This invention relates to a continuous conversion process and particularly to a continuous coking process which is effected in a liquid medium and the apparatus for effecting the process.

Coking or destructive distillation is a process for obtaining a highly carbonaceous solid from organic matter. The art of coking coal to form coke, and wood to form charcoal is well-known as is the art of forming petroleum coke from the higher boiling portions of a crude oil. Generally the coking process consists of heating the organic matter to be coked in the absence of air to drive off all volatile matter and to crack the less refractory substances to volatile substances whereby a distillate is formed and removed and a resulting coke remains. Coking is generally a batch operation in which a certain quantity of the organic material to be coked is placed in a coking chamber and all of the coking operations are performed on that particular batch after which it is discharged and replaced by a new batch.

The art of petroleum coking is characterized by the difficult problem of removing the coke product from the chamber in which it is produced. The manner of producing a petroleum coke is similar to that of producing coke from coal, and consists of pumping a liquid petroleum fraction into a coking chamber and subjecting it to high temperature to form a coker distillate, which is the volatile material passing overhead, and a solid, highly carbonaceous coke. When the operation is complete it is necessary to open the chamber, usually by removing the bottom, and to drill out the solid product. Various ingenious methods have been devised for removing the solid coke from the coking chamber such as placing a coiled chain in the coking chamber prior to the operation so that when the coking chamber is full of coke, it is necessary only to forcibly remove the chain, which is now embedded in the coke, to break loose at a substantially portion of the solid product. Another method of removing coke is to blast it out with high pressure hydraulic jets. At best, these methods are wasteful, crude, dirty and laborious. The batch operation herebefore described may not be successfully catalyzed since the catalyst would be embedded in the final product and could not be easily recovered. The lack of catalyst causes the process to be affected at high temperatures and further causes unfavorable product distribution in the coker distillate.

To overcome the difficulties enumerated above, continuous coking processes have been devised. Most of these processes are based on the use of coke, in particular form, as a contact material. The typical operation may be described as passing the petroleum fraction to be coked into contact with a fixed, fluidized or moving bed of particles of coke which are heated to the coking temperature whereby coke forms on the surface of the particles so that the production of coke is evidenced by an increase in the dimensions of the contact material. In order to successfully operate this type of process a continuous manner, there must be a continuous removal of coke particles, separation as to size, and return to the contacting zone. Although the continuous removal, size separation and return of coke particles to the reaction zone is a difficult operational step to achieve, it does not present the greatest problem in this type of manufacture. It seems that when a liquid petroleum fraction is coked, it passes from a liquid to a solid, in a continuous manner. In passing liquid to solid the fraction goes through all stages of plasticity including a sticky semi-solid stage when it will not be fluid enough to flow and yet not solid enough to be "dry" and non-agglomerating. As a result of this gradual although rapid transition from liquid to solid there is a point at which the material being converted will adhere tenaciously to anything it touches. Unfortunately, this point generally occurs in the immediate vicinity of the point of introduction into the reaction zone. A result of this it has been found that the hot metal at the point of introduction of the petroleum fraction into the coke zone will build up a layer of coke which, as the operation progresses, becomes increasingly thick, eventually clogging up equipment so that it is necessary to shut down.

Continuous coking operations are also thermal reactions wherein it is extremely difficult to control the composition of the product since no catalyst may be present in the reaction zone without causing impurities in the ultimate coke product. The limited commercial acceptance of a continuous coking process of this type is evidence of the great difficulty involved in such an operation.

It is an object of this invention to provide a method of continuously coking organic material wherein the material to be converted is never in contact with its container walls or other hot surfaces, thereby eliminating the "coking up" of equipment.

It is a further object of this invention to provide a continuous coking process wherein the coke is formed in a liquid medium thereby facilitating its removal from the reaction zone as well as providing a convenient medium for introducing heat into the reaction zone. It is still a further object of this invention to provide a continuous coking process which utilizes a catalyst from which the coke is readily separated, thereby allowing the process to be effected at lower temperature and furthermore improving the quality of the coker distillate. Other objects and advantages of this invention will be apparent from the following description.

It is an embodiment of this invention to provide a method of converting organic material which comprises passing the organic material into contact with and below the surface of a swirling mass of liquid having a higher specific gravity than the organic material and being substantially immiscible therewith, maintaining the swirling liquid at conversion conditions and withdrawing the resultant products.

