

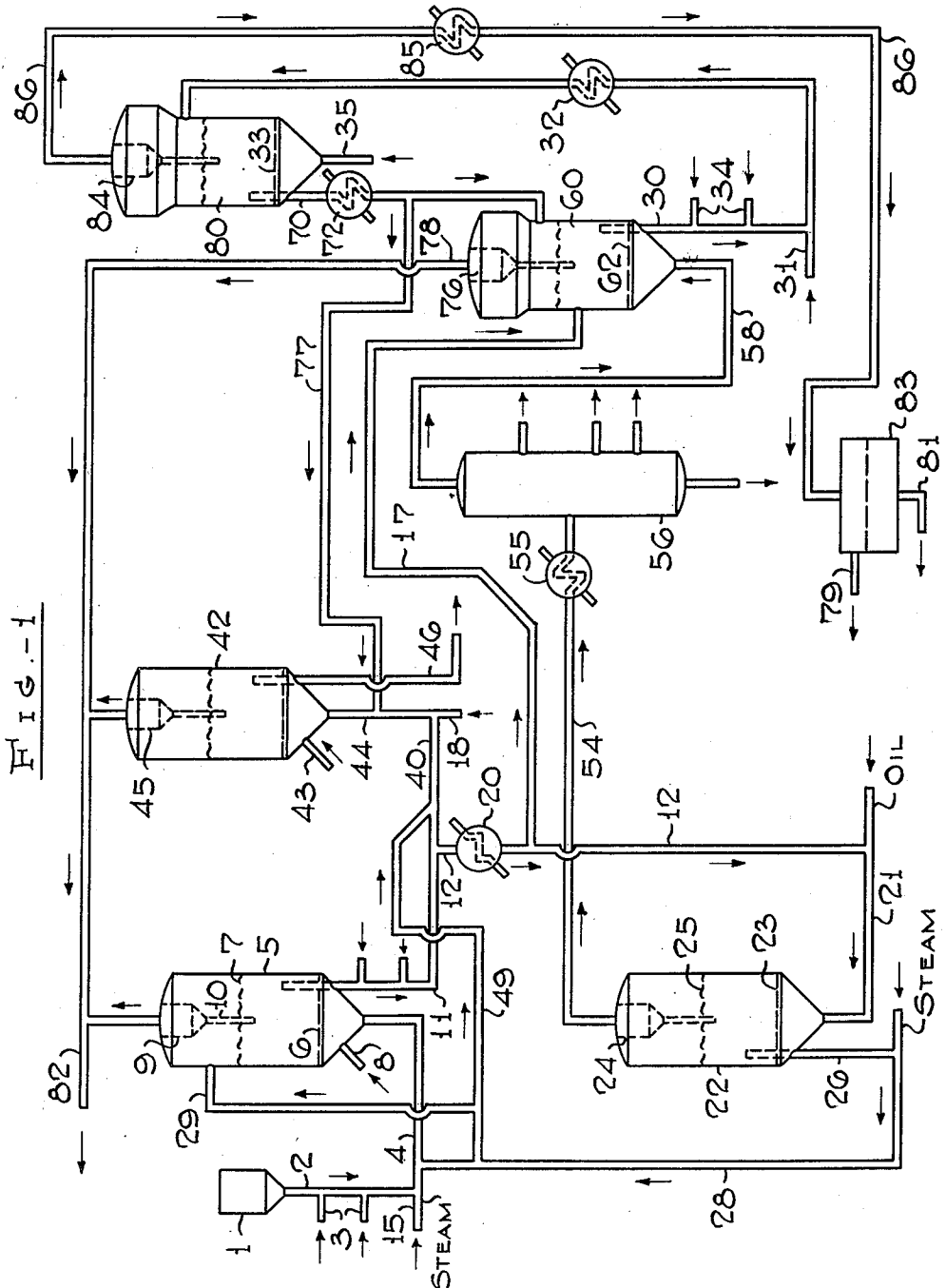
Nov. 25, 1952

S. B. SWEETSER

2,619,449

METHOD OF CATALYST PRODUCTION AND UTILIZATION

Filed Dec. 30, 1948



Sumner B. Sweetser Inventor

By J. Cashman Attorney

UNITED STATES PATENT OFFICE

2,619,449

METHOD OF CATALYST PRODUCTION
AND UTILIZATIONSumner B. Sweetser, Cranford, N. J., assignor to
Standard Oil Development Company, a corporation of Delaware

Application December 30, 1948, Serial No. 68,145

16 Claims. (Cl. 196—52)

1

The present invention relates to improvements in the production of a synthesis or fuel gas in combination with the preparation of catalytic material of high adsorptive capacity and for the employment of the same in processes requiring materials of high surface area. In particular, the invention relates to a method for producing water gas from coke or coal and employing the coke withdrawn from the water gas generator in catalytic reactions such as in reforming or cracking naphtha to improve the quality of the latter or in non-catalytic processes such as absorbing hydrocarbon constituents from tail gases of a hydrocarbon synthesis reaction.

