

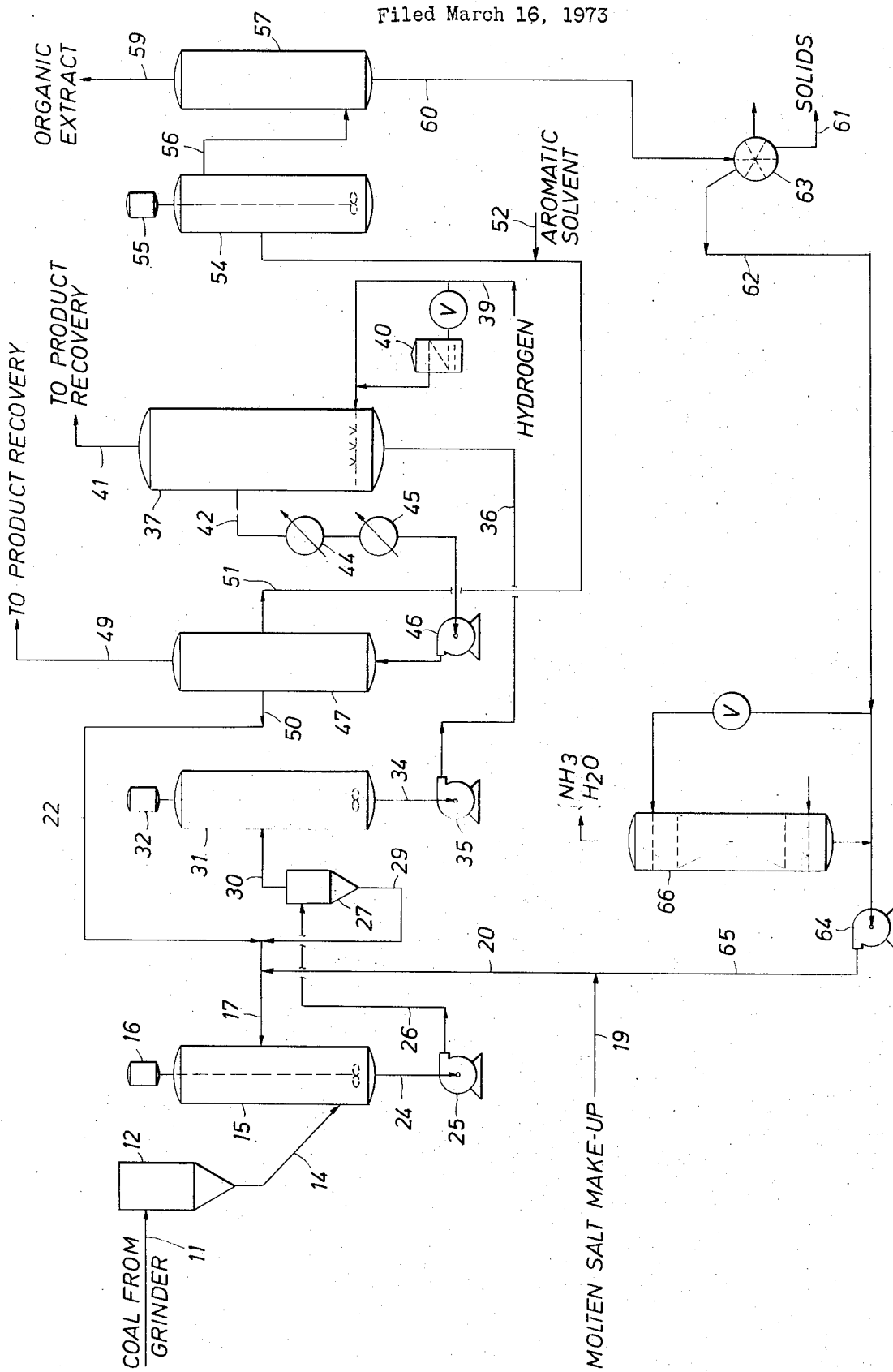
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HYDROCRACKING OF COAL IN MOLTEN ZINC IODIDE