It is another embodiment of this invention to provide a method of continuously coking an organic material which comprises passing said organic material into contact with and below the surface of a swirling mass of liquid having a higher specific gravity than the organic material and being substantially immiscible therewith, maintaining said swirling liquid at conversion conditions, separately withdrawing the resultant non-volatile product from the surface of said swirling liquid and the volatile product from above the surface of said swirling liquid.

It is another embodiment of this invention to provide a method of continuously coking an organic material which comprises passing said organic material into contact with and below the surface of a swirling mass of liquid having a higher specific gravity than the organic material and being substantially immiscible therewith, maintaining said swirling liquid at coking conditions, separately withdrawing a resultant coke from the surface of said swirling liquid and a coker distillate from above the surface of said swirling liquid.
It is another embodiment of this invention to provide a method of coking organic material which comprises passing the organic material into contact with and below the surface of a swirling mass of molten salt having catalytic properties, maintaining the swirling mass of molten salt at a temperature of from about 750° F. to about 2000° F. or more, separately withdrawing the resultant coke from the surface of the molten salt mass and a coker distillate from above the surface of the molten salt mass.

It is still another embodiment of the present invention to provide an apparatus for effecting the coking process which provides a means of contacting a petroleum fraction with a swirling molten medium so that the petroleum fraction does not come in contact with the container walls and to further provide a method of regulating the residence time of the petroleum fraction in the swirling medium.

To accomplish the objective of continuously coking an organic material within a chamber without contacting the organic material with the chamber in which it is coked, the present invention provides that the coking is done in the vortex of a swirling mass of molten medium. Since the coking up of equipment that causes shut downs is caused by deposits forming on the surface of the container walls which may be hot metals or refractory substances, and since the present invention provides a method of preventing the contact of the hot organic material with container surfaces, this invention substantially eliminates that difficulty. By introducing the organic material into a swirling mass of denser material, the centrifugal separator type of flow will cause the organic material to "float" towards the center of the swirling mass and thereby be converted remote from the container walls. Since the molten medium has no well defined surface for the coke to form on, it simply forms as a separate phase of lesser density that will float to the top of the swirling mass and accumulate there as a separate layer.

Any suitable molten contact material may be used including molten metals, molten salts, or other molten material that is substantially immiscible with the charge stock and of higher gravity. Some of these materials may include mercury, lead, low melting metal mixtures, fused salts including metal halides, sulfates, nitrates, etc., mixtures of metal salts and low melting metal salt mixtures in which catalytic salts are dissolved. It is particularly preferred that the molten medium comprises a catalytic molten salt so that the coker distillate formed in the reactions will be selectively cracked to form the more desirable products, for example, those boiling in the gasoline range. Some particularly effective molten salts that may be used are acidic metal halides, such as aluminum chloride, aluminum bromide, lead chloride, arsenic chloride, antimony chloride, thallium, iron chlorides etc. These may be used alone or in mixtures or dissolved in a low melting carrying medium such as a melt of lithium chloride-potassium chloride, lithium chloride-sodium chloride etc.

The present process must be effected at a temperature that is high enough to initiate the desired conversions. The temperature will usually be in excess of 750° F. and may range up to 2000° F. or more depending upon the type of conversion desired, the catalytic quality of the contact material and the characteristics of the charge stock. The cracking reactions are pressure by low pressure and so the pressure at which the process is effected may be atmospheric or slightly superatmospheric in order to facilitate the passage of materials from the reaction chamber. Pressures from atmospheric up to 15 to 20 p. s. i. or even up to 50 p. s. i. or more may be used.

