Feb. 17, 1959 J. F. MOSER, JR., ET AL 2,874,094

FLUID COKING PROCESS

Filed March 23, 1955

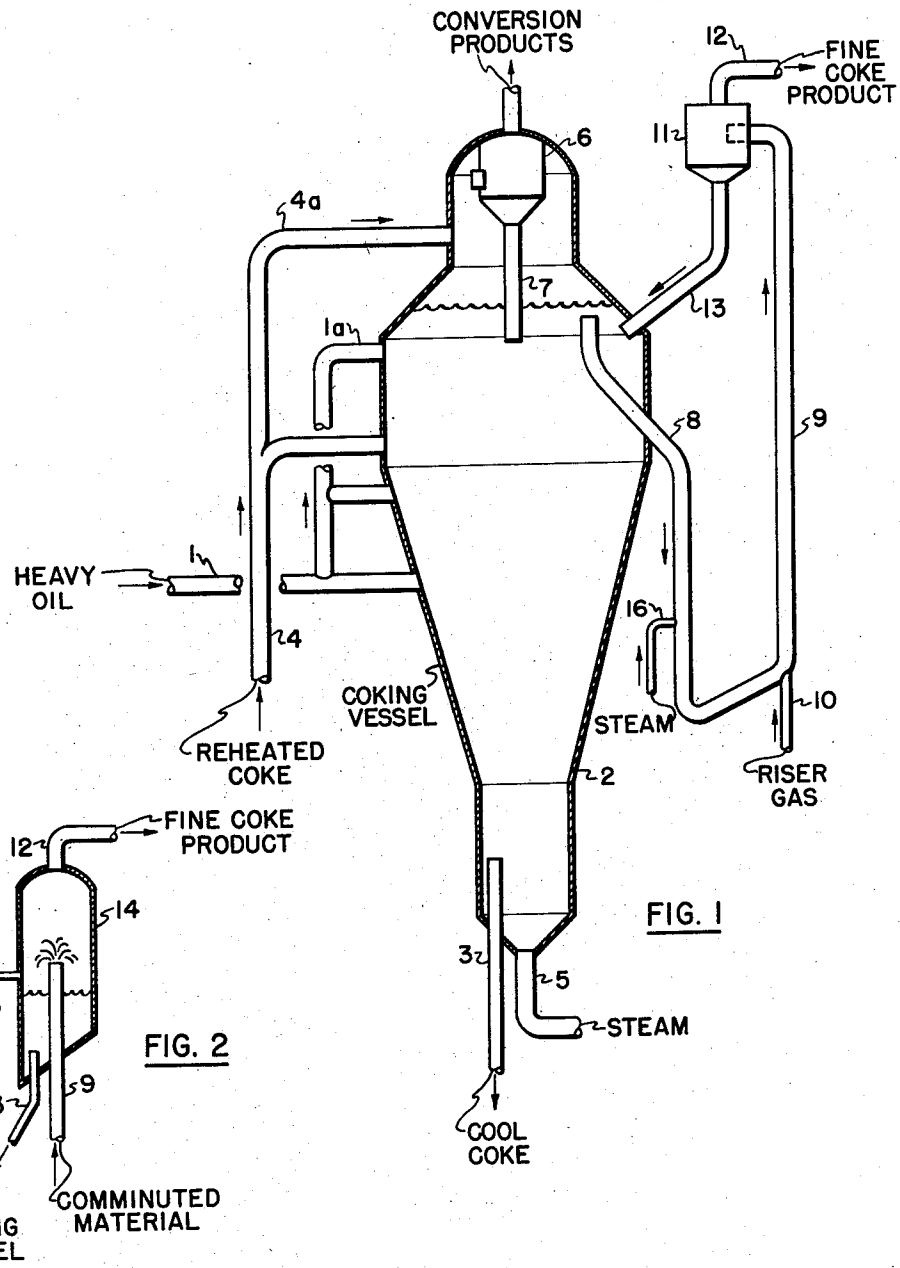


FIG. 1

FIG. 2

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United States Patent Office 2,874,094 Patented Feb. 17, 1959