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1

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HYDROCRACKING OF COAL IN MOLTEN ZINC IODIDE

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ABSTRACT OF THE DISCLOSURE

Coal is continuously hydrocracked in suspension in a continuous-phase molten salt predominating in zinc iodide, at a temperature of from about 300° C. to about 500° C. and under a pressure of from about 200 p.s.i.g. to about 3000 p.s.i.g. The molten zinc iodide contains a substantial proportion of alkali metal iodide as a melting point depressant, sufficient to lower the melting point from about 446° C., the normal melting point of zinc iodide, to substantially below 350° C. The molten zinc iodide catalyst also contains ammonia, ammonium iodide and water, in small proportions, resulting from hydrocracking the coal, all of which are also melting point depressants for zinc iodide. The slurry of coal in the molten catalyst system is prepared by first slurrying ground coal in at least 12 to about 25-fold proportions by weight molten iodide salt mixture predominating in zinc iodide and containing alkali metal iodide. The resulting slurry of coal in the molten salt mixture is then concentrated by separating a portion, at least one-third, of the molten salt mixture, to provide a still pumpable slurry of coal in molten salt, which is the charge to the hydrocracking zone. The separated excess molten salt is recycled to the primary slurrying operation to provide a portion of the molten salt for slurrying the coal. The molten salt mixture withdrawn from the hydrocracking operation is separated from volatile and normally liquid products of the reaction, and a major proportion thereof is recycled to the primary slurrying step. A minor proportion of the molten salt mixture is extracted with an aromatic solvent to remove resulting tar-like material and then filtered to remove solids, after which the separated molten salt is recycled to the primary slurrying operation.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the hydrocracking of coal in a slurry of coal in a molten catalyst system comprising predominately zinc iodide.

Description of prior art

An extensive amount of research and development work has been done by a number of workers on the conversion of coal to liquid hydrocarbon products. Much work has been carried out on the hydrocracking of coal in the presence of a continuous phase of molten zinc chloride as catalyst by workers at Consolidation Coal Company, under the sponsorship of the Office of Coal Research, U.S. Department of the Interior. Many publications have been based upon this work, including a number of patents, e.g., U.S. Nos. 3,355,376; 3,371,049; 3,594,329; 3,625,861 and British Pat. 1,095,851. Others have also been active in this field. U.S. Pat. 3,543,665 is directed to a similar process involving the use of various molten metal halides, particularly certain tri-halides of antimony, bismuth, and arsenic. Still further, U.S. Pats. 3,657,108 and 3,685,962 are directed to the regeneration of metal halide-ammonium halide complexes which are formed in the use of certain molten metal halides, including zinc iodide, in the hydrocracking of coal. It has also

2

been disclosed in U.S. 3,667,932, in the use of molten zinc halides in the hydrocracking of heavy oil fractions, that various advantages are obtained by the addition of various melting point depressants, such as the corresponding alkali metal halides to the molten zinc halide system.

In spite of the extensive efforts which have gone into attempts to develop practical catalytic processes for the conversion of coal to useful liquid hydrocarbon products, there still is no large-scale commercial application of any of these processes—no doubt due in large measure to the multiplicity of technical and economic problems which remain to be solved.

SUMMARY OF THE INVENTION

This invention provides a continuous process of hydrocracking coal in a slurry of coal in a multi-proportion of a molten mass predominating in zinc iodide by contacting the slurry with hydrogen at a pressure of about 200–3000 p.s.i.g. and at a temperature of from about 300° C. to about 500° C., in which the following combination of steps is involved:

(1) Continuously slurrying the coal in particulate form to a pumpable slurry in a circulating stream of an at least 12-fold weight proportion of a molten salt mixture, consisting essentially of zinc and alkali metal iodide under substantially non-cracking conditions and at a temperature substantially below the normal melting point of zinc iodide; the amount of alkali metal iodide being sufficient to give, with the zinc iodide present, a two-component mixture thereof having a first solidification point (melting point) below 350° C.;

(2) Separating at least about one-third of the molten salt mixture from the slurry and producing a concentrated, still pumpable slurry therefrom having a higher coal-solids content e.g., a molten salt to coal weight ratio of from about 7 to 12, and recycling the remaining portion of the molten salt mixture, depleted in coal, to the slurrying step;

(3) Subjecting the concentrated slurry to hydrocracking at a pressure of at least about 200 p.s.i.g., e.g., about 200–3000 p.s.i.g., and a temperature of about 300° to about 500° C. in the presence of hydrogen;

(4) Recovering the resulting hydrocracked products from the molten salt mixture and coal residue, including tar and ash;

(5) Separating and recycling a major portion of the molten salt mixture and suspended coal residue to the coal slurrying step; and

(6) Recovering a purified molten salt mixture from the remainder of the molten salt mixture and coal residue and recycling the recovered molten salt material to the coal slurrying step.

