

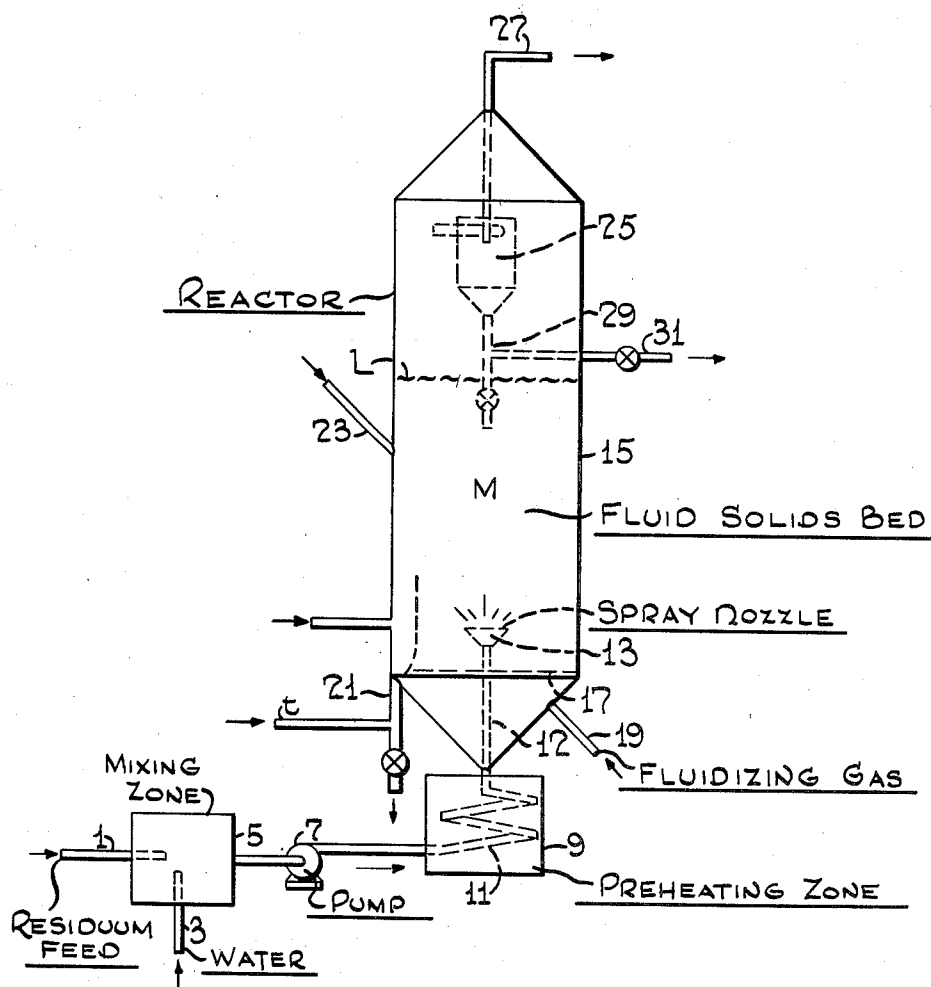
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COKING OF HEAVY HYDROCARBONACEOUS RESIDUES

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COKING OF HEAVY HYDROCARBONACEOUS
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The present invention relates to a method of treating hydrocarbons. Particularly, the invention pertains to a method of upgrading heavy hydrocarbon oils of the type of topped or reduced crude or similar heavy residues to produce lower boiling products of increased value including gas oil range hydrocarbons suitable as feed stocks for catalytic cracking, motor fuel range hydrocarbons, unsaturated and aromatic hydrocarbons suitable for chemicals production, etc. In its broadest aspect, the invention provides for the introduction of heavy residues of the type specified intimately mixed with water into a mass of subdivided solids maintained at temperatures conducive to the coking of the residua and the production of the desired lower boiling products.

