

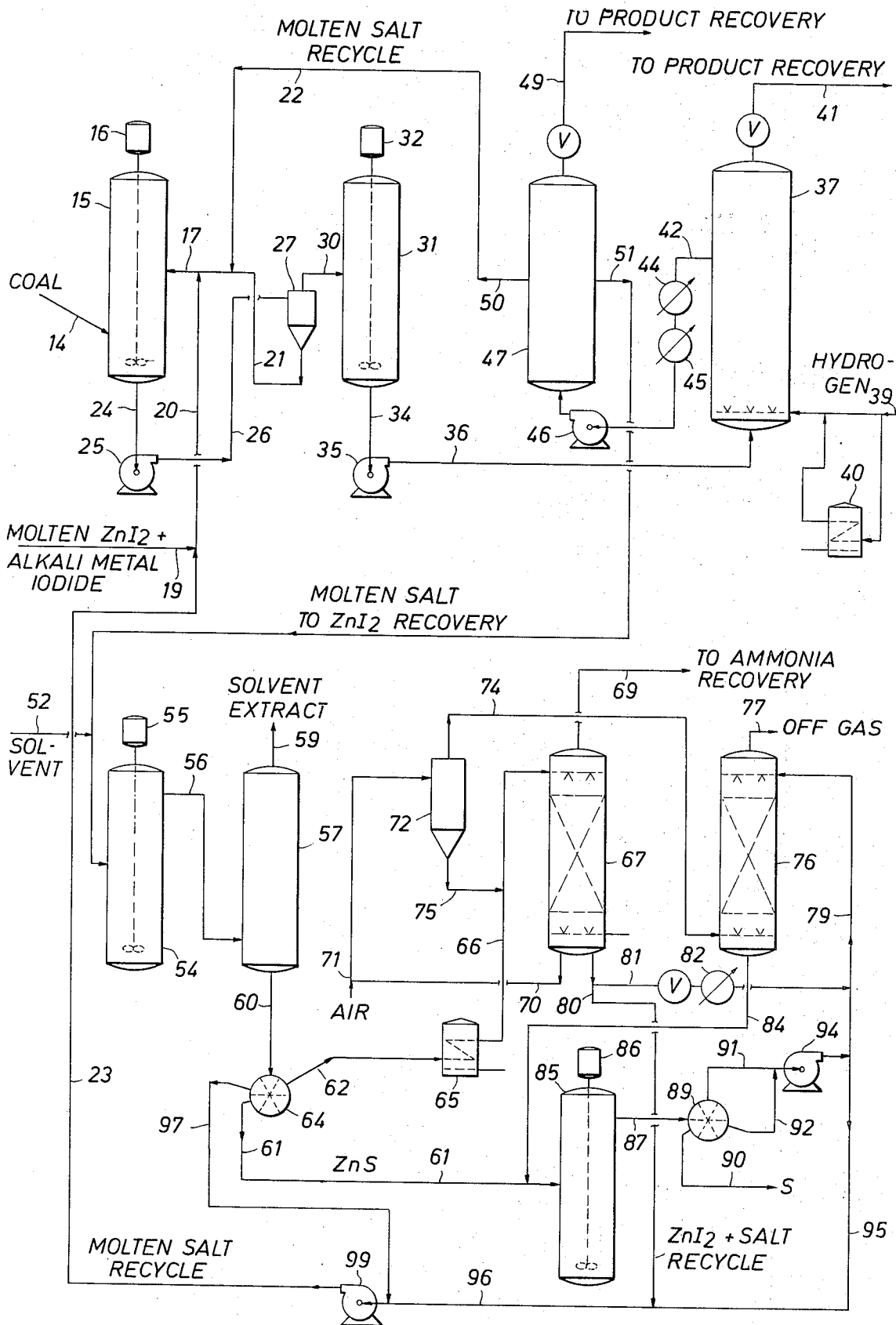
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R. A. LOTH ET AL

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HYDROCRACKING COAL IN MOLTEN ZINC IODIDE

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**HYDROCRACKING COAL IN MOLTEN
ZINC IODIDE**

Rene A. Loth, Spring, and Milton M. Wald, Houston,
Tex., assignors to Shell Oil Company
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6 Claims

ABSTRACT OF THE DISCLOSURE

Coal is slurried in a molten salt mixture predominating in zinc iodide and the coal is hydrocracked at a temperature of about 300°–500° C. and at a pressure of about 200–3000 p.s.i.g. in the presence of hydrogen. The molten salt mixture contains a substantial proportion of alkali or alkaline earth 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 hydrocracking converts nitrogen and oxygen in the coal to ammonia and water, respectively, the ammonia being converted in part to ammonium iodide. The generated water, ammonia and ammonium iodide all function as melting point depressants for zinc iodide. A major portion of the molten salt mixture, containing coal residue, including tar and ash, is recycled to the hydrocracking process. A minor proportion of the resulting molten salt mixture from hydrocracking is separated as a slip-stream and processed for recovery of the molten salt mixture thereof, and conversion of zinc sulfide and ammonium iodide formed from hydrocracking the coal, to recover the zinc and iodide contents thereof as zinc iodide, which is also recycled to the coal slurry operation.

