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PROCESS FOR COKING HYDROCARBONACEOUS LIQUIDS

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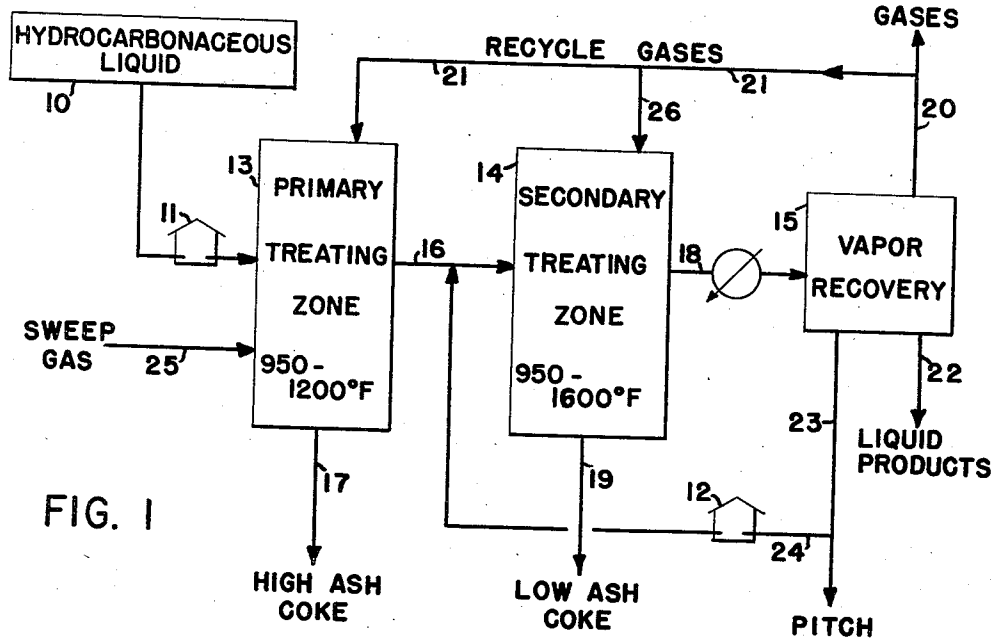



FIG. 1

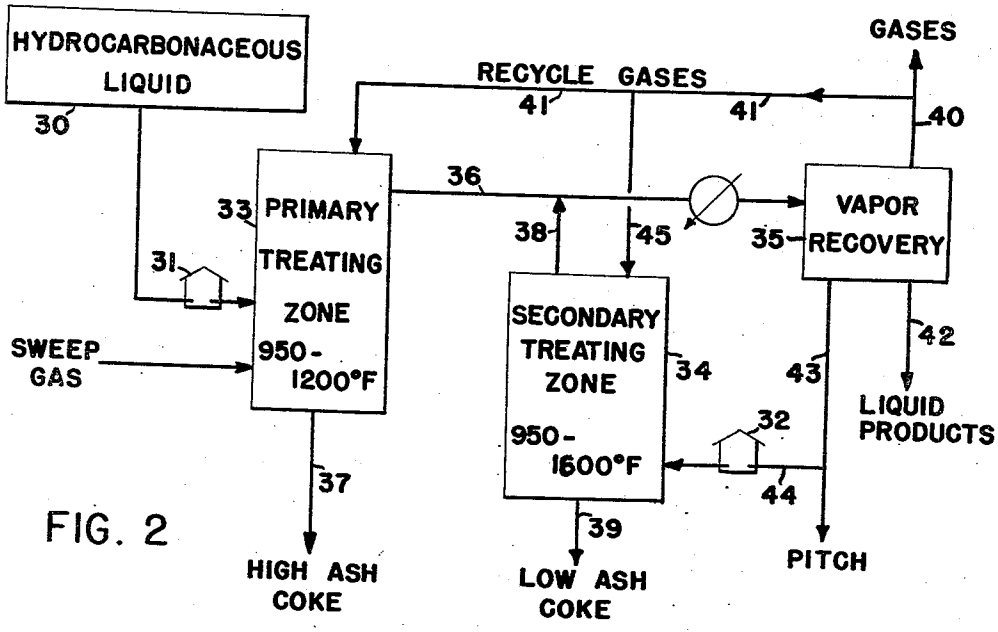



FIG. 2

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# PROCESS FOR COKING HYDROCARBONACEOUS LIQUIDS

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7 Claims. (Cl. 202—22)

The present invention relates to a process for coking ash-containing hydrocarbonaceous liquids. More particularly, it relates to a process of the continuous type for preparing low-ash-content coke from high-ash-content hydrocarbonaceous liquids.

