

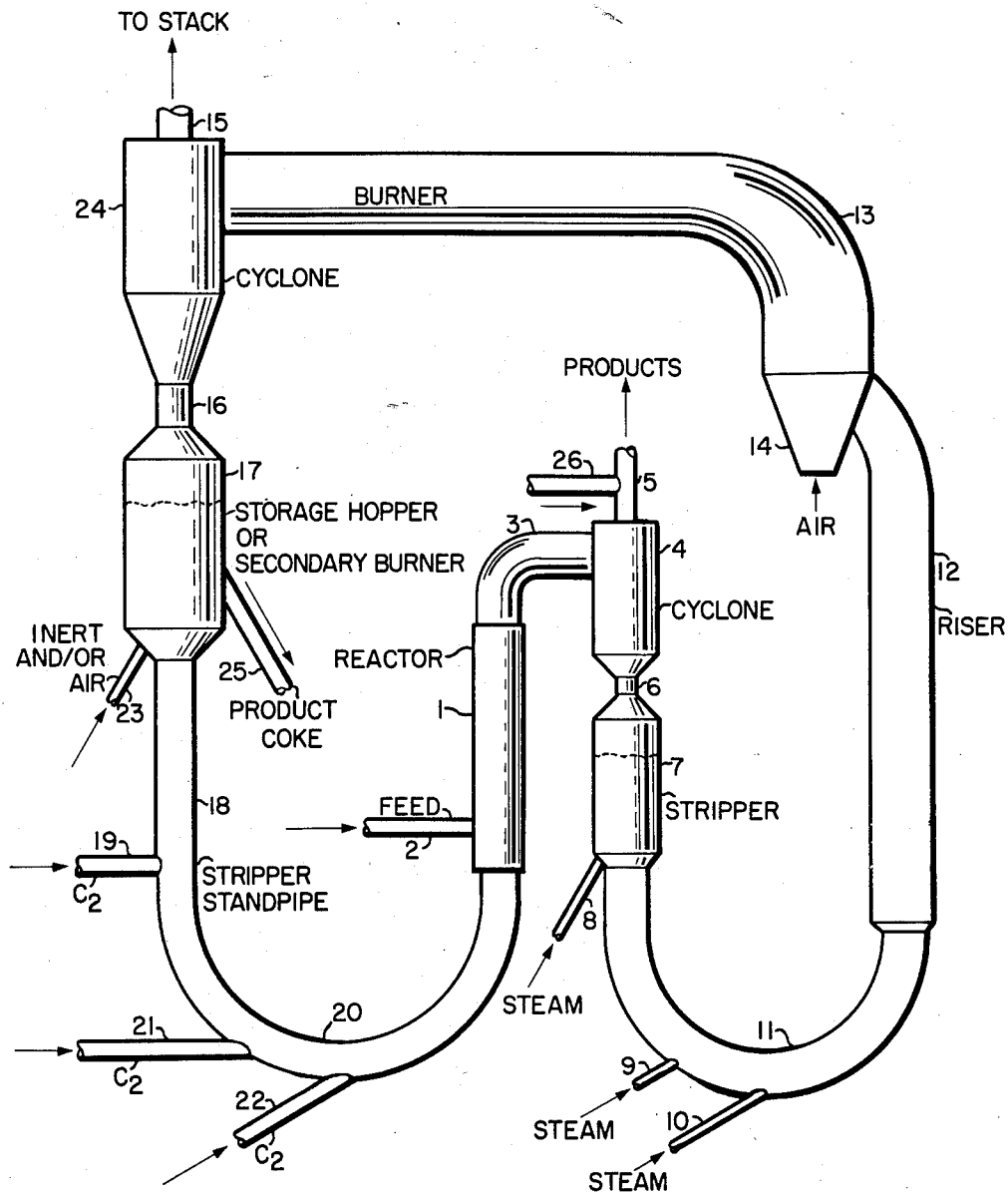
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USE OF NORMALLY GASEOUS HYDROCARBON FOR STRIPPING OF CIRCULATING COKE IN A FLUIDIZED COKING PROCESS

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**USE OF NORMALLY GASEOUS HYDROCARBON FOR STRIPPING OF CIRCULATING COKE IN A FLUIDIZED COKING PROCESS**

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6 Claims. (Cl. 202—14)

The present invention relates to an improved process wherein heavy hydrocarbon oils are contacted at elevated temperatures with finely divided inert particulate solids for the production of chemicals, principally gaseous unsaturated hydrocarbons, aromatics, and coke. More particularly, it relates to a process of this nature wherein hot circulating solids from the solids heating step are stripped with a normally gaseous hydrocarbon having at least two carbon atoms.