2,874,094

FLUID COKING PROCESS

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Application March 23, 1955, Serial No. 496,193

3 Claims. (Cl. 202—25)

This invention relates to the art of converting residual oils and similar materials by coking in a fluidized solids system. It is particularly concerned with the comminution of the contact solids used in the coking process whereby the size, size distribution and weight inventory of the contact solids are maintained substantially uniform and a finely divided coke product of boiler fuel size is obtained.

It is known to convert or upgrade heavy oils such as vacuum residua, shale oils, asphalts, tars, and cycle stocks by fluid coking processes to lighter and more valuable products. A conventional fluid coking process usually comprises a reaction zone containing a fluid bed of finely divided solids, usually coke produced by the process, maintained at a coking temperature by circulating the solids to an external heating zone and back. The heating zone customarily comprises a unit wherein the solids, which contain depositions of carbon, are reheated by partial combustion as a fluid bed, although other heating means may be used. The heavy oil feed is injected into the coking zone and undergoes vaporization and cracking with some of the feed being deposited on the contact solids and converted to coke. After having entrained solids removed, the vaporous conversion products are withdrawn overhead as product.

With substantially all of the heavy oils processed by fluid coking, an excess of carbon beyond that required to be burnt to meet heat requirement is produced. Thus the contact solids continue to grow in size and this continued growth will disrupt operations unless countering measures are taken. Measures taken in the past have included withdrawing, continuously or intermittently, a portion of the particles, preferably relatively coarse particles, to maintain the weight inventory of the contact solids substantially constant, and supplying to the system relatively fine particles, i. e., seed coke, to maintain the number, size and size distribution of the contact solids substantially uniform. This seed coke is usually obtained by comminuting in some manner, as by jet attrition grinding, a portion of the withdrawn product, or by comminuting the coke circulating in the process.

As much as 30 wt. percent or more of the heavy oil feed may end up as coke product. The principal profitable outlet for this coke product is as a fuel, e. g., boiler fuel. To use this fluid coke as a fuel requires that it be rather finely ground, below about 74 microns, in order to have it burn properly in conventional steam generating boilers. This size reduction is expensive because of the hardness of the coke.

The present invention is directed to the problems of contact solid growth and of producing a finely divided coke product, and proposes a novel solution therefor. It is predicated upon the discovery of the nature of the growth of the contact solid.

It has previously been appreciated that the finer portions of the contact solids, say below about 200 microns, readily agglomerate, or adhere together, forming substantially larger sized particles. Virtually no material below about 74 microns exists in the circulating coke stream. These agglomerates then are firmly cemented by the coking reaction. There is, then, a useless dissipation of fines by agglomeration that could better serve as individual growth nuclei. Agglomeration thus aggravates the problem of seed coke production.

The finer material which primarily enters into the agglomerates is continuously being produced in the coking process, mainly by the seed coke producing means but also by natural attrition in the fluid bed and circulation system and by the natural size reduction occurring in the burning unit that reheats the particles. Thus, there is continuously being produced a substantial amount of material below about 74 microns in size that, if it could be rescued and withdrawn from the process, would already be of boiler fuel size. This invention proposes a method by which this fine material can be separated and recovered as product, thereby permitting substantial economies to be realized.

It has now been discovered that fines, i. e., the finer portions of the contact solids, concentrate in the upper portions of the fluid coking bed. It is, therefore, in this upper portion where the agglomerates are predominately formed. Some agglomeration also occurs near points of feed injection. Further, it has now been found that freshly formed agglomerates are quite easily broken down or comminuted. If the agglomerates are allowed to remain resident in the fluid coking bed for over about 3 min., they are covered with fresh deposit of coke and become relatively hard and non-friable. To allow the agglomerates to gravitate to the base of the fluid coking zone, and to be there removed, as is customarily done, permits the agglomerates to fuse or bake into difficult to comminute particles.