Heretofore, heavy residues of the type mentioned above, particularly the residues from atmospheric or vacuum crude distillation have been subjected to thermal conversions, such as viscosity breaking or coking to produce lower boiling more valuable materials. Coking which is carried out at relatively more severe conditions is preferred when the direct production of relatively high proportions of hydrocarbons boiling below the gas oil range is desired. Sufficient coke is produced in this operation to supply by combustion thereof the heat requirements of the process. On the other hand, the coke produced gives rise to complications resulting from coke deposits on the walls of the coking vessels and in the transfer lines. To eliminate the frequent cleaning periods necessitated by excessive coke deposition subdivided inert adsorbent solids such as coke, pumice, kieselguhr, spent clay, sand, or the like have been admixed with the residuum feed to serve as a carrier for the coke and as a scouring agent preventing coke deposition on the equipment walls. The coke deposited on the solids may be burnt off in cyclic or continuous fashion to regenerate the solids and to supply the heat required for coking.

While fixed bed, moving bed and suspensoid systems may be used for this type of operation, the so-called fluid solids technique offers greatest advantages with respect to temperature control, heat economy, ease and continuity of operation as well as equipment dimensions. This technique involves the injection of the feed into a relatively dense highly turbulent bed of hot subdivided solids ranging in size from about 30 to about 400 mesh. Fluidization is accomplished by gases and vapors flowing upwardly through the bed at a linear superficial velocity of about 0.3–5 ft. per second to give the bed the appearance of a boiling liquid separated by a definite interface from an upper disperse phase. Volatile coking products are removed overhead while coke in the form of coke-carrying solids may be recovered directly from the fluidized bed. The heat required for coking may be supplied by indirect heat exchange, limited internal combustion within the fluidized bed or continuous circulation of coke-carrying solids between the coking zone and a separate coke-burning zone operated at a temperature above coking temperature.

While this technique affords superior heat control, substantial procedural improvements as well as better yields of desirable products as compared to other systems, its adaptation to commercial scale operation has been complicated particularly by the fact that in conventional operation fluidization becomes increasingly irregular in the course of the process and slugging and channelling of the bed becomes so excessive within a relatively short time as to force the interruption of the process. Extensive experimental work has demonstrated that this phenom-

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non is the result of particle agglomeration. The heavy feed stock cannot be completely vaporized prior to its introduction into the coking zone without excessive coke deposition in the heating coils and feed lines. A substantial proportion of the residuum feed must, therefore, be supplied in the liquid state. The individual particles in the bed are wetted by the oil and adhere to each other to form more or less loose aggregates which eventually are cemented together when the binding oil layer is coked. Even during the early wetting and agglomeration stage the bed volume decreases rapidly and fluidization gas continues to flow through channels in the wet mass. This situation is aggravated as coking proceeds until the fluid character of the bed is entirely lost.

The agglomeration effect has been found to be a function of the solids to oil ratio in the bed, the oil feed rate, the temperature and, to some extent, the character and particle size of the solids. In general, agglomeration and its detrimental effects are the more pronounced the lower the solids to oil ratio in the coking bed the higher the feed rate and the lower the temperature in the coking bed. Since these variables also determine the amount, character and quality of the coking products they cannot be used to control fluidization without simultaneously affecting other characteristics of the operation, which is usually undesirable.

Prior to the present invention it has been proposed to inject the liquid feed in a finely divided state, i. e. either by forcing it under pressure through a spraying nozzle or atomizing it with steam or inert gas, into the body or on top of the fluidized solids bed. Spraying of the feed on top of the fluid bed, though greatly reducing the agglomeration tendency, requires carefully controlled operating conditions to avoid entrainment of uncoked heavy feed constituents in the effluent vapors and gases of the coking zone which may lead to plugging of cyclones and pipes. Atomization of the feed under pressure and/or with atomizing gases into any portion of the bed is positively superior to bulk injection of the feed. However, experimental work has demonstrated that the degree of subdivision obtainable by conventional spraying and atomizing methods is insufficient to reduce agglomeration to a point permitting, particularly at temperatures up to about 1000° F., feed rates substantially in excess of 1.5 lbs. of feed per hour per lb. of solids in the coking zone (w./hr./w.) which are desirable in commercial operation. The present invention overcomes these difficulties.