Hydrocarbonaceous liquids, especially those derived through pyrolysis of carbonaceous solids, frequently contain substantial quantities of finely divided solids which are difficult to remove. These finely divided solids are particles of the original carbonaceous solids and partially pyrolyzed solids which become entrained in the pyrolysis vapors. It is not unusual for low temperature coal carbonization liquid products, for example, to contain as much as 15 to 25 percent by weight of these finely divided solid particles which contain all of the ash originally present in the particles prior to carbonization. The ash composition of these particles may be as much as 10 to 15 percent by weight.

As used herein, "ash" is defined as the non-combustible inorganic residue which remains following exhaustive combustion of the material.

Cokes produced by thermal treatment of these ash-containing hydrocarbonaceous liquids cannot be marketed as premium carbon sources because of their high ash contamination. The same problem arises in connection with utilization of the products of liquid phase coal hydrogenation, the liquid product resulting from solvent extraction of coal, the liquid product from oil shale pyrolysis, and like materials having relatively high-ash content.

To utilize these hydrocarbonaceous liquids as a premium solid carbon source, for use as an electrode carbon, for example, they must be converted into a coke having essentially no ash. Filtration of ash-containing solids from the hydrocarbonaceous liquids is difficult and expensive, if possible at all. The fine state of subdivision of the solids results in plugging of the pores of conventional filters; the viscous character of the liquids requires preliminary heating to permit passage through filters. Hence filtration is ordinarily not practiced.

Frequently the more valuable lower boiling liquid constituents of these hydrocarbonaceous liquids are first recovered as product by distillation. The undistilled residue of such distillation hereinafter will be referred to as pitch. In some instances, for example, this undistilled residue boils above 230° C.; in other instances the undistilled residue boils above 300° C.; the precise temperature of separation is determined by the proportions of the starting material and the demand for the lower boiling material. The high boiling undistilled residue usually is referred to as pitch.

I have discovered a method for preparing low-ash carbon solids from high-ash hydrocarbonaceous liquids by a two stage thermal treatment. The high-ash liquid is subjected to a primary thermal treatment under mild coking conditions at 950 to 1200° F. for preparing a high-ash coke containing essentially all of the ash-containing solids in the starting liquid together with a small portion of coke derived through thermal degradation of the more readily cokable constituents of the liquid. The uncoked components of the original liquid are recovered from the primary thermal treatment in vapor form, essentially free of ash containing materials. All or a portion of these uncoked vapors are subjected to a secondary thermal treatment under more severe coking conditions at 950 to 1600° F. The secondary thermal treatment produces an ash-free coke suitable as a premium carbon source together with non-condensable gases, low boiling liquid products, and an ash-free liquid residue which may be recycled to the secondary thermal treatment for further coking or may be recovered as a premium quality pitch, if desired. The ash-containing coke produced in the primary thermal treatment may be used as a fuel or as a low grade source of carbon, such as used in carbide production, metallurgical installations, and the like.



By the term coal as used herein, I comprehend all ranks of coal including anthracite, bituminous, sub-bituminous, lignite and the like. The present invention also finds utility in the treatment of liquid products resulting from the pyrolysis of oil shale.

The present process is applicable to those coking systems which are susceptible to controlled fractional coking, i. e., those systems which are of the "continuous" type rather than the "batch" type. The extent of coking which results in batch processing cannot be controlled with the precision required to realize the benefits of the present invention. Examples of batch processes are the sole-heated ovens in which a cokable, high boiling, hydrocarbonaceous liquid is heated under quiescent conditions to produce a solid block of residuum coke. Examples of continuous type processes are those coking systems carried out in fluidized beds, in moving solids beds, in rotating kilns and the like.

For a clear understanding of the present invention, its objects and advantages, reference should be had to the following description and accompanying drawings in which:

Figure 1 is a flow sheet illustrating the preferred embodiment of the present invention; and

Figure 2 is a flow sheet illustrating an alternative method for carrying out the present invention.

The apparatus shown schematically in Figure 1 includes a source of high-ash-feedstock **10**; heaters **11** and **12** for raising the temperature of liquid feedstock; a primary thermal treatment zone **13**; a secondary thermal treatment zone **14**; and a vapor recovery system **15** for separating non-condensable gases, liquids and unconverted pitch.