This invention is a continuation-in-part of the applicant's pending application Serial No. 123 filed January 2, 1948, now abandoned. In the latter there was disclosed a process whereby coke is continuously withdrawn from a water gas generator and used as a catalyst in chemical reactions requiring the use of highly adsorbent catalytic material such as catalytic cracking or reforming of hydrocarbons. It has now been found that the surface area of a low temperature coke undergoing gasification in the water gas reaction in the water gas generator goes through a maximum as shown in the following tabulation.

Surface area versus coke carbon content

Percent Carbon	Surface Area, Square Meters per Gram
84 (Fresh).....	0.04
56.....	680
27.....	360
17.....	200
5.....	60

This discovery has now been applied to the combination process of preparing hydrocarbon synthesis or fuel gas by coal gasification and also preparation of highly adsorptive char and employing the latter in chemical and non-chemical processes such as catalytic cracking or reforming of naphtha and/or gas oil hydrocarbons and adsorption of low molecular weight hydrocarbons. This discovery enables one thus to obtain both the highest possible surface area and concomitant activity of the char, and also to obtain maximum utilization of the carbon comprising the char.

In accordance with the present invention the water gas generation system is preferably operated in two or more stages and coke is withdrawn from the first stage for utilization in the catalytic or adsorption processes. The distribu-

2

tion of load between the stages is such that the coke withdrawn from the first stage has a surface area of at least about 500 square meters per gram. The balance of the coke not used for catalyst purposes is then sent to a subsequent water gas generation stage or stages and substantially consumed in the production of water gas for fuel or hydrocarbon synthesis gas generation purposes, in accordance with conventional water gas production techniques.

In one form of operation of this combination process employing the fluidized solids technique, steam and oxygen are injected into a reactor containing a fluidized bed of coal or coke under suitable conditions of temperature and pressure to obtain a conventional water gas reaction with the oxygen being the combustion agent for supplying the heat for maintaining the reaction. Fresh coke or coal is added to the first stage generator as required to maintain the desired inventory of the system. At the desired level of carbon content of the coke or desired extent of its surface area, the latter is continuously withdrawn from the first gasification stage. As required, a portion of this withdrawn carbon or coke of high surface area is then passed to a fluidized solids cracking or reforming reactor and/or to a fluidized solids adsorber. The balance of the carbon not sent to a subsequent catalytic or adsorption stage is then sent to a second gasification stage wherein the carbon content is reduced to any desired level in accordance with known and conventional coal gasification and water gas production techniques.

The hot carbonaceous solids withdrawn from the first stage water gas reactor and not sent to the second stage water gas reactor are passed through a standpipe and heat exchangers and, when they are to be used in naphtha cracking and reforming, are cooled, picked up by a stream of hydrocarbons to be cracked or reformed and are injected into a catalytic conversion zone where cracking or reforming of the hydrocarbons takes place under suitable conditions in fluidized form. Cracked or reformed products are withdrawn overhead and used catalyst is continuously withdrawn from the cracking or reforming zone, suspended in steam and returned to a water gas generation zone.

The carbon withdrawn from the first stage water gas generation zone is also advantageously employed in adsorbing and recovering the low molecular weight normally gaseous hydrocarbons produced in the cracking or reforming operation described above. This adsorption is most advan-

tageously performed by the fluidized solids technique as detailed more fully below.

