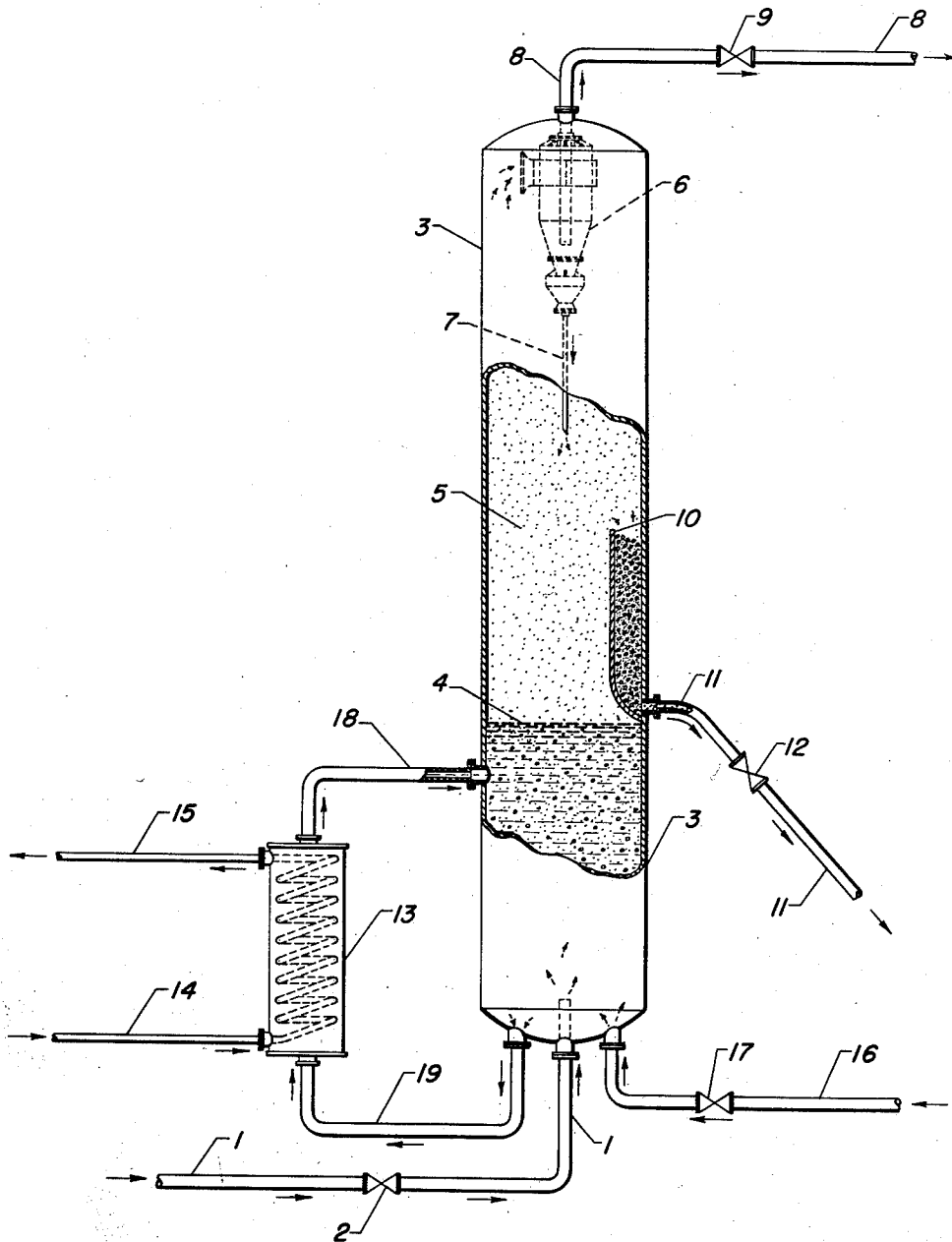


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HYDROCARBON COKING PROCESS

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HYDROCARBON COKING PROCESS

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This invention relates to a process for coking hydrocarbons and more particularly to a process for producing coke and lighter boiling constituents from an asphaltic petroleum fraction.

Asphaltic hydrocarbons such as reduced crudes and similar heavy residuum fractions are difficult to process because of undesirable tendencies to form solid materials when subjected to even moderately high temperatures. Asphaltenes contained in such stocks are heavy molecules of an aromatic nature which tend to polymerize to form solid carbonaceous deposits upon being heated, and these deposits are particularly known to form on hot surfaces such as heater tubes. Even if the stock is heated directly by contact with a solid cracking catalyst, for example, the asphaltenes rapidly polymerize and precipitate out of the charge stock as a carbonaceous material covering the active catalytic surface of the material. The extremely large quantities of coke that forms from such material must be removed by oxidation or other means to restore catalytic activity. These large quantities of coke represent lost material and also present processing problems such as fouling of equipment, excessive regenerator temperatures etc.