The material used as a feedstock in the present process is a hydrocarbonaceous liquid containing ash. The process is especially applicable to treatment of that fraction of low temperature carbonization tar boiling above 300° C. as well as treatment of the entire liquid product from low temperature carbonization, although it is preferable to remove at least the valuable constituents boiling below 230° C. for recovery prior to the present treatment since these materials are susceptible to thermal degradation to less valuable materials. The feedstock, quite viscous at ordinary temperatures, may be heated to facilitate its pumping through pipes. A heater **11** is provided for this purpose. The amount of preheat should be sufficient to reduce the viscosity of the liquid to permit pumping, yet not so high that coking occurs within the

heater. Preferably the liquid is preheated to a temperature in the range 200 to 800° F.

Preheated hydrocarbonaceous liquid is introduced into the primary thermal treating zone 13, maintained at a temperature of 950 to 1200° F. This primary treating zone is a suitable coking unit of the continuous type, e. g. a fluidized pitch coker, a downwardly moving bed pitch coker, a rotating kiln, a pug mill and the like. The primary zone 13 contains a mass of heated carbonaceous pebbles. These carbon pebbles supply the necessary surface area for deposition of a layer of coke from the liquid feedstock. It may be necessary from time to time to supply additional seed pellets as nuclei for the formation of additional carbon pebbles. Sweep gas is introduced into the primary treating zone 13 through a conduit 25 to allow regulation of the extent of coking occurring therein. The sweep gas serves to reduce the partial pressure of the vaporized feedstock and to facilitate removal of the vapors from the primary treating zone 13. Recycle product gases are preferred as sweep gases. The temperature, residence time and sweep gas rate in the primary zone 13 are regulated to allow only a minimum coking of the liquid portion of the feedstock.

As feedstock is introduced into the primary treating bed of carbon pellets, a film of liquid feedstock forms on the surface of each pebble. The substantial bulk of the feedstock is volatilized and recovered as a vapor through conduit 16. The finely divided ash-containing particles of the feedstock adhere to the moist surfaces of the carbon pellets and are incorporated into the carbon pellets during the subsequent coking of the liquid film resulting from its continued exposure to coking conditions in the primary zone 13. A portion of the carbon pebbles from the first zone is removed continuously or intermittently from the bed for screening. Oversize pebbles are removed as product high-ash coke and undersize pebbles are returned to the primary zone for additional size accretion through further coking. I prefer to limit production of high-ash coke in the primary zone to about 5 to 15 percent of the liquid portion of the feedstock by weight.

The total vapors resulting from the primary thermal treatment zone are passed through a conduit 16 to a secondary thermal treating zone 14, operated under more severe coking conditions at 950 to 1600° F. In the preferred embodiment shown in Figure 1, the secondary treating zone 14 may function as a liquid coker or may function concurrently as a liquid coker and as a reformer to upgrade in quality the uncoked products from the primary treatment. Where the secondary treating zone is to be operated as a concurrent liquid coker and reformer, its temperature should be maintained in the range of 1300 to 1600° F. Where the secondary treating zone is operated as a liquid coker, its temperature should be maintained in the range of 950 to 1200° F. to avoid thermal conversion of the uncoked constituents. The temperature of the secondary treatment zone (as a liquid coker) need not necessarily be higher than that of the primary treatment zone since the extent of coking can be effectively regulated through control of the sweep gas rate and vapor residence time. The secondary treating zone 14 contains a heated mass of carbon pebbles which supply the necessary surface for the additional coke formation. The pebbles in this instance are premium, essentially ash-free, carbon pellets.

The vapors entering the secondary treating zone 14 are essentially ash free. A portion of the vapors condenses to form a film upon the surface of the carbon pellets which is converted into coke on extended exposure to the processing conditions in the secondary zone 14. When the secondary treatment zone 14 is operated as a concurrent liquid coker and reformer, the uncoked components of the liquid experience a beneficial reforming which results from the severe thermal conditions maintained in the secondary zone 14. The resulting uncoked vapors are recovered through a conduit 18. A portion of the solid pellets in the secondary zone 14 is removed continuously or intermittently through a conduit 19 and screened. Oversize pellets are recovered as product, low-ash, premium carbon; undersize pellets are returned to the secondary zone 14 for additional size accretion through further coking.