Fines concentrate in the upper portion of the fluid bed for several reasons. The fine solids separated from the vaporous conversion products are normally returned to the upper portion of the bed. Also, the freshly reheated solids and the seed coke are usually returned to this portion. The fresh heavy oil feed to the fluid coking bed may also be injected into the upper portion to enhance the agglomeration of the fines.

In light of the above, it is an object of this invention to present to the art an improved fluid coking process. A more particular object is to develop a fluid coking process with means integral with the process for producing a finely-divided product of smaller average particle size than the size of the contact solids in the process.

These and other objects and advantages will become apparent as this description proceeds and the attached drawings, forming a part of this specification, are described in detail.

Figure I of the drawings illustrates diagrammatically one embodiment of the invention.

Figure II depicts an alternative method of separating the comminuted material from the conveying gas.

Briefly this invention proposes a method of counteracting the natural growth of the contact solids used in a fluid coking process which comprises withdrawing a stream of contact solids from the uppermost portion of the fluid coking bed. This stream contains a high proportion of freshly formed agglomerates. This stream is comminuted to break up the freshly formed agglomerates and to cause some cleavage of the particles forming the agglomerates whereby the average particle size of the stream is substantially reduced. A major portion or all of this comminuted material is then returned to the fluid coking bed.

Preferably, however, material finer than about 74 mi-

crons is separated from the comminuted material and withdrawn as net coke product of the process. In this manner, a coke product of boiler fuel size is readily obtained.

More particularly, this invention is concerned with an improved fluid coking process. The improved process comprises maintaining a fluid bed of particulate coke at a coking temperature in a coking zone. A heavy oil is injected into this fluid bed and undergoes vaporization and pyrolysis accompanied by the deposition of carbon on the particulate coke. The vaporous conversion products are withdrawn overhead from the fluid bed as product. A portion of the particulate coke is circulated to an external heating means, e. g., a fluid bed burner, and back to maintain the coking temperature. Another stream of particulate coke is stripped and withdrawn from the upper portion of the fluid bed. This stream contains a substantial proportion of the freshly formed agglomerates produced in the bed. This stream is then met with an upwardly directed high velocity gas jet which breaks up the agglomerates, produces seed coke and conveys the particles upwardly. The comminuting material is then separated in a separation zone, e. g., a rough cut cyclone elevated above the fluid bed. A major portion of the gas associated with the comminuted material and relatively fine particles are withdrawn from the separation zone as product, the rate of withdrawal of the fine particles being sufficient to maintain the weight inventory of the particulate coke in the process substantially constant. The remainder of the comminuted material is transferred to the fluid coking bed to maintain the number, size and size distribution of the particulate coke substantially uniform.

It is particularly preferred to use high velocity gas jets to reduce the agglomerates as other means of obtaining size reduction of the solids are not satisfactory, as will appear. It is more especially preferred to use supersonic jets to achieve break-up of the agglomerates.

With particular reference to the attached Figure 1, a preferred coking process incorporating the teachings of this invention will be described. A heavy oil which may be suitably preheated is injected into the coker **2** via line **1**. Recycled heavy ends separated from the vaporous coker effluent may be incorporated with this heavy oil. The oil feed comprises preferably a residual petroleum oil such as a top crude or a vacuum residua having an API gravity between about −5° and 20°, a Conradson carbon content between about 5 and 50 wt. percent and an initial boiling point between about 850° and 1200° F. As much as 50 wt. percent of this heavy oil can be injected via line **1***a* into the uppermost portion of the fluid bed to aid in the formation of agglomerates and to prevent loss of fines from the system.