In this combination process, the catalyst regenerator ordinarily associated with the cracking or reforming system, is entirely eliminated, the spent catalyst being returned to the water gas generator for conversion to CO and H₂. Thus the investment cost of a catalyst regenerator is entirely eliminated by this combination process. Another advantage of this process is the extreme cheapness of the catalyst and/or adsorbent. Conventional cracking or reforming catalysts cost about \$.15 to \$.50 a pound and conventionally activated carbons used in fluidized adsorption of normally gaseous hydrocarbons which are prepared by conventional means such as by physical or chemical processes by steam, zinc chloride, potassium sulfide, etc., are far more expensive than the material described in the present invention. In the present invention, since the catalyst is not used up in, but used by the process, the only cost is for heating it back to water gas generation temperature. Furthermore, the carbon which has gradually deposited on the catalyst in the gas oil cracking or naphtha treating step of the combination process, is advantageously utilized in the water gas reaction process, whereas in conventional processes, it is lost. Another obvious advantage of a plant in which both water gas is produced by coal or coke gasification and also in which naphtha is cracked or reformed, is that the light hydrocarbon gases resulting from naphtha treating processes, are readily adsorbed by the coke of high surface area produced by the gasification step in the first water gas production stage. Water gas may be generated by the so-called one or two vessel systems wherein the spent catalyst from the hydrocarbon conversion zone or deactivated adsorbent from the hydrocarbon fluidized adsorption zone may be sent either to the heating zone or water gas generation zone, preferably of the second stage system. The meaning of the terms "one vessel" and "two vessel" systems will be made more clear hereinafter. As used in the present invention "one vessel" refers to a water gas generation unit in which heat is produced within the gasification zone by an exothermic oxidation reaction. In a "two vessel" system, heat is generated in a separate exothermic reaction zone and transferred to the gasification zone of the water gas generation unit as the sensible heat of the circulating char. Thus in the present invention, any combination of "one vessel" and "two vessel" water gas generation units operating in series in two or more stages with coke draw-off between stages may be employed.

In one modification of the invention, the spent catalyst from the conversion zone is injected in the disperse phase near the top of the water gas generation zone so that the adsorbed hydrocarbons on the coke are cracked to lower molecular weight hydrocarbons and removed with product gas without being completely decomposed to carbon and hydrogen as they would then to be because of longer contact time if injected into the dense phase. By this method, the heating value of the product gas is appreciably increased. In another modification of the invention, the light ends from the cracking or reforming operation are mixed with the water gas to increase its calorific value as described more fully below. It is apparent that these two modifications are of importance when the product gases are to be

used for fuel rather than as hydrocarbon synthesis feed gases.

The spent coke used as catalyst in the cracking or reforming process, or the deactivated adsorption char is preferably recycled to the water gas generation zone. If the quantity of carbon withdrawn from the first stage and used as catalyst or adsorbent is small in relation to the total stream of carbon withdrawn from the first stage, the used catalyst from the subsequent chemical reaction is preferably recycled to the first water gas reactor, though under certain circumstances, it may be desirable to recycle the same to the second stage reactor. However, if such returned char represents a major portion of the material withdrawn from the first stage, the contaminated char is preferably returned to the second stage to maintain the high carbon content level of the first stage.

In the accompanying drawing are shown diagrammatically, systems in which modifications of the invention may be carried into effect.

The accompanying figure is a diagrammatic representation of a combination process incorporating a two stage water gas generation system. For illustrative, but not limiting purposes, both stages incorporate so-called "one-vessel" systems for water gas generation. It is understood that the two stages may comprise two "one-vessel" systems, two "two-vessel" systems or any combination of such systems.

Referring now to this figure, fresh coke or coal ground to a finely divided form, preferably capable of passing through a 60 mesh screen and even through a 100 mesh screen, is fed from a supply hopper 1 into a standpipe 2 which is provided with a plurality of taps 3 through which slow currents of air, superheated steam, or other aerating gas may be injected, in order to fluidize the coke or coal therein. The fluidized material is introduced into line 4 wherein it is dispersed and suspended in a stream of superheated steam containing spent catalyst introduced through line 23. The mixture of fresh coke or coal, spent catalyst, and steam is discharged into the bottom of water gas generator 5, the suspension entering below a screen or grid 6 and then passing upwardly. Due to the superficial velocity of said steam which is maintained within the limits of from about 0.2 to 3 feet per second, the coke or coal is formed into a dense, turbulent, ebullient mass resembling a boiling liquid and having a well defined upper level 7. An oxidizing gas such as oxygen is admitted through line 8, and may also be added to the fluidized stream in line 4 through line 15. The steam and carbonaceous material react to form water gas, a gasiform product containing carbon monoxide and hydrogen. The temperature in this zone is in the order of 1700° to 1900° F. and the gas pressure is preferably from atmospheric to about 40 p. s. i. g., although pressures up to 400 p. s. i. g. or higher may, under certain conditions, be employed. The heat required for the reaction is furnished substantially by the combustion of part of the carbonaceous solids in reactor 5 by the oxygen admitted through lines 8 and 15. The total supply of oxygen is carefully controlled to generate sufficient heat by combustion to satisfy the heat requirements of the process. It is understood that under the reaction conditions, when fresh coal is employed as the fresh feed it is coked in the fluidized bed in generator 5, so that the solid product subsequently withdrawn is referred to as coke rather than coal.