BACKGROUND OF THE INVENTION

Field of the invention

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

Description of the 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 catalytic hydrocracking of coal in the presence of a continuous phase of molten zinc chloride, particularly 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. 3,355,376; 3,371,049; 3,594,329; 3,625,861 and British Pat. 1,095,851. Others have also been active in the field. U.S. 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. 3,657,108 and 3,685,962 are directed to the regeneration of metal halide-ammonium halide complexes which are formed during the use of certain molten metal halides in the hydrocracking of coal. It has also been disclosed in U.S. 3,677,932, that various advantages are obtained by the addition of various melting point depressants, such as the corresponding alkali metal halides, to molten zinc halide systems used in the hydrocracking of heavy oil fractions.

Among the problems encountered in the catalytic hydrocracking of coal and coal extracts in the presence of molten halides is the conversion of a portion of the metal halide to metal sulfide, due to conversion of the sulfur in the coal to hydrogen sulfide, followed by its reaction

with the metal halide to form metal sulfide. This is particularly troublesome in the use of zinc halides because of the resultant loss of a portion of the zinc as zinc sulfide. Moreover, the iodine thus released from the zinc iodide, as hydrogen iodide, is converted by reaction with ammonia, formed from combined nitrogen in the coal, to ammonium iodide. The significance of this loss of zinc iodide may be better appreciated when it is considered that, for a plant which processes sufficient typical coal (containing 0.4% sulfur) to produce on the order of ten thousand barrels per day liquid hydrocarbons (which in reality is a small-scale operation compared to current petroleum refineries), would lose about 8,000 lbs. per hour of zinc iodide to zinc sulfide and ammonium iodide.

SUMMARY OF THE INVENTION

It has now been found that, in the hydrocracking of coal in a molten mass of a salt mixture predominating in zinc iodide and containing a sufficient amount of suitable melting point depressants, wherein the sulfur content of the coal is converted to hydrogen sulfide which reacts with a portion of the zinc iodide to produce insoluble zinc sulfide, and wherein the nitrogen content of the coal is converted to ammonia which is in part converted to ammonium iodide, the zinc and iodide values of the zinc sulfide and ammonium iodide, respectively, can be recovered for reuse in the hydrocracking process by the combined steps of:

(1) Separating the zinc sulfide from a portion of the molten salt mixture containing zinc sulfide and ammonium iodide,

(2) Reacting a portion of the molten salt mixture with oxygen (as in air) in an amount stoichiometrically equivalent to the separated zinc sulfide to convert a stoichiometric portion of zinc iodide to zinc oxide and iodine, and separately recovering the same,

(3) Reacting the recovered iodine with the separated zinc sulfide to form zinc iodide and sulfur, and recycling the zinc iodide to the hydrocracking process, and

(4) Reacting the zinc oxide recovered in step (2) with a portion of the molten salt mixture containing ammonium iodide to liberate ammonia and form zinc iodide and recycling the formed zinc iodide to the hydrocracking process.

The foregoing improved process is advantageous, not only in that zinc and iodide values are recovered which would otherwise be lost, but has the additional advantage that all the formed ammonia can be recovered as a valuable by-product. This is not the case with most conventional regeneration schemes which involve one or more combustion steps which destroy ammonia.

THE DRAWING

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

PREFERRED EMBODIMENT OF THE INVENTION

In accordance with the invention, a suitable slurry of coal in a molten salt mixture predominating in zinc iodide and containing an alkali or alkaline earth metal iodide as a pour point depressant (preferably an alkali metal iodide) is prepared in a mixing vessel and is then pressured and pumped at a selected reaction pressure, e.g. about 200 to about 3000 p.s.i.g., to a reactor vessel wherein the slurry is hydrocracked at an elevated temperature, e.g., about 300° to about 500° C., in the presence of added hydrogen. Products of the conversion are removed from the reaction mixture, some after transferring a portion of the liquid reaction mixture to a flash vessel. A portion of the resulting separated molten salt mixture is

recycled to the slurring operation, while a minor portion is removed as a slip-stream for purification and recovery of zinc iodide and zinc and iodine values. The slip-stream of molten salt mixture containing coal residue, ash, zinc sulfide, ammonia, and ammonium iodide is first solvent extracted to remove tar, then filtered to separate the insoluble zinc sulfide from the molten salt mixture. The separated molten salt mixture is heated and stripped to remove volatile or volatilizable components, including ammonia. Ammonia which is complexed with zinc iodide is thus substantially removed. A portion of the stripped zinc iodide-containing molten salt mixture is reacted with air thereby generating iodine and forming zinc oxide. While it is preferred to use the extracted, stripped molten salt mixture to generate iodine, the unstripped molten salt mixture, or ZnI_2 -containing molten salt from elsewhere in the system can also be employed to generate iodine. The iodine liberated by the air oxidation is recovered by absorption, preferably in an aqueous salt mixture, and the resulting solution is mixed with the previously separated zinc sulfide with conversion to zinc iodide and free sulfur. The resulting reaction mixture is filtered to separate the sulfur and other solids from the zinc iodide-containing stream.