It is, therefore, the principal object of the present invention to provide improved means for preventing excessive solids agglomeration in coking heavy hydrocarbonaceous residues in the presence of subdivided solids. Other and more specific objects and advantages will appear from the description of the invention hereinafter read with reference to the accompanying drawing.

In accordance with the present invention, the above mentioned objects and advantages are accomplished by spraying the residuum or other liquid hydrocarbonaceous feed intimately admixed with water into a fluidized bed of hot subdivided solids at an elevated temperature and pressure adequate to cause an instantaneous vaporization of the water entering the coking zone maintained at a lower pressure and/or higher temperature than that at which the oil-water mixture is introduced. The sudden vaporization and expansion of the water increases the dispersion of the residuum far beyond that obtainable by spraying alone independent of the particular spraying method used and its degree of dispersion.

Intimate mixtures of water and oil suitable for the purposes of the invention may be obtained by high velocity mixing and other conventional mixing methods. However, mixing processes producing emulsions of the oil and water and particularly procedures conducive to the formation of water-in-oil type emulsions afford consistently best results. When the feed is sprayed into the fluid coking bed in the form of a water-in-oil emulsion the shearing action of the expanding water on the surrounding oil portion of the sprayed droplet is substantially greater and the amount of water required for a satisfactory dispersion effect is greatly reduced, as compared with mere mechanical mixtures of oil and water

or even emulsions of the oil-in-water type. The spraying of oil-water emulsions and particularly of water-in-oil type emulsions into the bed of subdivided hot solids is, therefore, the preferred embodiment of the invention.

Emulsions suitable for the purpose of the invention may be produced in any manner known per se, for example by high-velocity or jet mixing particularly in the presence of emulsifiers such as alkali, alkaline earth, aluminum or other metal derivatives of fatty acids, rosin acids, naphthenic acids, sulfite liquors, etc. or of even those acid constituents present in the residuum feed itself or after air blowing, to form water-in-oil emulsions containing about 5-35% by weight of water. This emulsion is preheated under pressure to the highest possible temperature at which the water remains liquid at the prevailing pressure and at which no substantial coking of the oil feed takes place. Preheat temperatures above about 500° F. and approaching but not substantially exceeding 700° F. are suitable for this purpose at pressures of about 700-3500 p. s. i. g. At these conditions, the emulsion is sprayed through one or more spray nozzles of any conventional design directly into the body of hot subdivided solids maintained at coking temperatures and fluidized by an upwardly flowing gasiform medium in any manner known per se. As the result of the substantially lower pressure, usually atmospheric or close thereto, and the substantially higher temperature of usually about 800°-1400° F. maintained in the coking zone the highly superheated water portion of the sprayed droplets vaporizes and expands instantaneously with almost explosive force to cause an infinitely fine dispersion of the oil portion. When so operating, fluidization difficulties due to agglomeration may be completely avoided even at oil feed ratios as high as 5 w./hr./w. and at coking temperatures as low as 800° F. Solids to oil ratios low enough to permit practically desirable reactor dimensions may be used. In addition the selectivity of the conversion toward desirable low boiling products is substantially increased due to the more intimate contact between feed and fluidized solids.

Having set forth its objects and general nature, the invention will be best understood from the more detailed description hereinafter wherein reference will be made to the drawing, the single figure of which is a schematic illustration of a system suitable to carry out a preferred embodiment of the invention.

Referring now to the drawing, the system illustrated therein essentially comprises a mixing zone 5, a preheating zone 9, and a fluid type coking zone 15. In operation, a liquid crude residuum, such as bottoms from atmospheric or vacuum crude distillation and water are supplied through lines 1 and 3, respectively to mixing zone 5. The relative feed rates of residuum and water may be so controlled that about 5-50 lbs., preferably about 5-10 lbs., of water are fed per 100 lbs. of residuum. The water may contain about 0.1-5% of an emulsifier, such as calcium or aluminum soaps. Mixing zone 5 may be of any conventional design suitable for the production of emulsions. For example, zone 5 may be a colloid mill or a high velocity stirred mixing zone maintained at a temperature of 200°-400° F. and a pressure of 15-250 p. s. i. a.