5

The gaseous products are withdrawn from generator 5 through a dust separator 9 such as a cyclone which has a dip line 10 extending below the upper level 7 of the fluidized bed for returning separated dust particles. The water gas may be treated for the removal of sulfur or other impurities and then delivered to storage, preferably after combination with the product from second stage water gas generator 42.

The hot carbonaceous solids are allowed to remain within reactor 5 for a sufficient period of time to attain the surface area desired, usually greater than 500 square meters per gram, and then the hot carbonaceous solids are continuously withdrawn from water gas generator 5 through aerated bottom draw-off pipe 11 which extends above grid 6. The period of residence of the coke or coal within reactor 5, in order to attain the high surface area desired, depends upon a plurality of operating factors such as type of coal fed, temperature of gas generation, ratio of steam to coke fed in the reactor, solids hold-up time, etc. In accordance with the invention and depending upon the size of the subsequent cracking, reforming and/or adsorption operation, part of the stream of hot carbonaceous solids is passed through line 12 and through suitable heat exchangers where the temperature of said solid stream is reduced to about 1200° F. As a heat exchange medium, steam which is to be superheated for use in generating water gas in generator 5 and/or generator 42, is advantageously employed. Some cooling is also effected by using low temperature steam as aeration gas in standpipe 12. Another portion of hot carbonaceous residue of high surface area may be withdrawn as a side stream through line 17 and employed in the fluidized solid operation of adsorbing light hydrocarbons from the cracking process as detailed more fully below. The balance of the hot carbonaceous residue which is now to be substantially completely converted to water gas, is withdrawn through line 40. Superheated steam is added to the carbonaceous material to disperse and suspend the same and to convert it into a form capable of flowing through pipes, valves and similar equipment much like a liquid. Steam for fluidizing may be admitted through line 18. The fluidized stream is passed through line 40 into the lower portion of a water gas generator 42 which is essentially the same type as vessel 5 and it is fitted at its lower end with an inlet line 43 for admitting oxidizing gas such as oxygen. Said oxidizing gas may also be added to the fluidized stream in line 40 through line 44.

The fluidized carbonaceous material in generator 42 is in the form of a dense, turbulent mass fluidized by the upwardly flowing gases and superheated steam. The gasification of the carbon by the steam in the second stage reactor proceeds rapidly to form carbon monoxide and hydrogen. The heat required for the endothermic gasification reaction in this "one vessel" unit is supplied by the combustion of part of the carbonaceous solids in reactor 42 by the oxygen admitted through line 43 and/or 44. The total supply of oxygen is carefully controlled to generate sufficient heat by combustion to satisfy the heat requirements of the process. The temperature maintained in the reaction zone 42 is in the range of about 1700° to 1900° F. and the pressure may be up to 400 p. s. i. g. or higher. The gasification products are withdrawn through a dust separator 45 such as a cyclone and may go directly to product storage, to purification for sulfur removal and

6

to the hydrocarbon synthesis plant with or without being first blended with the gasification products from the primary water gas reactors. If the water gas is to be used as a fuel gas, it may be further enriched with normally gaseous hydrocarbons to increase its calorific content in a manner described more fully below.

Within second stage reactor 42, the coke is consumed in the gasification reaction to any desired residual carbon content, and ash or residue is discharged through line 46.