Other high boiling material contained in such stocks besides the asphaltenes, is capable of forming coke when treated either thermally or catalytically. Coke may also be formed by converting non-asphaltene material such as long straight chained molecules, however, more severe treatment is required since the molecules must first be cracked and the olefinic fragments polymerized to form coke. Since coking of the non-asphaltic material requires rather severe conditions and since both non-asphaltic and asphaltic material are present in some charge stocks, it may be seen that it is difficult to process such a stock since conditions at which asphaltenes cause trouble in the operation are not severe enough to convert the other material. Therefore, if a conventional coking process were to be performed on an ordinary asphaltic reduced crude, heating the reduced crude to a high enough temperature to cause coking of the non-asphaltic material would cause precipitation of the asphaltenes with the resultant difficulties. Contrary wise if only the conditions necessary to precipitate asphaltenes were obtained, the non-asphaltic material would remain unconverted.

The hereinbefore described state of circumstances suggests a two-stage operation, the first of which processes asphaltenes and the second of which processes non-asphaltenes. It is an object of this invention to provide a single unitary process which not only processes both the asphaltic and non-asphaltic material contained in an asphaltic charge stock but does so with inter-related steps to obtain improved results over a two-stage operation as well as a reduction in the number of processing stages.

It is an embodiment of this invention to provide a coking process which comprises passing an asphaltic charge stock beneath the surface of a molten medium maintained in the lower portion of a coking zone at

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coking conditions, precipitating asphaltic material as finely divided particles, collecting said precipitated particles at the surface of said molten medium, entraining said particles in an ascending gas stream to form a fluidized bed in an openly communicating superimposed zone, contacting vapors of unprecipitated material with said fluidized bed of particles to convert said unprecipitated material to coke and lower boiling material and separately recovering a coker distillate and solid coke particles.

In the process described in the above embodiment the charge stock, when introduced below the surface of a suitable molten medium is converted in two ways. First the asphaltene material contained in the charge stock is precipitated into finely divided or atomized solid particles and second, the non-asphaltene material is either thermally cracked to form lower boiling material or merely vaporized. The small particles of solidified asphaltene material, being less dense than the molten medium in which they are disposed, float to the surface and form a layer of individual small particles. These particles, when contacted with an ascending gas stream, are entrained therein and pass into the upper portion of the vessel wherein they are maintained as a fluidized bed. The fluidized particles present a large surface upon which vapors of the ascending non-asphaltic material are adsorbed and converted to lighter material and coke so that the net result of the process is to produce lower boiling material and coke particles whose diameters are continuously increasing as a result of continuous conversion. The lower boiling material or coker distillate is removed from the vessel and the coke particles are also removed at whatever rate is desired to maintain a given inventory of coke in the fluidized bed. The amount of coke maintained in the coking zone may be regulated by the velocity of the ascending gas stream, that is the coke and coker distillate may be drawn off together and subsequently separated and the amount of material in the fluidized bed regulated by the rate at which the gaseous material is passed through the vessel, or in a preferred operation the coker distillate may be drawn off through a suitable separation device so that only coker distillate is removed and the coke particles are separately withdrawn through suitable collection wells maintained in the vessel. The latter embodiment is the preferred since the former embodiment would preferentially withdraw smaller particles which should serve as nuclei for more coke formation rather than large particles which are more difficult to fluidized. When a collection well is maintained in the coking zone it is preferably maintained in the lower portion thereof but above the surface of the molten medium of course, so that the particles that settle more readily, that is the larger and denser particles, are the first withdrawn while the particles which settle least readily, that is the smaller and lighter particles, are maintained as a fluidized bed at an elevation above the collection well.

The molten medium to be used may be catalytic or non-catalytic in nature. A molten medium is used primarily so that there are no distinct surfaces upon which precipitated asphaltenes may form as a deposit. The advantages of a molten medium are apparent when one observes that a charge stock such as reduced crude that is discharged beneath the surface of a molten medium at proper conditions is converted to atomized solid particles and vapors even without the necessity of distributing means such as spray heads, etc. at the point of introduction. Although it is not definitely known, it is thought that the precipitating action comprises a local agglomeration of the asphaltene molecules in small particles which are separated by the liquid portion of the charge. When the liquid evaporates it leaves distinct particles of extremely small dimensions. Since the

molten material has no distinct surfaces, the asphaltenes, while passing through the various stages of liquid, plastic, tacky solid and eventually hard, dry solid, will assume the shape of a sphere or spheroid due to the normal operation of surface tension upon a liquid suspended in an immiscible fluid. As a result, as hereinbefore stated, the asphaltenes form as minute, hard dry particles rather than as a deposit upon the walls of the heater.