As previously discussed, the utility of molten zinc iodide as a medium for the hydroconversion of coal is well known. In such processes coal may be directly introduced as such with hydrogen into the hydrocracking zone containing the molten salt mixture. Alternatively, the coal may be first slurried in the molten salt mixture and then introduced into the hydrocracking zone. The present invention concerns an improved hydrocracking process in which the weight ratio of molten salt to coal in the slurry employed to transport the coal to the reactor, and the weight ratio of coal to molten salt mixture in the reactor per se, are controlled in such a manner as to achieve a high degree of efficiency and to avoid unnecessary material handling, heating and cooling. In accordance with the invention, ground coal (e.g., 60–300 mesh) is intimately mixed with at least about a 12-fold, preferably 15 to 25-fold, proportion by weight of a molten zinc iodide-containing salt mixture thereby forming a pumpable slurry which is transported to the reaction zone under

substantially non-cracking conditions, i.e., under conditions of low temperature, e.g., 250°–300° C., so that undesirable thermal conversion of the coal into tar and other heavy products is avoided. Before entering the reactor, at least about one-third of the slurry, preferably one-third to two-thirds, is separated from the balance of the slurry, and the coal therein concentrated to produce a still pumpable slurry containing no more than about a 7 to 12-fold by weight proportion of the molten salt mixture relative to the slurried coal. This concentrated slurry enriched in coal is fed to the reactor while the remaining portion of the slurry, containing a lesser proportion of coal, is recycled to the coal slurring step. It has been found that concentration of the slurry can be very effectively accomplished by use of a series of liquid cyclones (hydroclones) because of the difference in specific gravity of the molten salt and the coal in the slurry. Centrifuges or comparable separators can also be employed to increase the concentration of coal in the slurry.

In further accordance with the invention, hydrocracking is effected at a pressure of about 200–3000 p.s.i.g., preferably 1000 to 3000 p.s.i.g., and a temperature of about 300° to 500° C., preferably 400° to 450° C. The hydrocracked products are separated from the molten salt mixture and recovered. A major portion of molten salt mixture containing minor amounts of coal residue and other impurities is recycled from the reaction zone to the slurring step and utilized for slurring further amounts of coal. The remainder of the salt mixture is preferably subjected to one or more purification steps as hereinafter discussed before recycle to the slurring step. The invention will now be further described by reference to the accompanying drawing.

THE DRAWING

The sole figure of the accompanying drawing is a schematic flow diagram illustrating a preferred embodiment of the invention.

PREFERRED EMBODIMENT OF THE INVENTION

Referring to the drawing, previously ground and dried coal is supplied by line 11 to a coal hopper 12 from which the coal is delivered by line 14 to a slurry mixer 15, provided with a stirrer operated by motor 16. The coal is intimately mixed and slurried with molten salt supplied by line 17. Molten salt for start-up of the operation, and make-up salt after the process is in continuous operation is supplied through lines 19, 20, and 17. The molten salt is predominately zinc iodide containing a sufficient proportion of alkali metal iodide, together with some ammonium iodide resulting from the subsequent reaction of the coal and to some extent a small proportion of water, to insure that the molten salt mixture is sufficiently fluid at non-cracking conditions for the coal, for example, at about 250°–300° C. (preferably about 250° C.).

It may be determined that a mixture of zinc iodide and lithium iodide containing about 33% weight lithium iodide has a melting point of about 250° C.; a mixture of zinc iodide and sodium iodide containing about 13% weight sodium iodide is molten at 250° C.; a mixture of zinc iodide and potassium iodide containing about 9% weight potassium iodide has a melting point of about 250° C.; and water to the extent of about 6% by weight in zinc iodide lowers the melting point of the zinc iodide to about 200° C. At a weight ratio of molten salt to coal of at least 12 to about 25, the molten salt having the required low melting temperature, a readily pumpable slurry is obtained. The weight ratio of molten salt to coal in the slurry mixture is preferably about 15 to about 25, and more preferably about 20. This slurry is transferred through line 24, by a circulation pump 25 via line 26 to a series of liquid cyclone separators, represented by a