The portion of carbonaceous solids of high surface area withdrawn from first stage generator 5 which is not passed to the second stage generator nor withdrawn through line 17 as adsorbent material for light hydrocarbon adsorption described below, and which is to be used as a cracking or reforming catalyst, is passed through standpipe 12 and heat exchanger 20 as described above and the solids cooled to about 1200° F. are picked up in line 21 by the hydrocarbon stream which is to be cracked or reformed and the mixture is injected into a second reaction zone 22, where cracking or reforming of the hydrocarbons takes place under suitable reaction conditions in the fluidized form. In general, cracking operation in 22 may be carried out both on synthesis gas oil and on petroleum fractions whereas in the case of naphtha reforming, the feed is usually a petroleum cut. Reactor 22 which may be a conventional fluid solids reaction vessel consists essentially of a cylindrical chamber fitted at its lower end with a conical base to which the stream of naphtha or gas oil and cracking or reforming catalyst may be admitted through line 21, a grid 23 for dispersing the stream and a dust separator 24. Reactor 22 is operated preferably at about 1000° to 1100° F. when reforming naphtha and about 50 to 100 degrees lower when cracking gas oil. The pressure maintained in reactor 22 is dependent upon the pressure maintained in the first stage water gas generator 5. It is desirable that the hydrocarbon conversion zone and the water gas generation zone be operated at essentially the same pressure as it is mechanically not generally feasible to circulate fluidized solids between widely different pressure levels. In hydrocarbon converter 22 the solid carbonaceous high surface area particles are suspended and fluidized by the upwardly flowing gasified oil or naphtha stream and are maintained in an ebullient state resembling a boiling liquid having a clearly defined upper level 25. As a result of the cracking or reforming operation, carbon is deposited on the surface of the catalyst thereby inactivating the latter. For effective operation of the hydrocarbon conversion unit the residence time of the catalyst in the hydrocarbon conversion unit is 2 to 10 minutes if a gas oil cracking operation is carried out, and 5 to 20 minutes if naphtha is being reformed. The reaction products are withdrawn upwardly through dust separator 24 and are passed through heat exchange equipment to the products recovery system which is described in more detail below.

Used catalyst which has accumulated a carbonaceous deposit is continuously withdrawn from reaction zone 22 through line 26 which extends through screen or grid 23 into the dense catalyst bed. The spent catalyst is discharged into 28, suspended by steam, and is transferred to line 4 and thus recycled to first stage water gas generator 5. If desired, instead of trans-

ferring used catalyst to generator 5 it may be passed to second stage generator 42 through lines 49 and 40. As hereinbefore indicated the ash in the system is controlled by removal through line 46. Fresh coke or coal is added and ash containing solids is withdrawn from the system at such a rate as to maintain an equilibrium mixture of about 50 to 80% carbon on the carbonaceous solids withdrawn from first stage generator 5.

Returning now to the cracked or reformed products withdrawn overhead from hydrocarbon conversion zone 22, the vaporized cracked or reformed products are passed through line 54 to a cooler 55 and thence to fractionation tower 56. Within tower 56, fractionation by any known process may be used to separate higher and heavier hydrocarbons from low molecular weight hydrocarbons boiling in the range of about C₅ and below. Thus overhead from tower 56 is withdrawn the hydrocarbon fraction boiling below about 100° F. and this mixture is passed via line 58 to fluidized adsorber 60. From fractionator 56 cuts comprising heating oil, gas oil, and gasoline may be withdrawn as side streams and further processed in any conventional method known in the art.

Fluidized adsorption vessel 60 is preferably in the form of a vertical cylinder with a conical base having a grid or screen 62 to support the bed of fluidized adsorption char and to provide suitable distribution for the gasiform fluidizing medium, here the light hydrocarbons, uncondensable gases, and inert gases. As required, carbon of high surface area may be withdrawn from line 12 via line 17 and passed to adsorber 60. Within adsorber 60 a mass of the finely subdivided solid adsorbent which, if desired, may have undergone a screening or classifying process (not shown) wherein particles larger than about 60 mesh and smaller than about 325 mesh may have been rejected, is maintained in the form of a dense, turbulent mass having a well defined upper level. Adsorbent material may be added not only through line 17 but also from desorber 80 through line 70. Desorbed carbon is supplied to an upper portion of vessel 60 from stripper vessel or desorber 80 through line 70 and cooler 72. In order to provide a countercurrent action between the adsorbent char and the upflowing gasiform medium, adsorber 60 preferably contains packing material such as ceramic rings or other inert material known in the art. The superficial velocity of the gas within adsorber 60 is such as to maintain the finely divided adsorbent in a fluidized condition. The pressure within 60 is of the same order of magnitude or only slightly lower than that maintained in hydrocarbon conversion reactor 22.