The molten material used may be a molten metal, a molten salt, a combination of salts, or any other suitable material which has the characteristics of being chemically inert towards the charge stock, liquid at the operating conditions and stable at the operating conditions of the process. Suitable molten media may include mercury, lead, low melting alloys such as Woods metal or solder or molten salts such as sodium chloride, potassium chloride, lithium chloride, magnesium chloride, combinations of these chlorides which may or may not form low melting mixtures, such as lithium chloride-potassium chloride, sodium chloride-magnesium chloride, cobalt sulfide-cobalt chloride, etc. The molten salt may also be combined with molten salts having catalytic activity such as halides of lead, manganese, tin, antimony, cadmium, zinc, silver, nickel, cobalt, and others. The use of catalytic material as the molten medium or in addition to the inert molten medium will generally increase the rate at which reactions occur as well as to produce a more selective coker distillate, that is one containing a greater amount of material boiling in the gasoline range and a lesser amount of material being converted to normally gaseous compounds.

The process of this invention is preferably effected at temperatures of from about 800° F. to about 1400° F. or higher and will usually be operated at from about 950° F. to about 1050° F. It is preferred that the charge stock is introduced into the molten salt in the cold condition or in a slightly pre-heated condition, said pre-heat preferably being obtained from a heat exchange relationship with another process stream. The process may or may not be effected under pressure but will probably be effected under a slight superatmospheric pressure, say from about 10 p. s. i. to 100 p. s. i., to facilitate the flow of materials from the reaction chamber. The pressure maintained in the reaction zone may be exerted by the normally vaporous material from the charge stock by itself or it may be exerted by a gas containing other material admixed therewith. Normally the material in the charge stock that is vaporized will form a sufficient volume of gas to cause fluidization of the precipitated asphaltene particles, however, if greater degree of fluidization is desired an additional gas may be added beneath the surface of the molten medium to aid in fluidization. Inert gases such as nitrogen, carbon dioxide, steam, etc. may be added to increase the volume of ascending gas or gases which also act as a reactant such as carbon monoxide, hydrogen and others may be added. When hydrogen is added to the reaction zone, the coker distillate will be a more saturated product and hence a more stable one since the operation of the mass action law will cause additional hydrogenation to occur in the unsaturated cracked product.

Oxygen or oxygen-containing gas such as air might also be provided to the coking zone to perform the double function of providing additional fluidizing gas to the process and autothermically providing endothermic reaction heat. Thus, when a mixture of charge stock and air, for example, is charged to the lower portion of the reaction zone or when charge stock and air are charged separately to the lower portion of the reaction zone, a portion of the charge stock will be oxidized thereby heating the molten medium and the charge stock contained therein to reaction conditions as well as to provide additional fluidizing gas in the form of carbon oxides, water vapor, and nitrogen. When the process is not operated autothermically other heating means must be provided and these

may be any of the conventional well known methods. Heat may be provided to the molten medium by a heat exchange means disposed in the lower portion of the reaction zone or by an electrical immersion type heater or the like. It is preferred that when indirect heat is supplied to the reaction zone it is through the medium of an external side arm type reboiler so that the incoming charge stock does not contact the heating means, but the heat is supplied to the reaction zone by a circulating stream of the molten medium. Preventing contact of the charge stock and the heater prevents the formation of carbonaceous deposits upon the heater.

It may be economical to provide for a method of recovering the catalytic material which is entrained in the overhead gases or adsorbed on the coke. When the catalytic or contact material is a molten salt it will generally be most readily recovered from the gas by scrubbing the gas and the liquid condensed from the gas with water. Similarly, the catalysts may be recovered from the solid coke by leaching with water. The solution of catalyst and water resulting from such a recovery process may then be evaporated and the recovered catalytic salt again returned to the reaction zone or the solution may be concentrated by evaporation and recharged to the reaction zone as a concentrated solution so that evaporation takes place within the reaction zone causing additional volumes of gas to rise through the fluidized bed in the form of the steam from the salt solution.

The accompanying drawing further illustrates the process of the present invention, however, it is not intended that the drawing shall limit the invention to the particular process or materials herein described.