The coking zone **2** contains a fluidized bed of finely divided inert particles, preferably particulate coke produced by the process. The dense bed has a definite upper level with a dilute or disperse phase thereabove. The coke has a particle size between about 20 and 800 microns, preferably between about 40 and 400 microns. The fluidized bed is maintained at a temperature between 850° and 1600° F., preferably between about 900° and 1100° F. To do this, cool coke particles are withdrawn via line **3** after having been stripped of the occluded hydrocarbons and are circulated to an external heating means, e. g., a transfer line burner. Reheated coke particles are returned to the reactor at a temperature of about 100° to 300° F. above the coking temperature by line **4**. A portion of these reheated coke particles can be introduced into the disperse phase of the reactor via line **4***a* to prevent coking of overhead equipment as has become conventional in the art.

The fluidized bed is maintained as such by the upflowing hydrocarbon gases formed by the coking of the oil feed and by steam added to the base of the vessel via line **5**. When using finely divided coke of about 40 to 400 microns and a superficial velocity of about 1 to 2 ft. per second, the density of the fluidized bed will be about 35 lbs. per cu. ft. but may vary between about 15 and 60 lbs. per cu. ft.

Vaporous conversion products are removed overhead and passed through cyclone separating system **6** located in the top interior of the reactor. More than one cyclone separator may be used and the separator may be arranged exteriorly of reactor **2**. The separating system **6** removes the fine solids entrained from the fluid bed and also the hot solids injected into the disperse phase via line **4***a*. These separated solids are returned to the upper portion of the fluid bed via line **7**.

According to this invention, a portion of the fluid bed is continuously withdrawn from near the upper portion of the bed by standpipe **8**. One or more points of withdrawal can be used as is necessary to capture the freshly formed agglomerates. This withdrawn stream is stripped of occluded hydrocarbons by admitting steam via line **16** to standpipe **8**. The solids flow around the base of the standpipe to riser **9** in a manner known by the art. At the base of the riser **9**, the solids are engaged with a lift or riser gas supplied by line **10**. This gas may comprise any suitable gas such as steam, flue gases, other inert gases, air, etc. This riser gas is admitted to conduit **9** as a high velocity gas jet having the velocity of at least 500 ft. per sec. This high velocity gas primarily reduces freshly formed agglomerates but it also creates some seed coke by cleavage of the particles. The riser gas conveys the comminuted material upwardly to rough cut cyclone **11** or its equivalent. Materials finer than about 74 microns along with the riser gas are separated and removed from the cyclone via line **12**. This fine coke comprises the net coke of the process and is withdrawn in amounts sufficient to maintain the weight inventory of the solids in the system substantially constant. The coarser solids separated from the comminuted material are returned to the upper portion of the fluid coking bed via line **13**.

It is preferred to introduce riser gas via line **10** as a supersonic jet, i. e., at velocities equal to or greater than the velocity of sound in the gas under the conditions of the riser. This is because the supersonic jet primarily causes shearing between adherent particles forming the agglomerate and does not so much result in direct cleavage or fracture of the particles. Lower velocity jets, i. e., subsonic jets, are also satisfactory but generally are less efficient i. e., a greater amount of energy is required to obtain the same extent of comminution. High velocity jets are preferred in any case over other grinding means such as hammer mills, as other grinding means act primarily to cause cleavage or fracture of the individual discrete particles. In some instances, the use of high velocity jets in conjunction with targets may be favored depending upon the degree and extent of comminution desired.

The rate of circulation of particles to the grinding device lies between about 100 to 300 wt. % of the fresh feed rate to the unit. This rate is sufficient to meet seed coke requirements of the process and to produce a finely divided coke product. The jet velocity can vary from 500 to 3000 ft. per sec. with operations in the higher ranges being preferred. If steam be the riser-attriter gas used approximately 0.005 to 0.020 lbs. of 450 p. s. i. steam per lb. of coke circulated through the grinding device will be consumed. Although the agglomerates circulated through the grinder may be termed loosely adherent, their degree of adherency is such that it requires an appreciable amount of energy to cause them to break apart. Thus it has been found that natural agitation in the fluid beds and in the circulation system does not cause breaking up of any appreciable amount of the agglomerates formed. Thus more severe treatment of these agglomerates is required as proposed by this invention.