The gasiform fluidizing medium which has now been scrubbed substantially free of hydrocarbons containing three or more carbon atoms is now withdrawn upwards from above the disperse phase in adsorber 60. Adsorbent fines entrained by the upflowing gas stream are substantially removed by the expanded section of adsorber 60 where gas velocity is sufficiently decreased so that the gas will no longer support any significant quantity of solids and most of the entrained particles drop back into the fluidized mass. The scrubbed fluidizing medium which comprises mostly C₁ and C₂ hydrocarbons is passed through gas-solids separating equipment such as cyclone 76 and is withdrawn overhead through line 78.

If it is desired to use the water-gas for fuel

rather than for hydrocarbon synthesis, the calorific value of the gas is substantially increased by adding thereto, the C₁ and C₂ gases resulting from the cracking or reforming operation which are efficiently recovered and separated from valuable higher boiling hydrocarbons in the manner described and which have been removed from fluidized solids adsorption vessel 60 through line 78. These gases are mixed with the CO and H₂ gases resulting from the water-gas reaction in line 82 and a fuel gas of high B. t. u. content is thus obtained. In another modification of the invention the used catalyst from the hydrocarbon conversion zone 22 may be directly injected in the disperse phase near the top of water-gas generation zone 5 by passage through lines 28 and 29 so that adsorbed hydrocarbons on the coke are cracked to low molecular weight hydrocarbons and removed with the product gas without being decomposed completely to carbon and hydrogen as would tend to be the case if injected into the dense phase.

Returning now to the absorption unit 60, a stream of char wherein are adsorbed lower molecular weight hydrocarbons such as C₃ and higher is continuously withdrawn from adsorber 60 through line 30 which extends into the fluid bed above grid 62. The solids are picked up by a stream of steam in line 31 and are conveyed via heater 32 to an upper portion of stripper vessel 80 which is preferably located in a position elevated in respect to adsorber 60. To aid in the conveyance of the solids through the lines, aeration fluid such as steam may be supplied through aeration taps 34.

Stripping vessel 80 is a tower of design similar to adsorber 60 comprising a lower conical and upper expanded section and supplied with distribution grid 33 and similarly containing trays or packing material to effect countercurrent flow of the solid material with respect to the stripping steam admitted through line 35. In stripper 80 fluidized conditions are maintained and stripping of the adsorbed hydrocarbons from the adsorption medium occurs while the latter is in the form of a dense fluidized bed. The pressure in stripper 80 is of the same order of magnitude as in adsorber 60 and the temperature such that all of the adsorbed hydrocarbon material is desorbed by the steam. If desired, additional heat may be supplied to stripper 80 through external or internal steam coils (not shown).

Finely desorbed carbon particles are continuously withdrawn from the fluidized bed in stripper 80 through line 70, passed through cooler 72 and then to the upper section of adsorber 60 for further adsorption of light hydrocarbons from the overhead gases from fractionator 56.

From above the dense bed in stripper 80, steam and desorbed hydrocarbons are passed through a gas solids separator 84 and thence the vapors are passed through line 86 and cooler 85 to separator 83. In the latter equipment, condensation of steam and of relatively higher boiling hydrocarbons occurs. The lower aqueous layer may be withdrawn through line 81 and discarded and the hydrocarbons layer passed via line 79 to the gasoline recovery system for further processing if desired, or for blending to produce high octane motor fuel. From time to time as the adsorbent carbon loses activity, spent carbon may be withdrawn from line 70 via line 77 and passed to line 40 for gasification in water gas generator 42.

It will be understood that the embodiment of the invention as described above admits of nu-

merous modifications apparent to those skilled in the art. Thus instead of coke or coal, any carbonaceous materials which on heat treatment in the water gas generator produce a high surface area carbonaceous solid may be used. Heat exchange systems may be installed in the process to effect heat economies and to adjust temperatures in the respective reaction zones. Furthermore, the catalytic and non-catalytic properties of the char when produced as in the process of the present invention by a water gas reaction are not limited to the catalytic cracking or conversion of hydrocarbons and to adsorption of low molecular weight hydrocarbons. For example, the char may be used in place of bauxite for the treatment of hydrocarbons synthesis products in order to eliminate oxygen and to improve gasoline stability. If desired, the char withdrawn from reactor 5 may be impregnated with another catalytic material or with a promoter promoting various types of chemical reactions and then employed in such reactions.