The emulsion so formed is withdrawn from mixing zone 5 by means of pump 7 and passed to preheating zone 9 at a pressure of about 700-3500 p. s. i. g., preferably about 1600 or 2000 to 3000 p. s. i. g., to be preheated therein to about 500°-700° F. Preheating zone 9 may be a conventional pipe furnace, heat exchanger, or the like in which pipe or coil 11 is heated by hot combustion gases, product gases or the like. Coil 11 discharges into pipe 12 provided with a conventional spray nozzle 13 arranged in the lower portion of coking reactor 15 above suitable gas distributing means such as a perforated grid 17. Reactor 15 contains a mass M of subdivided solids such as coke, sand or the like having an average particle size of about 50-100 mesh. Mass M is maintained in reactor 15 at about atmospheric pressure in the form of a dense, highly turbulent, fluidized solids bed having an upper interface L by a fluidizing gas such as steam, hydrocarbon gases or vapors, etc. introduced through line 19 and grid 17 in amounts sufficient to establish a linear superficial gas velocity within reactor 15 of about 0.3-1.5 ft. per second. The temperature of mass M may be maintained at about 800°-1400° F., preferably about 800°-950° F., suitable for coking, par-

ticularly low temperature coking, in any manner known per se. For example, coke-carrying solids may be withdrawn through a conventional standpipe 21 aerated and/or stripped by gas injected via taps *t*. Solids so withdrawn may be suspended in air, passed to a combustion zone (not shown) to be heated therein to a temperature about 50°-200° F. above coking temperature and then returned via line 23 to mass M. Systems of this type are well known in the art of reduced crude coking as demonstrated by such patents as U. S. 2,436,160; U. S. 2,485,315 and others. Therefore, no detailed description of the manner of heat supply which has no particular bearing on the present invention is required. Lines 21 and 23 may also serve, respectively, the recovery of product coke and the supply of make up solids.

Returning now to spray nozzle 13, the highly superheated water-in-oil emulsion is dispersed through nozzle 13 under the high preheating pressure into mass M at a feed rate which may be between about 1.5 and 5 w./hr./w. or higher, based on residuum feed alone. Immediately upon leaving nozzle 13 the ejected emulsion droplets are torn apart by the sudden conversion of the superheated water into steam under the influence of the pressure reduction. The infinitely small oil particles thus formed are almost instantly coked in contact with the hot solids particles of mass M without wetting these particles to any appreciable extent. Particle agglomeration is thus avoided. While excellent results may be obtained over a wide range of spraying efficiency of nozzle 13, it is desirable so to design the nozzle that the size of the original droplets formed will be below about 10 microns. Spray nozzles of the shear-jet or pressure type are suitable for this purpose. The vaporous coking products are carried by the fluidizing gas overhead from mass M and may be withdrawn from reactor 15 via suitable gas-solids separation means such as cyclone separator 25 and line 27 to be passed to conventional product recovery and/or catalytic cracking equipment (not shown). Solids fines separated in separator 25 may be returned to mass M via dip-pipe 29 or discarded via line 31.

The system illustrated in the drawing permits of various modifications. For example, instead of providing a separate preheating zone 9, pipe 12 may be so arranged within mass M to permit sufficient residence time of the feed emulsion in indirect heat exchange with mass M to attain the desired preheating temperature. More than one spray nozzle may be used which may be arranged at the same or at different levels within mass M to permit perfect distribution of the feed over the contact solids. If desired, heat may be supplied to mass M by carrying out a limited combustion therein or by indirect heat exchange with suitable heating fluids all in a manner known per se. Other mixing systems such as stirred batch mixers, homogenizers, or jet mixers may be used in place of the mixing zone 5 as described above.