single cyclone 27, wherein the slurry is separated into an overhead fraction (withdrawn through line 30) which is more concentrated in coal and a bottom fraction containing the more dense excess molten salt which is withdrawn through line 29 and returned by line 17 to slurry mixer 15. The slurry withdrawn from the slurry mixer has a typical specific gravity of about 2.6 at about 250° C., whereas that in line 30 discharging into slurry surge vessel 31 and eventually withdrawn therefrom as the reactor charge has a typical specific gravity of about 2.14 at 250° C. Removal of a portion of the molten salt, having a higher density than the coal, results in the more concentrated slurry having a lower density.

The thus prepared concentrated slurry is maintained as such in slurry surge vessel 31, provided with a stirrer powdered by motor 32. The slurry is withdrawn therefrom through line 34 and pumped by reactor charge pump 35, whereby the pressure of the slurry stream is raised to about 2500–2600 p.s.i.g., through line 36 to the bottom of the reactor 37. Hydrogen is supplied to the reactor by line 39 (for start-up purposes the hydrogen is passed through heater 40). The reaction mixture is maintained in the reactor at a temperature of about 300°–500° C., preferably about 400°–450° C., and typically at about 420° C. The exothermic heat of the hydrocracking process is sufficient to maintain the desired reaction temperature. Reactor 37 is maintained partially filled with the slurry and resulting liquid products, with a gas phase in the upper portion of the reactor. Vapors in the upper portion of the reactor are withdrawn through a suitably valved and controlled line 41, and suitably processed for separation and recovery of the components thereof.

The flow rate of the slurry into the reactor and the withdrawal of liquid through line 42, taking into consideration the relative size of the reactor, are selected to provide a residence time in the reactor of from about 15 to about 30 minutes. The temperature in the reactor may be such that the addition of very little, if any, melting point depressant is required to maintain the zinc iodide in the molten state therein. This may be adequately provided in the reactor by ammonium iodide which results from conversion of nitrogen-containing components of the coal, and water which results from conversion of combined oxygen in the coal, to the extent that they remain in the zinc iodide under the conditions in the reactor (a substantial amount of each does remain dissolved—functioning as very effective melting point depressants for the zinc iodide).

The liquid reaction mixture of molten salt, liquid reaction products and suspended coal residue, including heavy tar and ash, is withdrawn through line 42 and cooled in heat exchangers 44 and 45, then passed through a suitable expansion device, as indicated by slurry expander 46, and passed to a flash vessel 47 at a pressure of about 40–60 p.s.i.g., the temperature having been reduced to about 250° C. The flashed and vaporized products are removed by a suitably valved and controlled line 49, and subsequently processed for separation and recovery of the products thereof, as will be understood from the prior art.

As representative of the conversions which can be effected in the process, the hydrocracking of coal in a zinc iodide-potassium iodide salt mixture containing about 9% by weight potassium iodide, at a weight ratio of salt to coal of about 8, at 420° C. and a pressure of 2000 p.s.i.g., for a time of about 30 minutes, gave rise to the following products in grams per 100 grams of moisture and ash-free (MAF) coal: 3.5 grams of C₁–C₂ hydrocarbons; 27.2 grams of C₃–216° C. B.P. hydrocarbons, and 27.7 grams of a 216° C.–400° C. B.P. hydrocarbon fraction.

The molten salt mixture in flash vessel 47, containing a small portion of what might be called coal residue, including tar and ash, is divided into two streams, one withdrawn through line 60 and the other through line 51. The major portion, about 70–90% by weight of the total

5

(typically about 80%), is withdrawn through line 50 and recycled to the slurry mixer through lines 22 and 17. The remainder of the molten salt mixture is withdrawn through line 51 and is mixed with a suitable aromatic hydrocarbon solvent from line 52, and thoroughly mixed in extractor-mixer 54 provided with a stirrer powered by a motor 55. The resulting mixture is passed through line 56 to settler 57, wherein the organic extract of aromatic solvent containing dissolved tar is separated and removed through line 59.