Figure II illustrates an alternative separating means that may be used in place of rough cut cyclone **11**. The

comminuted material in riser **9** may be injected into disperse phase zone defined by veseel **14**. In this zone, the particles are classified by disperse phase elutriation. Additional classifying gas, e. g., steam may be admitted to the zone **14** by line **15**. To obtain overhead from this zone material below about 74 microns in size, superficial gas velocities in the range of 0.2 to 0.5 ft. per second are used. The coarser material falls out of the gas to the base of the vessel and is returned to the coking zone by line **13**. The elutriated finer coke is withdrawn overhead along with the elutriation gas through line **12**.

The following example will serve to illustrate this invention. About 2300 bbls./day of residual oil having an API gravity of 4.5°, a Conradson carbon content of 24 wt. % and an initial boiling point of about 1000° F., preheated to about 600° F., is injected into coking vessel **2** via line **12**. About 5,000 lbs./hr. of steam are admitted to the vessel via line **5** to serve as stripping and fluidizing gas. The solids/oil circulation rate is about 8/1, and the coking temperature is maintained at about 950° F. Approximately 15 tons of coke at a fluidized density of 40 lbs. of cubic ft. is maintained in the coking vessel **2**. The pressure at the cyclone inlet is 6 p. s. i. About 25 wt. % of the residual oil is converted to carbon and deposited on the solids. The remainder of the oil is converted to vapors which are withdrawn overhead as product through cyclone separator **6**.

Under these conditions, approximately 70,000 lbs./hour of coke is withdrawn 2 ft. below the upper bed level by line **8** and circulated through the grinding device. This withdrawn material is stripped and allowed to pass to the base of standpipe **8** which is located 40 ft. below the upper bed level. This is sufficient to build up the pressure at this point to 21 p. s. i. The contents of line **8** are then met with the riser gas. About 840 lbs./hr. of 450 p. s. i. steam is admitted via line **10** at a velocity of 3000 ft./ sec. to the base of riser **9**. This sufficiently comminutes the circulating coke. The gas and about 800 lbs./hr. of a fine coke product having a size below roughly 74 microns and a median particle size of 25 microns are separated from cyclone **11** from the comminuted material, and are withdrawn as product. The remainder is returned to the reactor. Table I illustrates the particle size and particle size distribution of the various circulating coke streams in the process.

Table I

Wt. percent smaller than—	In fluid bed	Circulated to jet comminuting (via line 8)	Net coke product (in line 12)	Seed coke to reactor (in line 13)
800 microns	100	100	----------	100
400 microns	93	94	----------	94
295 microns	78	80	----------	78
246 microns	61	64	----------	61
175 microns	29	33	----------	32
147 microns	15	18	100	21
74 microns	1	2	93	5
20 microns	0	0	30	0
Median particle size, microns	215	205	25	200

This table shows the relative degree of fineness of the boiler fuel size product (net coke product) obtained and of the seed coke compared to the size of the coke used in the fluid coking bed. The table also shows the extent of comminution obtained by the high velocity jet in line **8**.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. In the fluid coking process wherein the natural growth of the contact solids of the fluidized coking bed is counteracted by removing contact solids from the fluidized coking bed, comminuting removed solids to reduce their particle size, and returning so comminuted solids to said fluidized coking bed, the improvement which comprises withdrawing said contact solids from the upper portion of said fluid coking bed wherein there is contained a high proportion of fine particles and freshly formed agglomerates, and subjecting said freshly formed agglomerates to comminution whereby particle size reduction is accomplished with reduced effort.

2. The improvement of claim 1 wherein entrained solids separated from the vaporous conversion products of said fluidized coking bed are returned to the upper portion of said fluidized coking bed.

3. The improvement of claim 1 wherein said comminuted solids are returned to the upper portion of said fluidized coking bed.

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