It is known in the art to coke heavy hydrocarbon oils at elevated temperatures for the production of gaseous unsaturated hydrocarbons and coke. The coking unit or reactor usually consists of a fluidized system, e. g., a transfer line which constitutes the reaction zone or a fluidized bed reactor. Staged reactors can also be employed. In a typical operation the heavy oil to be processed is injected, usually in finely divided liquid form, into the transfer line reaction zone containing a high velocity confined stream of hot suspended inert particulate solids, preferably coke particles. In the reaction zone the feed is vaporized by the heat of the particles and is cracked for controlled short periods of time. The gaseous or vapor products are taken off overhead.

Coke, which is deposited upon the heat carrying particles, is withdrawn from the reactor along with said particles and transported by a fluidizing gas to a suitable reheater such as a transfer line or a fluid bed burner. The temperature of the solids is raised in this heating step so as to supply heat for the cracking or coking reaction. This heat can be obtained by burning a portion of the product coke or by direct heat exchange such as burning of added gaseous or liquid fuel in the presence of the coke of other solids. The net coke made is withdrawn as product while the major portion of the coke is returned to the reactor.

Heavy hydrocarbon oil feeds suitable for the process include heavy crudes, atmospheric or vacuum crude bottoms, pitch, asphalt, cracked residua, other heavy hydrocarbon petroleum residua or mixtures thereof. Coal tar bottoms may be treated by the process, as well as other analogous heavy oils. Typically such feeds can have an initial boiling point of about 700° F. or higher, an A. P. I. gravity of about 0 to 20°, and a Conradson carbon residue content of about 5 to 40 wt. percent. (As to Conradson carbon residue see ASTM Test D-180-52.)

It is preferred to operate with solids having a particle size ranging between 100 and 1000 microns in diameter with a preferred average particle size range between 150 and 400 microns. Preferably not more than 5% by

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weight of the solids have a particle size below about 75 microns, since small particles tend to agglomerate or are swept out of the system with the gases. While other inert particles such as sand, pumice, Carborundum, etc. can be used, coke produced in the process is usually preferred.

One of the chief problems associated with this type of process, as practiced heretofore, is that the circulating coke from the heating step contains occluded gases such as carbon dioxide and carbon monoxide as well as nitrogen and oxygen from the combustion. The occluded gas usually amounts to at least about 10 s. c. f./ton of coke circulated and results in more than about 3 vol. percent dilution of the C<sub>2</sub> and lighter gases. The oxygen can also be present in the chemisorbed form. The term "occluded" as used herein therefore connotes chemisorbed gases as well as entrained, adsorbed, etc. gases. These gases when released in the reactor undesirably dilute the product gases. Oxygen, furthermore, is a good catalyst for the polymerization of diolefins. Yields of such desirable products as butadiene, piperylene, and the like are, therefore, reduced by oxygen getting into the reactor from the burner.

An additional problem encountered in the process is that the coke product produced from high sulfur feeds are also high in sulfur content. In general the sulfur content of the coke product from the coking process is about 2 times the sulfur content of the residuum feed from which it is produced. The sulfur content of coke from sour residua can range from 5% to 8% sulfur or more. The high sulfur content of the coke product poses a major problem in its efficient utilization. For most non-fuel or premium fuel uses a low sulfur content coke, e. g., below about 3 wt. percent sulfur, is required. For example, low sulfur content coke is desired for the manufacture of phosphorous, for the production of calcium carbide, for lime burning in the manufacture of soda ash or other alkalis, for various metallurgical applications, and for the production of electrode carbon for various electrochemical applications such as the manufacture of aluminum, high grade steel and the like.

