein the dispersion of said oil is developed by highly turbulent flow of the

mixture at a temperature within the range of about 300 to 1000° F.

5. The process of claim 2 wherein said cracking catalyst comprises an iron group metal.

6. The process of claim 2 wherein said cracking catalyst comprises nickel.

7. The process of claim 2 wherein said combined stream is contacted with said catalyst at a pressure within the range of about 100 to 1500 pounds per square inch gauge.

8. A process for the generation of a fuel gas of high calorific value which comprises subjecting a carbonaceous fuel to partial combustion to form a gas comprising carbon monoxide and hydrogen at a temperature within the range of about 1800 to 3500° F. and at a pressure within the range of about 100 to 1500 pounds per square inch, mixing said gas comprising carbon monoxide and hydrogen with a dispersion of heavy oil in steam to form a combined stream at a temperature within the range of 1000 to 1600° F., said dispersion of heavy oil in steam being formed by introducing a heavy oil into a stream of steam in proportion within the range of about 20 to 300 percent by weight of steam basis the weight of heavy oil and passing the resulting mixture of oil and steam at a velocity in excess of 20 feet per second through a tubular conduit having a length at least 100 times its inside diameter effecting dispersion of said oil in said steam while maintaining a portion of said oil in the liquid phase, contacting said combined stream with an iron group metal cracking catalyst at a temperature within the range of about 1000 to 1600° F., and recovering a composite gas of relatively high heating value as product of the process.

9. The process of claim 8 wherein said mixture of oil and steam is subjected to heating in at least a portion of said tubular conduit to a temperature within the range of about 300 to 1000° F.

10. The process of claim 8 wherein said iron group metal comprises nickel.

11. The process of claim 8 wherein said combined stream is contacted with said catalyst at a pressure within the range of about 100 to 1500 pounds per square inch.

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