The ash-free vapor product from the secondary treatment zone 14 passes through a conduit 18 to the vapor recovery system 15. Non-condensable gases are recovered through a conduit 20 for further processing, for use as fuel, or for disposal. If desired, a portion of the non-condensable gases may be returned through conduits 21 and 26 to provide the sweep gas for controlling the coking rate in the primary treating zone 13 and the secondary treating zone 14 respectively. Low boiling liquid products are recovered through a conduit 22, e. g. those boiling below 300° C. High boiling residue, e. g. pitch boiling above 300° C., is recovered through a conduit 23 as an ash-free reformed pitch. This reformed, ash-free pitch is valuable in itself as an electrode binder, an impregnant, a roofing material, or any of the similar applications currently satisfied by high temperature carbonization pitches. If desired, a portion of the ash-free reformed pitch may be recycled through a conduit 24 and heater 12 for further coke production and reforming in the secondary thermal treating zone 14. A portion of the pitch in conduit 23 must be removed as product since the thermal treatment introduces a refractory property to the ash-free pitch, preventing its recycle to extinction via continued coking.

To avoid the operability problems which arise from the use of a moving bed contacting technique for the primary coking process, the primary thermal treatment zone 13 may be conducted under fluidized conditions. The fluidized technique provides a convenient means for regulating sweep gas rates to control the extent of coking in the primary zone. To produce the lump form coke product demanded in the market, the secondary thermal treating zone may be operated as a downwardly moving bed.

The alternative embodiment of the present invention illustrated in Figure 2 is adapted to the treatment of ash-containing hydrocarbonaceous liquids and particularly to the treatment of a wide boiling range fraction of said liquids without the necessity for preliminary removal of valuable low boiling constituents. The apparatus shown in Figure 2 includes a source of feedstock 30; heaters 31 and 32 for elevating the temperature of liquid feedstock; a primary thermal treating zone 33; a secondary thermal treating zone 34; and a vapor recovery system 35. The primary thermal treatment zone 33, in structure, operation and function corresponds to the primary zone 13 of Figure 1.

Feedstock from the source 30 is heated in the heater 31 to a pumpable temperature and subjected to mild coking conditions at 950 to 1200° F. in the primary thermal treatment zone 33. High-ash coke pellets are recovered through a conduit 37. Uncoked vapors are recovered through a conduit 36 and sent directly to the vapor recovery system 35 for recovery of non-condensable gases through a conduit 40 and recovery of low boiling liquid products through a conduit 42. By avoiding treatment of these vapors under the more severe conversion conditions of the secondary treating zone 34, loss of valuable low boiling tar acids from the feedstock is minimized. High boiling residue pitch, ash-free, is recovered through a conduit 43 and passed to the secondary thermal treating zone 34 through a conduit 44 and heater 32. The secondary treatment zone 34, operated at a temperature of 950 to 1600° F., corresponds in structure, operation and function to the secondary treatment zone 14 shown in Figure 1. Low-ash coke pellets are recovered through a conduit 39 and volatilized portions of the ash-free pitch are recovered through a conduit 38 and fractionated in the vapor recovery system 35.

Recycling of non-condensable gases through conduits 41 and 45 to each of the thermal treatment zones, permits

independent control over the coking rate occurring in each of the treatment zones.

To illustrate the present invention, results of operation according to Figure 1 will be reported by way of example. The feedstock was low temperature carbonization pitch boiling above 230° C. The pitch, produced in a fluidized low temperature carbonization process, contained 9 percent solids by weight and 0.78 percent ash by weight. Pitch, preheated to 320° F., was passed downwardly through a primary coker maintained at 1000° F. and containing a downwardly moving bed of devolatilized coke pellets which had been screened to pass through a standard No. 8 mesh and be retained on a standard No. 16 mesh. The pellets were prevented from adhering through the action of a rotating stirrer.

For every 100 lbs. of pitch feedstock, 16.8 lbs. of high-ash coke were produced in the primary coker vessel. This product coke had an ash-content of 4.5 percent by weight. 97 percent of the ash in the feedstock appeared in the product coke.

83.2 lbs. of vapors were removed from the primary coking vessel and passed without condensation upwardly through a secondary reforming vessel containing a downwardly moving bed of devolatilized coke pellets which had been screened to pass through a standard No. 8 mesh and be retained on a standard No. 16 mesh. The reformer was maintained at a temperature of 1450° F.; no mechanical agitation of the bed was provided. The 83.2 lbs. of primary coker vapors were subjected to the reformer conditions for a contact time of 4 to 5 seconds. 20 lbs. of low-ash coke and 63.2 lbs. of vapors were produced in the reformer vessel. Product coke pellets from the secondary zone had an ash content of 0.115 percent by weight. 20 lbs. of ash-free pitch boiling above 230° C. were available for recycle or for use as premium quality pitch. 43.2 lbs. of gas, liquor and low boiling distillates were recovered.

A material balance for the described operation is presented in Table I.