The conventional methods of removing sulfur from coke from ordinary sources with gaseous reagents have in general not been too satisfactory. The results are even poorer when these procedures are applied to fluid coke, i. e. coke produced by the fluid process coking of oil. Delayed coke is more porous than this fluid process coke and the interstices are more connected and larger than in such coke. A treating gas consequently has relatively easy access to the sulfur. Coke from a continuous process such as fluid coking is laminar in structure and particles may comprise some 30 to 100 superposed layers of coke. Thus, it is difficult for a reagent to penetrate more than a few outer layers of a typical particle. These difficulties are even further compounded because of the beforementioned usually higher than normal sulfur content of coke which is derived from high sulfur petroleum feeds.

This invention provides an improved process for overcoming these difficulties in the high temperature coking of heavy hydrocarbons especially petroleum oils, for the production of so-called chemicals or low molecular weight unsaturates and aromatics. The process comprises continuously stripping at least a portion and preferably all

of the hot circulating coke, as it passes from the coke heating step, with a normally gaseous hydrocarbon having at least 2 carbon atoms. The stripping is conducted in such a manner so as to remove a major proportion, i. e., more 90 vol. percent, of the occluded gases from the circulating coke before it reaches the reactor. This, among other things, prevents the occluded gases from giving rise to the beforementioned difficulties.

The reason for the improved operation of this invention is believed to be as follows.

The stripping gas of C<sub>2</sub> or higher hydrocarbon first displaces the combustion gases from the burner. Next, because of the temperatures involved, the hydrocarbon cracks and olefins, free radicals, and nascent hydrogen are formed. These olefins and/or the nascent hydrogen and/or free radicals react very actively with any sulfur or oxygen associated with the hot coke. Some of the cracked stripping gas passes into a burner where it can be burned as fuel, thus reducing the coke-burning requirements and maximizing the production of a high-quality coke.

The normally gaseous hydrocarbons utilized for the stripping process have at least two carbon atoms and thus normally include C<sub>2</sub>, C<sub>3</sub>, and even C<sub>4</sub> hydrocarbons. Use of hydrogen or methane is undesirable since any portion of these gases which passes to the reactor would dilute the reactor products and make the recovery of ethylene, which usually is one of the more valuable products of the process, more difficult. C<sub>2</sub> and heavier hydrocarbons are partially dehydrogenated and/or cracked to yield ethylene. The saturated C<sub>2</sub> to C<sub>4</sub> hydrocarbons are preferred as stripping gases. These stripping gases can be utilized in a relatively pure form or in the impure form as they ordinarily come in readily available refinery streams such as liquefied petroleum gas or effluent from an olefin polymerization plant. For example, the deethanizer gas from such a plant having the following composition could be used:

	Mol. percent
Methane-----	6
Ethylene-----	5
Ethane-----	88
Propane-----	1

The stripping gas is preferably used in at least one volume and preferably 2 v./v. based on the circulating coke. This amount is sufficient to prevent any appreciable portion of the occluded gases from entering the reactor.

This invention will be better understood by reference to an example in the flow diagram shown in the drawing.

In the drawing, conduit 1 is a transfer line reactor through which the reactant system flows in the form of a high velocity confined stream. A heavy oil feed, e. g., an East Texas vacuum residuum having a Conradson carbon number of 24 wt. percent, preheated to a temperature of 600° F. enters the transfer line reactor through line 2 although a plurality of points can be used. The hot stripped fluidized coke, entering the transfer line reactor from the heater, is at a temperature of 1500° F. and is transported in through the transfer line reactor at a high velocity, e. g., 60 ft./sec. so that the contact time of the resultant hydrocarbon vapors is 0.5 second from the point where the feed is introduced to the quench point, and the reactor outlet temperature is 1300° F. The reaction system is thus maintained for a period of time to obtain the desired reaction. In the reactor gaseous unsaturated hydrocarbons such as ethylene, propylene, butadiene, isoprene, etc., are evolved, the residuum feed is cracked, and the carbonaceous residue, mostly coke, is deposited in one or more thin layers on the original solid particles which are usually and preferably of the same material.

The solids are transported through the reactor by the

combined action of the fluidizing gas added through lines 21 and 22 plus the gases evolved by cracking. The coke particles together with the vaporous products are then sent through outlet line 3 into a suitable separator, shown here as a conventional cyclone 4 or any suitably rapid solids/vapor separating device. The gaseous products are taken overhead through line 5 whereas the hot coke discharges through line 6 into a stripper-hopper 7. Quench media such as tar bottoms, feed material, etc. can be injected through line 26.