An example of this use is the impregnation of the char with a sulfide of tungsten or molybdenum to produce a sulfactive hydrogenation catalyst. A further example is the impregnation of char with silver or vanadium for use as an oxidation catalyst.

While the foregoing description and exemplary operations have served to illustrate specific applications of the invention, modifications apparent to those skilled in the art are within the scope thereof.

What is claimed is:

1. The method of conducting chemical reactions employing a highly adsorbent carbonaceous material which comprises passing a stream of finely divided carbonaceous solid material selected from the group consisting of coal and coke passing through a 60 mesh screen from an external source into an initial gasification zone, forming a fluidized mass of solids therein, subjecting said mass to a gasification reaction with steam at a temperature within the range of about 1700°-1900° F. for a sufficient period of time to form a volatile product comprising carbon monoxide and hydrogen and a solid gasification residue of high surface area of at least about 500 square meters per gram and containing on the average about 50-80% carbon, withdrawing said volatile product from said initial gasification zone, withdrawing the said residue from said initial gasification zone, charging a portion of said withdrawn residue to a separate zone wherein it is maintained in the form of a fluidized mass, contacting said last-named fluidized mass in said last-named zone with hydrocarbons at conditions conducive to the deposition of carbonaceous deposits on said last-named mass, passing the balance of the material withdrawn from the initial gasification zone to a second gasification zone, and subjecting said material in said second gasification zone to a gasification reaction with an oxidizing gas at about 1700°-1900° F. to produce a fuel gas.

2. An improved process for producing valuable fuels which comprises passing a stream of finely divided carbonaceous solid material selected from the group consisting of coal and coke passing through a 60 mesh screen into a gasification zone, forming a fluidized mass of solids therein, subjecting said mass to a gasification reaction with steam at temperatures of from about 1700°-1900° F. for a time sufficient to produce a gas rich in H₂ and CO and a solid gasification residue of at

least about 500 square meters per gram surface area and containing on the average about 50-80% carbon, withdrawing from said gasification zone a gas rich in H₂ and CO, separately withdrawing from said gasification zone a stream of said residue, passing a portion of said stream into a hydrocarbon conversion zone, contacting said portion in said conversion zone with hydrocarbons boiling in the gas oil range at hydrocarbon conversion conditions and separately withdrawing a hydrocarbon fuel comprising gasoline from said conversion zone.

3. The process of treating carbonaceous solids which comprises subjecting finely divided carbonaceous solids selected from the group consisting of coal and coke in a reaction zone in the form of a dense turbulent fluidized mass to a water gas reaction with steam, continuing said reaction until the average carbon concentration of said solids is reduced to about 50-80 wt. per cent and recovering from said zone a solid gasification residue of said reduced average concentration having a surface area of at least 500 square meters per gram.

4. The process of producing a high calorific fuel gas which comprises passing a stream of finely divided carbonaceous solids selected from the group consisting of coal and coke and steam into a water gas generation zone, maintaining said solids in said zone as a fluidized bed at water gas generation conditions, withdrawing from said zone a gas rich in CO and H₂, withdrawing from said zone a stream of carbonaceous solid particles of high surface area, passing at least a portion of said solid particle stream into a hydrocarbon conversion zone, maintaining a fluidized bed of said particles in said zone, contacting said particles with hydrocarbons at temperatures of from about 950° to 1100° F. in said conversion zone, withdrawing said particles from said zone, injecting at least a portion of said particles into said water gas generation zone at a point above said bed so as to strip adsorbed hydrocarbons from said solids and crack said stripped hydrocarbons to low molecular weight hydrocarbons, and withdrawing said cracked hydrocarbons along with a gas rich in CO and H₂.

5. The process of producing a high calorific fuel gas which comprises passing a stream of finely divided carbonaceous solids selected from the group consisting of coal and coke and steam into a water gas generation zone, maintaining said solids in said zone as a dense fluidized bed at water gas generating conditions, withdrawing from said zone a gas rich in CO and H₂, withdrawing from said zone a stream of finely divided carbonaceous solid particles of high surface area, passing at least a portion of said solid particle stream into a hydrocarbon conversion zone, maintaining a fluidized bed of said particles in said zone, contacting said particles with hydrocarbons at temperatures of from about 950° to 1100° F. in said conversion zone, maintaining a contact time of said particles with said hydrocarbons for about 2 to 20 minutes, removing from said conversion zone a gas comprising C₁ and C₂ hydrocarbons, withdrawing carbonaceous particles from said hydrocarbon conversion zone, injecting said particles into said water gas generation zone at a point above said dense fluidized bed so as to strip adsorbed hydrocarbons from said solids and crack said stripped hydrocarbons to low molecular weight hydrocarbons, withdrawing said cracked hydrocarbons along with the gas rich in CO and H₂, and adding to said

11

mixture of gases, the gas comprising C₁ and C₂ hydrocarbons withdrawn from said hydrocarbon conversion zone.