Since the organic material is of a lesser density than the contact material it is preferred that the organic material be introduced into the lower portion of the contacting vessel so that it rises therethrough. The organic material is preferably introduced in a finely subdivided form so that there is a maximum of contact between the molten medium and the organic material. The molten material which may be introduced as liquid petroleum, gaseous petroleum, gaseous gas, or other volatile material, may be extruded into the lower portion of the contacting zone or passed through a spray head so that small particles are formed. The molten medium is preferably introduced tangentially into the contacting zone so as to form a swirling mass. It is contemplated that the molten medium is introduced at an intermediate point in the column and that it is discharged from the column both through an overflow conduit and a lower discharge point which is located in the contacting zone below the point of organic material introduction. By proportioning the amount of molten medium that discharges through the overflow means and through the lower discharging means as well as by selecting the proper intermediate point of the column to introduce the molten medium, the rate at which the organic material rises through the column may be controlled. For example, the flow may be countercurrent when the overflow is introduced at a point high on the column. If the overflow of salt discharged through the lower discharge means is far greater than that discharged through the overflow means. The apparatus provides for a downwardly spiraling mass of salt which causes the rising subdivided organic material thereby providing a contact time of organic material and molten medium by causing the organic material to float upward against a descending liquid stream. When a lower salt introduction point is used and the proportion of overflow is increased, it may be seen that the molten salt will have a general downward spiraling motion and will be in rough concurrent flow with the organic material thereby providing for a relatively shorter contact time. The apparatus may be so constructed to provide for any given contact time by introducing the salt through one or several of many intermediate points and by providing both upper and lower discharge means for the salt.

It is preferred that the upper portion of the contacting zone is laterally expanded to provide for a greater inventory of coke in the upper portion of the zone. The overflow mechanism hereinbefore mentioned is preferably of sufficient diameter to provide for the overflow of salt and discharge of accumulated coke. The overflow conduit passes into a salt accumulating zone wherein the salt accumulates with a layer of coke on top. It is contemplated that the layer of coke may be removed from the salt by some mechanical means in this accumulating zone.

The accumulating zone may be a convenient place for providing the necessary heat of reaction to the salt. The salt may be heated by any suitable means such as direct fire, heat exchange with hot fuel gases etc. It is also contemplated that the reaction may be operated in an autotermic manner by introducing oxygen or oxygen-containing gases into the contacting zone so that a portion of the organic material is burned up or providing heat for the reaction of the remainder of the material.

A particularly suitable apparatus for effecting the process of the present invention may comprise a vertically elongated vessel of circular cross section to facilitate a centrifugal separator type swirling flow of the liquid medium contained therein. The cylindrical vessel may be laterally expanded in the upper portion to form a contacting region where the non-volatile product from the process may accumulate. The level of molten medium may be maintained and the discharge of non-volatile product may be effected by providing a large diameter overflow conduit to the upper enlarged portion of the vessel passing downwardly from the enlarged portion to a separation and accumulation zone where the non-volatile material may separate from the liquid medium in an area of relative tranquility. The accumulation zone may simply be a vessel having sufficient capacity to substantially reduce the velocity of the stream passing there-
through containing a means, mechanical or otherwise, for removing the nonvolatile phase from the surface of the liquid medium.

The liquid contact medium circulates from the vessel, to the accumulator and back to the vessel, returning to the vessel from the accumulator through a conduit that enters the vessel tangentially so that the circulation of the liquid medium imparts the swirling motion to the material in the vessel. The swirling motion may be obtained by mechanical means, such as an impeller, in addition to the tangential inlet, however, it is preferred to regulate the centrifugal motion by regulating the rate of liquid circulation. As hereinbefore described, the reaction vessel is provided with a liquid discharge conduit in the lower portion for regulating the flow characteristics of the liquid medium within the reaction vessel.

The feed stock to the reaction vessel enters in the lower portion through a suitable distributing device which causes the charge stock to disperse into sub-divided cones.

The liquid medium may enter the reaction column tangentially at one or many points. For a particularly versatile apparatus, the reaction vessel may be provided with a plurality of tangential inlets, which are fed from a common header and provided with suitable valves. The flow characteristics of the liquid medium in the reaction vessel may be regulated by using all or some of these inlets. For example, when it is desired to have a downward swirling flow of liquid having high angular velocity, a single upper inlet may be used to pass liquid into the vessel at a high velocity and a substantial proportion of the liquid medium passing from the column may pass from the lower discharge conduit. Conversely, when it is desired to have an upwardly spiraling flow of liquid medium having a low angular velocity several or all of the tangential inlets may be used to pass liquid into the column at relatively low velocity and a large proportion of the liquid medium may be discharged from the column through the overflow conduit.