Other normally gaseous hydrocarbons are injected through lines 8, 9, and 10 for the stripping and transporting of the coke from the reactor side. Steam can be used at this point since the temperature is from 100° to 300° F. lower than in the burner-stripper and the reaction of coke and steam is less active and product contamination less serious. The stripped coke is then transported through a U-bend or other suitable communicating means 11 and through a conduit such as riser 12 to a high temperature conduit 13. The latter operates as a transfer line burner.

The coke flowing through lines 11, 12, and 13 is fluidized or carried as a suspension of suitable density, e. g. 1 to 20 lb./cu. ft. while maintained in the form of a high velocity confined stream. Air enters through line 14. Alternatively to burning coke a stream of extraneous fuel, e. g., natural gas or fuel oil, may be injected if it is desired to maximize the coke yield. The temperature of the coke is raised to about 1500° F. so as to supply the heat for the cracking reaction, the velocity being about 60 ft./sec. and the residence time in the transfer line burner about 1.5 seconds. The coke and combustion products are then sent into an upper separator or cyclone 24. Flue gases are removed upwardly through line 15, they may be passed downwardly if desired, whereas the hot circulating coke is sent through line 16 into a hopper 17. The hot coke in this hopper 17 is kept fluid by inert gas and/or air injected through one or more lines, e. g. line 23, in addition to the vapors from the stripping section 18. Hopper 17 also serves as a secondary burner, if a combustion supporting gas such as air is employed, since the air used for fluidization will tend to burn any carbon monoxide, hydrogen or hydrocarbons rising from the stripper-standpipe 18. The fluidized coke from hopper 17 next passes by gravity into a stripper standpipe 18 where it is stripped with a predominantly C<sub>2</sub> hydrocarbon cut entering through line 19 injected preferably at least one pipe diameter before the solids enter U-bend 20. The C<sub>2</sub> cut can be preheated, if desired, by heat exchange with the hot flue gas going to the stack. This same hydrocarbon gas is used to keep the solids fluidized, i. e., to circulate the coke through U-bend 20 or other connecting means to transfer line reactor 1. This stripping and circulating gas counter-currently displaces occluded gases such as carbon dioxide, carbon monoxide, and nitrogen from the circulating solids. Because of the temperature of the circulating coke the stripping gas partially cracks or is dehydrogenated to olefins, free radicals and nascent hydrogen. These olefins and/or free radicals and/or nascent hydrogen react with any sulfur and oxygen present. The displaced combustion gases, the sulfur and oxygen products, and a large part of the cracked stripping gas passes up the standpipe 18 to storage hopper 17 where the combustible portion is burned. The residual gases are discharged through stack 15.

The major proportion of occluded gases are thus removed so that where additional fluidizing hydrocarbon gas is injected, such as through lines 21 and 22, there is no problem of releasing the objectional combustion gases and other contaminants into the reactor. The cracked products evolving from the contacting of the circulating coke in the U-bend pass into the transfer line reactor 1 and join the main product vapors. Product coke is withdrawn through line 25.

A typical product yield is presented below.

Product Yields

Stripping of Circulating Coke from Burner	No Stripping	"Conventional" Stripping	Improved Method of Stripping Typical of Invention
Residuum Feed Rate, B/D	16,000	16,000	16,000
Coke Circulation Rate, Tons/Hr.	1,400	1,400	1,400
Stripping Gas	None	Steam	( <sup>1</sup> )
Fluidizing Gas to U-bend	Steam	Steam	( <sup>1</sup> )
Stripping Gas Rate, S. C. F. H.		55,000	55,000
U-bend Fluidizing Gas Rate, S. C. F. H.	180,000	180,000	180,000
Product Yields, Wt. percent on Resid. Feed:			
Nitrogen	0.31	0.03	0.03
CO+CO <sub>2</sub>	0.16	0.25	0.01
Hydrogen	0.40	0.42	0.56
Methane	6.9	6.9	7.6
Ethylene	10.6	10.6	13.7
Ethane	2.7	2.7	5.0
Propylene	8.7	8.7	8.8
Propane	0.4	0.4	0.4
C <sub>2</sub> and lighter	30.2	30.0	36.1
Butadiene 1-3	2.2	2.2	2.4
Butylenes	4.1	4.1	4.1
Butanes	0.6	0.6	0.6
Total C <sub>5</sub> 's	4.0	4.0	4.1
Benzene	2.2	2.2	2.2
Total C <sub>6</sub> /430° F. (ex. Benzene)	13.4	13.4	13.1
Tar (430° F.-)	26.8	26.8	26.8
Coke (excess over that burned)	5.8	5.0	6.8
Mol. percent Ethylene in C <sub>2</sub> and lighter	33.9	33.8	34.7
Wt. percent Sulfur in coke	7.0	7.0	2.5