While in the foregoing description reference has been made mainly to fluid type coking which is the preferred embodiment of the invention, it should be understood that the invention has a more general applicability. Substantial advantages may be secured by feeding heavy hydrocarbonaceous residues intimately mixed with water in accordance with the invention to subdivided solids masses of all types whenever particle agglomeration is to be avoided. For example, the invention may be employed to advantage in connection with coking operations of the moving bed type. Other modifications within the spirit of the invention may appear to those skilled in the art.

The invention will be further illustrated by the following specific example.

Example

An emulsion formed by intimately mixing in a colloid mill 100 parts of 2.4% South Louisiana vacuum residuum and 25 parts of water containing 0.5% of aluminum oleate is preheated to about 600° F. at 1600 p. s. i. g. pressure and sprayed into a bed of fluidized coke maintained at a temperature of 950° F. and essentially atmospheric pressure. A separate stream of steam equivalent to 25 parts of water is fed into the fluid solids bed below the point of feed injection in order to maintain this lower section of solids fluid. Under these conditions a feed rate, based on residuum, of 3 w./hr./w. can be main-

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tained until the run is voluntarily terminated without fluidization difficulties.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. In the process of coking heavy hydrocarbon oils in contact with preheated particulate heat-carrying solids in a low pressure coking zone, wherein said oil is converted at least substantially in liquid phase whereby said solids tend to become wetted with said oil to such an extent as to adhere together, the improvement which comprises forming an intimate mixture of said oil with 5 to 35% by weight of water, heating said mixture in liquid phase under elevated pressure to a temperature sufficient to cause substantially instantaneous vaporization of the water upon release of the mixture from said pressure, and releasing the heated mixture into said low pressure coking zone so as to permit said water to vaporize and expand substantially instantaneously to achieve extremely fine dispersion of said oil in said zone.

2. The process of claim 1 in which said liquid mixture is injected into said mass in finely divided form.

3. In the process of coking heavy hydrocarbonaceous residues in contact with a dense, fluidized mass of subdivided solids maintained at coking temperatures of about 800 to 1400° F. and about atmospheric pressure, the improvement which comprises preventing formation of viscous oil coatings on said solids sufficient to cause substantial coherence of said solids by preforming an intimate liquid mixture of said residues with 5 to 35 weight percent of water, preheating said mixture under a high preheating pressure to a temperature closely approaching the boiling point of water at said preheating pressure, but below a level conducive to substantial coking of said oil, and suddenly releasing the preheated pressurized mixture into contact with said solids at much lower pressure to cause extremely fine atomization of said oil.

4. Process according to claim 3 wherein said preheating pressure is between 700 and 3500 p. s. i. g.

5. In the process of coking heavy hydrocarbonaceous residues in contact with a dense, fluidized mass of subdivided solids maintained at coking temperatures of about 800 to 1400° F. and about atmospheric pressure, the

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improvement which comprises substantially preventing agglomeration of said subdivided solids due to deposition of wet oil coatings thereon by emulsifying said residues with water in a ratio to form an emulsion containing 5 to 35 weight percent of water, preheating the emulsion formed under an elevated pressure of about 700 to 3500 p. s. i. g. to a temperature above about 500° F. and closely below the boiling point of water at said elevated pressure, but below a level conducive to substantial coking, and spraying said preheated emulsion into said mass at a temperature and pressure conducive to the instantaneous vaporization of said emulsified water upon entering said mass.

6. The process of claim 5 in which said emulsion is of the water-in-oil type and contains an emulsifier selected from the group consisting of aluminum and calcium soaps.

7. The process of claim 6 in which said preheating temperature is substantially lower than the temperature of said mass.

8. Process according to claim 5 wherein the preheating pressure is between 1600 and 3000 p. s. i. g. and the preheating temperature is 500 to 700° F.

9. The process of claim 5 in which said emulsion is sprayed to a droplet size of less than 10 microns diameter.

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