When the reaction to be effected is endothermic it may be necessary to apply heat to the liquid medium. It is extremely desirable to heat the liquid medium rather than the charge stock to eliminate the undesirable thermal effects caused by contacting charge stock with hot metallic surfaces such as those found in heaters. The liquid contact medium may be heated by ordinary heat exchange methods while in the accumulator or the accumulator may be exposed to direct flames. It is also within the scope of this invention to effect the reaction autogenously by introducing a stream of oxygen-containing gas into the reaction vessel thereby oxidizing a portion of the charge and supplying the heat necessary to cause the rest to react.

In the upper portion of the reaction vessel, at a point above the overflow conduit, there will of course be a volatile product discharge conduit for carrying volatile products overhead. When the reaction vessel is operated at a superatmospheric pressure, this conduit will contain a valve which will control the pressure in the reaction vessel.

The overflow conduit may contain a means of introducing a stripping gas into an intermediate portion thereof for the purpose of removing volatile material from liquid medium or non-condensable material passing therethrough. The stripping gas may be any inert gas such as steam, nitrogen, flue gas etc.

Even though the process of this invention is primarily directed towards the production of coke, it may be observed that a large yield of useful volatile overhead product, called byproduct coke, will be realized. In ordinary processes for producing coke, the coke distillate has characteristics conforming roughly to thermally cracked gasoline, having low octane rating, a high degree of unsaturation, being of relatively straight chain structure and extremely unstable in storage. When the process of the present invention employs a catalytic sub-
stance as a liquid contact medium, the characteristics of the coker distillate conform closely to those of a catalytically cracked gasoline. The catalytically produced coker distillate is superior in quality, and hence more valuable as a by product, than the thermally produced coker distillate since it has a higher octane rating, has a lesser degree of unsaturation, is more highly branched in structure and is more stable in storage. Besides enhancing the value of the product, the use of a catalytic substance as a liquid medium enables the reactions to be effected at a lower temperature thereby causing a saving in the initial cost and upkeep of heating equipment.

The accompanying drawing is presented to illustrate one particular embodiment of the process and apparatus of this invention but is not intended to unduly limit the invention to the particular process and apparatus illustrated.

Referring now to the drawing, which for the sake of simplicity illustrates the process of coking a high boiling petroleum fraction, the charge stock passes through line 1 into the lower portion of vessel 3 and through distributing nozzle 2. The stream flowing from distributing nozzle 2 is a series of finely divided droplets of petroleum which passes upwardly through reaction vessel 3. Reaction vessel 3 contains a molten salt having catalytic effects and is filled to a level 4 which is regulated by the intake end of overflow conduit 6. Molten salt vessel 3 tangentially through at least one of the lines 13, 15, 17, 19, and 21 containing valves 14, 16, 18, 20, and 22 respectively. It is contemplated that the molten salt supplied to vessel 3 through the appropriate line enters tangentially at a relatively high velocity thereby imparting to the mass of molten salt contained in vessel 3 a swirling circular motion in a roughly horizontal plane. The swirling motion of the dense molten column causes a centrifugal type operation in which the less dense petroleum “floats” towards the middle of the column and rises therethrough out of contact with container walls. The tangential inlets to column 3 are supplied with molten salt from line 12 which is common to all of them.

The overflow from vessel 3 passes through the hereinbefore mentioned conduit 6 and into salt accumulator 8. Line 6 may contain line 7 entering into a horizontal line thereof which supplies line 6 with a suitable stripping gas when such stripping gas is desired. When the operation conditions are such that volatile matter might pass through conduit 6, steam, nitrogen, flue gas or other inert gases may pass into conduit 6 through line 7 thereby preventing the escape of volatile material into salt accumulator 8. In chamber 8 a level of salt is maintained upon which is floating the involatile material resulting from the conversion process. The involatile material is substantially “dry” coke which may be described as coke that is completely in the solid phase having no tendency to further react or to agglomerate.