<sup>1</sup> Deethanizer Overhead.

This table shows how the recoveries of ethylene, butadiene and coke are substantially increased by the process of this invention. The sulfur content of the coke is low-  
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order to express this invention more fully the following conditions of operation of the various components are set forth below.

Conditions in reactor 1

	Broad Range	Preferred Range
Temperature, °F.	1,200-2,000	1,300-1,500
Superficial Velocity of Fluidizing Gas for Reactor, ft./sec. at Reactor Inlet	7-50	10-25
Superficial Velocity of Fluidizing Gas in Transfer Line Reactor, ft./sec. at Reactor Outlet	10-150	25-100
Vapor Contact Time (Feed Inlet to Quench Point), sec.	0.05-5.0	0.1-3.0
Hydrocarbon Partial Pressure at Reactor Outlet, p. s. i. g.	1-50	8-15

Conditions in burner 13

	Broad Range	Preferred Range
Temperature, °F.	1,300-2,100	1,400-1,700
Superficial Velocity of Fluidizing Gas in Transfer Line Burner, ft./sec.	10-150	25-100

The advantages of the process of this invention will be apparent to those skilled in the art. The oxygen is kept

out of the reactor preventing any loss in diolefin yield due to polymerization. Undesirable diluent gases such as carbon monoxide, carbon dioxide and nitrogen are kept out of the reactor product. Sulfur is removed from the coke. The cracked stripping vapors carried into the reactor are valuable and easily recovered products. These same vapors when carried into the burner section can be burned as fuel thus decreasing the coke-burning requirements.

In addition, consumption of coke by the water gas reaction from the utilization of steam as a stripping or fluidizing gas is eliminated. Steam at the high temperatures encountered in the system would gasify about 3% of the coke product. It also would increase the heat requirements of the burner due to the endothermic gasification reaction. Large quantities of carbon monoxide and hydrogen would be discharged in the hopper or secondary burner. Reactor products would also undesirably be diluted with the gasification products.

It is to be understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. In a process for converting a heavy hydrocarbon oil to low molecular weight normally gaseous unsaturated hydrocarbons, aromatics, and coke by the steps of contacting the oil charge stock with fluidized, inert, particulate solids in a reaction zone at a temperature of 1300° to 2100° F. wherein the oil is converted to product vapors and carbonaceous solids are continuously deposited on the particulate solids; removing product vapors from the reaction zone; heating the circulating particulate solids removed from the reaction zone in a separate heating zone to increase the temperature of such solids to at least 1400° F.; returning circulating heated solids from the heating step to the reaction zone to supply heat thereto and wherein the particulate solids from the heating step contain occluded gases including carbon dioxide, carbon monoxide, and oxygen, the improvement which comprises removing a major proportion of the occluded gases from the circulating coke from the heating step before it reaches the reaction zone by stripping the circulating coke from the heating step with a normally gaseous hydrocarbon having at least two carbon atoms.

2. The process of claim 1 in which the inert particulate solids are coke.

3. The process of claim 2 in which the normally gaseous hydrocarbon is utilized in an amount of at least 1 v./v. based on the circulating coke.

4. The process of claim 3 in which at least 90 vol. percent of the occluded gas are removed from the circulating coke.

5. The process of claim 1 including the additional step of burning combustible components of the cracked stripping gas so as to additionally supply heat to the particulate solids.

6. The process of claim 1 in which the normally gaseous hydrocarbon stripping gas comprises predominantly ethane which is dehydrogenated to ethylene during the stripping step.

No references cited.