The extracted catalyst melt containing suspended solids is transferred by line 60 to a suitable pressure filter 63, wherein the solids are separated and removed by the line 61 and the liquid, comprising molten salt, is withdrawn by line 62, stripped as desired in stripper 66 to remove ammonia and water, and pumped by pump 64 through recycle line 65 to line 20 and line 17 and thence back to the slurry mixer.

Certain advantages of this invention will appear from a consideration of certain factors which are involved in a suitable large-scale operation from the conversion of coal to liquid hydrocarbon products suitable to be used directly as fuel or to be further converted into materials which are directly useable as such. For example, it has been determined that for a coal conversion plant to produce the equivalent of about 100,000 barrels per day of liquid hydrocarbon products, which might be considered to be comparable to a moderate petroleum refinery unit, something on the order of 22,000 tons per day of coal would need to be processed. In order to hydrocrack that amount of coal in a molten zinc iodide catalyzed process according to this invention, it would require a circulating stream of molten salt to the reactor of the order of 22 million pounds per hour, under the favorable ratio of molten salt to coal of about 10 to 1. But, in order to provide the initial slurry of the coal for suitable handling, the coal would require approximately twice as much molten salt for the initial slurrying operation at the non-cracking conditions. Thus, it is clear that it is highly advantageous to provide a process which does not require passing all of the molten salt originally required to produce the slurry through the hydrocracking reaction zone.

What is claimed is:

1. In a continuous process of hydrocracking coal in a slurry of coal in a major proportion of a molten salt mixture predominating in zinc iodide by contacting the slurry with hydrogen at a pressure of about 200 to 3000 p.s.i.g. and at a temperature of from about 300° C. to about 500° C., the improvement which comprises the combined steps of:

- (1) continuously slurrying coal in particulate form to a pumpable slurry in a circulating stream of at least a 12-fold proportion of a molten salt mixture consisting essentially of zinc iodide and alkali metal iodide under substantially non-cracking conditions and at a temperature substantially below the normal melting point of zinc iodide, and the amount of alkali metal iodide being sufficient to give with the zinc iodide present a two-component mixture thereof having a first solidification point below 350° C.,

6

- (2) separating at least about one-third of the molten salt mixture from the slurry and producing a concentrated, still pumpable slurry therefrom having a molten salt to coal weight ratio of from about 7 to 12, and recycling the remaining portion of the molten salt mixture, depleted in coal, to the slurrying step,
- (3) subjecting the concentrated slurry to hydrocracking at a pressure of about 200–3000 p.s.i.g. and at a temperature of about 300° to about 500° C. in the presence of hydrogen,
- (4) recovering the resulting hydrocracking products from the molten salt mixture and coal residue,
- (5) separating and recycling a major portion of the molten salt mixture and suspended coal residue to the slurrying step, and
- (6) recovering a purified molten salt mixture from the remainder of the molten salt mixture and coal residue and recycling the recovered molten salt mixture to the coal slurrying step.

2. The process of claim 1 wherein the coal is slurried in step (1) with 15 to 25 parts by weight, based on the coal, of the molten zinc iodide-alkali metal iodide mixture.

3. The process of claim 2 wherein from one-third to two-thirds of the molten iodide salt mixture is separated from the slurry to produce the concentrated slurry which is hydrocracked.

4. The process of claim 3 wherein the concentrated slurry is hydrocracked at a pressure of about 1000–3000 p.s.i.g. and at a temperature about 400° to 450° C.

5. The process of claim 4 wherein the portion of the molten salt mixture and suspended coal residue separated and recycled to the coal slurrying step is from about 70 to 90% by weight of the total.

6. The process of claim 1 wherein concentration of the molten salt mixture separated from the slurrying step (2) is effected with the use of a liquid cyclone separator.

7. The process of claim 1 wherein the purified molten salt mixture recovered in step (6) is purified by extraction with an aromatic hydrocarbon solvent.

8. The process of claim 7 wherein the extracted molten salt mixture is stripped to remove ammonia and water.

9. The process of claim 2 wherein the coal is slurried in about 20 parts by weight of the molten salt in step (1), about one-half of the molten salt is separated from the slurry in step (2), and is concentrated to a molten salt to coal weight ratio of about 10, the concentrated slurry is hydrocracked at about 400°–450° C. and a pressure of about 2500–2600 p.s.i.g. in step (3), and about 80% of the molten salt mixture is separated and recycled in step (5).

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