6. The process of treating carbonaceous solids which comprises subjecting carbonaceous solids selected from the group consisting of coal and coke in a reaction zone to a water gas reaction with steam, continuing said reaction until the average carbon concentration of said solids is reduced to about 50-80 wt. per cent and recovering from said zone a solid gasification residue of said reduced average carbon concentration having a surface area of at least 500 sq. meters per gram.

7. The process of producing fuel gas and activated char from carbonaceous solids which comprises subjecting carbonaceous solids selected from the group consisting of coal and coke in a gasification zone to a water gas reaction with steam, continuing said reaction until the average carbon concentration of said solids is reduced to about 50-80 wt. per cent, withdrawing from said zone a fuel gas containing H₂ and CO, and recovering from said zone a solid gasification residue in the form of activated char of said reduced average carbon concentration having a surface area of at least 500 sq. meters per gram.

8. The method of producing volatile fuels which comprises passing a stream of finely divided carbonaceous solids selected from the group consisting of coal and coke into the first stage of a system consisting of at least two separate gasification stages, forming a fluidized mass of solids in said first stage, subjecting said mass to a gasification reaction with steam at a temperature within the range of about 1700°-1900° F. for a sufficient period of time to form a gasiform product comprising CO and H₂ and a solid adsorbent gasification residue of a high surface area of at least about 500 sq. meters per gram having an average carbon concentration of about 50 to 80%, withdrawing said residue from said first stage, charging a portion of said withdrawn residue to a separate zone wherein it is maintained as a fluidized mass, carrying out a hydrocarbon conversion process in said last-named zone requiring the use of high surface area solids and causing a reduction in the surface activity of said solids, passing another portion of said withdrawn residue to a second stage of said system, subjecting said other portion in said second stage to a gasification reaction with an oxidizing gas to produce a fuel gas at about 1700°-1900° F., withdrawing carbonaceous solids of reduced surface activity from said separate zone and returning at least a portion of said withdrawn solids to said system to convert therein at least a substantial portion of their carbon content into a fuel gas.

12

9. The method of claim 8 wherein said process is a hydrocarbon conversion reaction in the course of which carbonaceous deposits are formed on the solids in said separate zone.

10. The method of claim 8 in which said withdrawn solids are returned to said second stage.

11. The process of claim 1 in which carbonaceous solid material is withdrawn from said hydrocarbon contacting zone and said last-named withdrawn material is recycled to said first-stage gasification zone.

12. The process of claim 1 in which carbonaceous solid material is withdrawn from said hydrocarbon contacting zone and said last-named withdrawn material is recycled to said second stage gasification zone.

13. The process of claim 2 wherein heat is supplied to said gasification zone by feeding oxygen to said zone.

14. The process of claim 2 wherein a portion of said stream of high surface area carbonaceous solids withdrawn from said gasification zone is passed to a fluidized solids adsorption zone and is employed in adsorbing light hydrocarbon vapors and gases.

15. The process of claim 14 wherein said light hydrocarbon vapors and gases are produced in said hydrocarbon conversion zone.

16. The process of claim 2 comprising maintaining a fluidized bed of said solids in said hydrocarbon conversion zone by a stream of vaporized normally liquid hydrocarbons boiling in the gas oil range, maintaining a residence time of said particles in said zone of from about 2 to 20 minutes, maintaining a temperature in said zone of from about 950°-1100° F., and withdrawing valuable liquid and gaseous hydrocarbons from said conversion zone.

SUMNER B. SWEETSER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,875,199	Parkman	Aug. 30, 1932
2,436,938	Scharmann et al.	Mar. 2, 1948
2,443,714	Arveson	June 22, 1948
2,445,328	Keith	July 20, 1948
2,482,187	Johnson	Sept. 20, 1949
2,476,472	Arnold et al.	July 19, 1949

OTHER REFERENCES

Godel, "Chemical Engineering," July 1948, pages 110-111.