Salt accumulation vessel 8 may contain heater 28 which furnishes the necessary heat of reaction for the process. The salt in accumulator 8 passes through line 10 and pump 11 into the before mentioned line 12 which supplies the tangential inlet conduits chamber 3. Vessel 3 may be provided with outlet conduit 23 in the lower portion thereof which passes through pump 24 and into line 25 discharging into salt accumulator 8. The total flow of salt entering through one or several of the tangential inlets to column 3 must be discharged from column 3 either through line 6 or through line 23. By proportioning the flow through one or both of these lines, one may regulate the direction of flow of the molten salt in the column, that is whether it shall spiral upwardly, downwardly, or swirl in a horizontal plane. When it is desired to increase the contact time of the organic material to be converted with the molten medium, for example when the accumulated non-volatile material on level 4 is not dry coke, the proportion of salt
passing through line 23 may be increased so that the hydrocarbons entering distributing nozzle 2 must float upwardly opposed to a descending stream. Conversely, when a lesser contact time is desired a greater proportion of the salt leaving column 3 is discharged into overflow line 6 whereby an upwardly spiraling stream of molten salt is in vessel 3 so that the organic material entering through distributing nozzle 2 will float upwardly concurrent with the molten salt.

When a petroleum fraction is to be coked there will result from the process a coker distillate which is comprised of the more volatile hydrocarbons contained in the petroleum to be coked as well as reaction products from the conversion such as cracked gasoline and the normally gaseous hydrocarbons. At the conditions in vessel 3 this material will be in the vapor state and will be passed overhead through line 26 and condenser 27 which liquefies the normally liquid constituents of the stream.

Condensed gas passing from the upper portion of salt accumulator 8 is provided to remove the non-volatile product or coke from the process. The coke overflooding from vessel 3 through line 6 will accumulate on the relatively tranquil surface maintained in accumulator 8 and may be removed through conduit 9 either by overflow or by any suitable mechanical device 30.

When it is desired to operate the present process autothermically, line 29 may be provided which preferably enters column 3 tangentially in the lower portion thereof. Line 29 may contain oxygen or oxygen-containing gases which will oxidize a portion of the hydrocarbons in the feed stock thereby supplying sufficient heat of reaction for the conversion of the remainder of the charge stock.

The gas used may be air or air enriched with oxygen or air diluted with flue gas or other inert.

Although this process has been described primarily in relation to a coking operation wherein an organic substance such as a high boiling petroleum fraction, coal, wood, etc. is subjected to conversion conditions in a molten medium and converted to coke and coker distillate, it may find use in other conversion processes including catalytic cracking of a petroleum fraction to form a lower boiling petroleum fraction, reforming a gasoline fraction to form a gasoline having higher octane number and improved characteristics, distilling and converting shale oils by subjecting finely ground shale to conditions of high temperature in a molten medium, polymerizing low boiling hydrocarbons to form higher boiling hydrocarbons etc.

We claim as our invention:

1. The method of continuously converting organic material which comprises introducing said organic material into the lower portion of a vertically elongated swirling mass of liquid having a higher specific gravity than said organic material and being substantially immiscible therewith, passing the organic material upwardly through the central portion of said swirling mass, maintaining said swirling liquid at coking conditions, separating the resulting coke from the surface of said swirling liquid and a coker distillate from above the surface of the liquid.

2. The method of continuously converting organic material which comprises introducing said organic material into the lower portion of a vertically elongated centrifugally swirling mass of liquid having a higher specific gravity than said organic material and being substantially immiscible therewith, passing the organic material upwardly through the central portion of said swirling mass, maintaining said swirling liquid at coking conditions, separating the resulting coke from the surface of said swirling mass and a coker distillate from above the surface of the liquid.

3. The method of continuously coking organic material which comprises introducing said organic material into the lower portion of a vertically elongated centrifugally swirling mass of liquid having a higher specific gravity than said organic material and being substantially immiscible therewith, passing the organic material upwardly through the central portion of said swirling mass, maintaining said swirling liquid at coking conditions, separating the resulting coke from the surface of said swirling liquid and a coker distillate from above the surface of the liquid.

4. The method of continuously coking organic material which comprises introducing said organic material into the lower portion of a vertically elongated centrifugally swirling mass of liquid having a higher specific gravity than said organic material and being substantially immiscible therewith, passing the organic material upwardly through the central portion of said swirling mass, maintaining said swirling liquid at coking conditions, separating the resulting coke from the surface of said swirling liquid and a coker distillate from above the surface of the liquid.