*Table I*

| | Percent ash |
|---|---|
| Feedstock: 100 lbs. pitch | 0.78 |
| Products: | |
| 16.8 lbs. coke | 4.5 |
| 20.0 lbs. coke | 0.115 |
| 20.0 lbs. pitch | zero |
| 43.2 lbs. gas, liquor and distillate. | |

The original feedstock contained 9 percent by weight of solids in which the ash constituents were concentrated. Based on the 91 lbs. of liquid pitch in the feedstock, 18.6 percent by weight was converted to a high-ash coke and 22 percent by weight was converted to a low-ash coke. An additional 22 percent by weight of the liquid portion of the feedstock was recovered as a pitch available for the production of additional coke by recycling if desired.

According to the provisions of the patent statutes, I have explained the principle, preferred construction and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. The method of preparing low-ash coke from an ash-containing hydrocarbonaceous liquid which comprises passing said liquid through a first mild coking zone at 950 to 1200° F., recovering a high-ash coke therefrom, separately continuously removing therefrom the uncoked portion of the feedstock as a substantially ash-free vapor, passing at least the high-boiling portion thereof through a second thermal treating zone at 950 to 1600° F., recovering a low-ash coke and separately continuously removing the uncoked vapor from said second zone.



2. The method of preparing low-ash coke from an ash-containing hydrocarbonaceous liquid boiling above 300° C. which comprises passing said liquid through a first mild coking zone at 950 to 1200° F., recovering a high-ash coke therefrom, separately continuously removing therefrom the uncoked portion of the feedstock as a substantially ash-free vapor, passing all of said ash-free vapor through a second thermal treating zone at 1300 to 1600° F., recovering a low-ash coke and separately continuously recovering uncoked vapors from said second zone.

3. The method of preparing low-ash coke from an ash-containing hydrocarbonaceous liquid boiling above 300° C. which comprises passing said liquid through a first mild coking zone at 950 to 1200° F., recovering a high-ash coke therefrom, separately continuously removing therefrom the uncoked portion of the feedstock as a substantially ash-free vapor, passing all of said ash-free vapor through a second thermal treating zone at 1300 to 1600° F., recovering a low-ash coke therefrom, separately continuously removing therefrom the uncoked vapors from said second zone, recovering non-condensable gases from said uncoked vapors and recycling at least a portion thereof to said first mild coking zone as sweep gas for limiting high-ash coke production therein to 5 to 15 weight percent of the liquid portion of the feedstock.

4. The method of preparing low-ash coke from an ash-containing hydrocarbonaceous liquid which comprises passing said liquid through a first mild coking zone at 950 to 1200° F., recovering a high-ash coke therefrom, separately continuously recovering therefrom the uncoked portion of the feedstock as a substantially ash-free vapor, recovering non-condensable gases, low boiling distillate and high-boiling residue from said ash-free vapor, passing said high-boiling residue continuously through a second thermal treating zone at 950 to 1600° F., and recovering a low-ash coke and separately continuously recovering the uncoked vapors from said second zone.

5. The method of preparing low-ash coke from an ash-containing hydrocarbonaceous liquid which comprises passing said liquid through a first mild coking zone at 950 to 1200° F., recovering a high-ash coke therefrom, separately continuously recovering the uncoked portion of the feedstock as a substantially ash-free vapor, recovering non-condensable gases, low-boiling distillate and high-boiling residue from said ash-free vapor, passing said high-boiling residue continuously through a second thermal treating zone at 950 to 1600° F., recovering a low-ash coke and separately continuously recovering the uncoked vapors from said zone, recycling at least a portion of said non-condensable gases to said first zone as sweep gas for limiting high-ash coke production therein to 5 to 15 weight percent of the liquid portion of the feedstock.

6. The method of preparing low-ash coke pellets from an ash-containing hydrocarbonaceous liquid which comprises passing said liquid at 950 to 1200° F. through a first mild coking zone containing a bed of particulate carbonaceous solid pellets, passing sweep gas through said first zone to control deposition on the pellets therein of a coke layer containing 5 to 15 percent by weight of the liquid portion of the feedstock together with substantially all of the ash from the feedstock, recovering a high-ash coke from said first zone, separately continuously recovering therefrom the uncoked portion of the feedstock as a substantially ash-free vapor, passing said ash-free vapor at 1300 to 1600° F. through a second thermal treatment zone containing a bed of particulate, essentially ash-free carbonaceous solid pellets, recovering essentially ash-free carbonaceous solid pellets from said second zone, retaining uncoked vapors in said second

zone for a sufficient time to achieve reforming, and continuously recovering the uncoked, reformed vapors from said second zone.

7. The method of claim 6 in which the ash-containing hydrocarbonaceous liquid is derived from coal.


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