Referring now to the drawing which will describe the process in relation to the conversion of a reduced crude and a catalytic molten medium comprising lithium chloride, potassium chloride, and tin chloride for the sake of simplicity, charge stock passes through line 1 and valve 2 into the lower portion of coking zone 3. In coking zone 3 a molten mixture of potassium chloride, lithium chloride and tin chloride is maintained at a level 4 at a temperature of 800° F. to about 1400° F. and the reduced crude charge stock rises through the salt mixture and is therein converted. The precipitated asphaltenes resulting from conversion rise through the molten medium and float on the top thereof wherein they are entrained and fluidized in vapors of the unprecipitated material from the reaction zone, the solid particles forming fluidized bed 5 in the upper portion of coking vessel 3. The vaporized material which holds the coked particles in suspension is partially adsorbed on the surface of the coked particles and is thus maintained at conversion conditions for sufficient time for thermal reactions to occur which cause craking and some polymerization which results in more coke formation. The coker distillate resulting from this process is withdrawn from vessel 3 through cyclone separator 6 which separates the stream into a particle stream returning through stand pipe 7 to the fluidized bed and a gaseous product stream which is withdrawn through transfer line 8 containing valve 9.

The larger, heavier coked particles, or those which have been maintained in the fluidized bed the longest, settle more rapidly than the lighter particles which, by elutriation, rise to the upper portion of chamber 3, and said heavier particles are collected in collection well 10 disposed in a lower intermediate portion of chamber 3, collection well 10 is connected to conduit 11 and valve 12 through which a net coke make is withdrawn from the process.

The present illustration shows heater 13 connecting to chamber 3 by lines 18 and 19 and containing lines 14 and 15 for the circulation of a heating medium, disposed external to the coking zone. The heater shown is a natural circulation, indirect heating type and as herein-

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before described in the specification, may be replaced with immersion type heaters, direct heaters, or internal heaters. Line 16 and valve 17 will provide for the introduction of an extraneous gas stream which may be inert or a reactant in the process. When line 16 carries oxygen to the process it may be unnecessary to provide for additional heat with heater 13 in which case heater 13 may be not used or totally eliminated from the process.

I claim as my invention:

1. A coking process which comprises passing an asphaltic charge stock beneath the surface of a molten medium maintained in the lower portion of a coking zone at coking conditions, precipitating asphaltic material as finely divided particles, collecting said precipitated particles at the surface of said molten medium and entraining them in an ascending gas stream to form a fluidized bed in an openly communicating superimposed zone, contacting vapors of unprecipitated material with said fluidized bed of particles at a temperature and for a time sufficient to convert said unprecipitated material to coke and lower boiling material and separately recovering said lower boiling material and said solid coke particles.

2. A coking process which comprises passing an asphaltic charge stock beneath the surface of a molten medium maintained in the lower portion of a coking zone at a temperature of from about 800° F. to about 1400° F., precipitating asphaltic material as finely divided particles, collecting said precipitated particles at the surface of said molten medium and entraining them in an ascending gas stream at least partially comprising vapors of unprecipitated material to form a fluidized bed in an openly communicating superimposed zone, contacting vapors of unprecipitated material with said fluidized bed of particles at a temperature and for a time sufficient to convert said unprecipitated material to coke and lower boiling material and separately recovering a coker distillate and solid coke particles.

3. The process of claim 2 further characterized in that said ascending gas stream comprises unprecipitated material in the charge stock and extraneous hydrogen,

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4. The process of claim 2 further characterized in that said coking zone is maintained at reaction temperatures by adding to said coking zone, concurrently with the charge stock, oxygen-containing gas, the reaction products of which form a portion of said ascending gas stream.

5. The process of claim 2 further characterized in that said ascending gas stream comprises the unprecipitated material of the charge stock and an inert gas.

6. A coking process which comprises passing an asphaltic charge stock beneath the surface of a molten medium maintained in the lower portion of a coking zone at coking conditions, precipitating asphaltic material as finely divided particles, collecting said precipitated particles at the surface of said molten medium and entraining them in an ascending gas stream to form a fluidized bed in an openly communicating superimposed zone, contacting vapors of unprecipitated material with said fluidized bed of particles at a temperature and for a time sufficient to convert said unprecipitated material to coke and lower boiling material, withdrawing said lower boiling material from said coking zone through a separation means disposed in the upper portion thereof and separately withdrawing solid coke particles from a collection zone disposed above the level of said molten medium in an intermediate portion of said coking zone.

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