5. The method of continuously converting organic material which comprises introducing said organic material into a reaction zone containing a vertically elongated centrifugally swirling mass of molten salt maintained at coking conditions, passing the organic material upwardly through the central portion of said swirling mass, tangentially introducing said molten salt into said reaction zone whereby the swirling motion is imparted to the mass in said reaction zone, separately withdrawing the resultant non-volatile product from the surface of said swirling mass and a volatile product from above the surface of said swirling mass.

6. The method of continuously coking organic material which comprises introducing said organic material into a reaction zone containing a vertically elongated centrifugally swirling mass of molten salt maintained at coking conditions, passing the organic material upwardly through the central portion of said swirling mass, tangentially introducing said molten salt into said reaction zone whereby the swirling motion is imparted to the mass in said reaction zone, separately withdrawing the resultant non-volatile product from the surface of said swirling mass and a volatile product from above the surface of said swirling mass.

7. An apparatus for converting organic materials in the presence of a molten medium which comprises in combination a vertically disposed elongated cylindrical vessel, an accumulating chamber, an overflow conduit passing from the upper portion of said vessel downwardly into said accumulating chamber a particle overflow conduit passing from the upper portion of said accumulating chamber and a liquid discharge means passing from the lower portion of said accumulating chamber through conduit means to a plurality of vertically disposed intermediate tangential inlets to said cylindrical vessel, lower reactant inlet and upper product outlet means connected with said cylindrical vessel, liquid outlet means disposed in the lower portion of said cylindrical vessel in a position lower than said reactant inlet, and conduit means connecting said lower liquid outlet to said accumulating chamber.

8. The apparatus of claim 7 further characterized in that said lower reactant inlet means is provided with a distributing nozzle.

9. The apparatus of claim 7 further characterized in that the upper portion of said vessel is laterally expanded and said overflow conduit passing from said enlarged zone contains means for introducing stripping gas into an intermediate portion thereof.

10. The apparatus of claim 7 further characterized in that means for introducing oxygen-containing gas is provided to an intermediate section of said cylindrical vessel.

11. The apparatus of claim 7 further characterized in that heating means is provided to said accumulating chamber.

12. The apparatus of claim 7 further characterized in that mechanical means is provided to the upper portion of said accumulating chamber to facilitate the removal of solid material.
13. An apparatus for converting organic materials in the presence of a molten medium which comprises a vertically elongated cylindrical vessel having a reactant inlet at its lower portion and a vapor outlet at its upper portion, an accumulating chamber, an overflow conduit extending from the upper portion of said vessel to said chamber, means for passing molten medium from the lower portion of said vessel to said chamber, means for removing solid particles from the upper portion of said chamber, and means for removing molten medium from the lower portion of said chamber and for discharging the same tangentially into said vessel at an intermediate point in the height thereof between said reactant inlet and said overflow conduit.

14. An apparatus for converting organic materials in the presence of a molten medium which comprises a vertically elongated cylindrical vessel having an enlarged upper portion, a reactant inlet at the lower portion of the vessel and a vapor outlet in said enlarged upper portion thereof, an accumulating chamber, an overflow conduit extending from said enlarged upper portion of said vessel to said chamber, means for passing molten medium from the lower portion of said vessel to said chamber, means for removing solid particles from the upper portion of said chamber, and means for removing molten medium from the lower portion of said chamber and for discharging the same tangentially into said vessel at an intermediate point in the height thereof above said reactant inlet and below said enlarged upper portion.

15. An apparatus for converting organic materials in the presence of a molten medium which comprises a vertically elongated cylindrical vessel having a reactant inlet at its lower portion and a vapor outlet at its upper portion, an accumulating chamber, an overflow conduit extending from the upper portion of said vessel to said chamber, means for passing molten medium from the lower portion of said vessel to said chamber, means for removing solid particles from the upper portion of said chamber, an inlet conduit connected tangentially to said vessel at an intermediate point in the height thereof between said reactant inlet and said overflow conduit, and means for supplying molten medium under pressure from said chamber to said inlet conduit.

References Cited in the file of this patent

UNITED STATES PATENTS

866,084 Stgiltz September 17, 1907
2,015,083 Oberle September 24, 1935
2,050,772 Wait August 11, 1936
2,334,583 Reeves November 16, 1943
2,624,697 Clouse et al. January 6, 1953