The zinc oxide resulting from the iodine generation step is combined with the molten salt mixture containing ammonium iodide fed to the stripper, with the result that the zinc oxide displaces ammonia from the ammonium iodide to recover the iodide as zinc iodide.

Referring now to the drawing which represents a preferred embodiment of the invention, ground and dried coal is supplied by line 14 to a slurry mixer 15, provided with a stirrer powered by motor 16. A molten salt mixture predominating in zinc iodide, and also containing as pour point depressants alkali or alkaline earth metal iodide, ammonium iodide and water, is supplied to the slurry mixer through line 17, various portions of the molten salt mixture being provided via lines 19, 20, 21, 22 and 23. For efficient operation the slurry prepared in slurry mixer 15 contains from about 12 to about 25 parts by weight of molten salt mixture for each part by weight of coal. The slurry is transferred by pump 25, through line 26 to a plurality of liquid cyclone separators represented by the single cyclone 27, wherein from $\frac{1}{3}$ to $\frac{2}{3}$ of the molten salt mixture is separated and withdrawn from the bottom and transferred by line 21 to line 17 to the slurry mixer. The resulting concentrated coal slurry containing molten salt and coal in a weight ratio of from about 7 to 12, preferably about 10, is transferred by line 30 to a slurry surge vessel 31, provided with a stirrer powered by motor 32. The concentrated coal slurry is transferred by line 34, reactor charge pump 35, which raises the pressure to about 2600 p.s.i.g., and line 36 to the reactor 37. The initial slurry mixtures are formed at a pressure of about 30–60 p.s.i.g. and at a temperature of about 250°–300° C.

Hydrogen is supplied to the reactor 37 by line 39 (for initial start-up, passed through heater 40) and the hydrocracking in reactor 37 is carried out at a temperature of from about 300–500° C., preferably 400°–450° C., typically about 420° C. A fluid body of molten salt mixture, liquid reaction products and suspended coal and coal residue, including tar and ash, is maintained in the reactor with vapor space near the top thereof. Vapors are removed through valved line 41 and delivered to suitable equipment for product recovery. Condensed phase material is continuously withdrawn from the reactor through line 42, cooled by heat exchangers 44 and 45 and expanded in expander 46 into flash vessel 47, from which vaporized products are removed through valved line 49 and sent to suitable product recovery facilities. The resulting molten mass in the flash vessel 47 is at a temperature of about 250°–300° C. and a pressure of 30–60 p.s.i.g. and is primarily molten zinc iodide con-

taining alkali metal iodide, ammonium iodide and/or other melting point depressants, and suspended therein a minor proportion of unconverted coal, coal residue, and zinc sulfide.

A major portion, generally 70–90%, of the molten salt mixture in 47 is withdrawn through line 50 and recycled for further use in producing the coal slurry. The remainder of the molten salt in 47, generally from 10–30%, is withdrawn through line 51 and passed to a clean-up and recovery system. The molten salt mixture is mixed at about 250°–300° C. with a suitable lower boiling aromatic solvent from line 52, intimately mixed in extractor mixer 54, provided with a stirrer powered by motor 55, and the mixture transferred through line 56 to settler 57, from which the resulting solvent extract is withdrawn through line 59 and the molten salt mixture raffinate withdrawn from the bottom thereof through line 60. The extracted material in line 60 is filtered in filter 64, with suitable washing as desired, and the separated solid mix of zinc sulfide, coal, char and ash is transferred by line 61 to converter 85. The wash solvent, suitably molten or aqueous zinc iodide, is removed by line 97 and recycled in the system. The filtered molten salt is transferred by line 62, heated from about 250°–300° C. (the temperature of the previous extraction) in heater 65 to about 300–500° C., typically about 400°–410° C., and passed by line 66 to stripper 67 wherein volatile material, particularly ammonia, is stripped by means of an inert gas, such as nitrogen. A portion of stripped molten salt mixture at 300–500° C., e.g., 410° C., is transferred by line 70, mixed with air from line 71, to iodine generator 72. The amount of air is preferably selected to be sufficient to produce an amount of iodine which will be sufficient to convert the separated zinc sulfide to zinc iodide; at least a stoichiometric amount is required. A substantial excess of iodine is undesirable since additional facilities would be required to recover it. Accordingly, from about 100 to 110% of the stoichiometric amount has been found to be suitable. The liberated iodine is conveyed through line 74 to iodine absorber 76 wherein it is absorbed in an aqueous zinc iodide solution provided by line 79, originating principally from filter 89. The iodine absorption is effected at about 80°–100° C., preferably about 90° C. and 20–30 p.s.i.g. pressure. The absorbed iodine in the zinc iodide solution is withdrawn through line 84 and passed to the converter 85 wherein it is reacted at about 130° C.–170° C., preferably about 150° C., with the zinc sulfide to form zinc iodide and free sulfur. Converter 85 is provided with a stirrer powered by motor 86. The resulting conversion mixture is transferred by line 87 to filter 89 wherein the insoluble solids, including free sulfur, are separated via line 90 and the filtrate is withdrawn through line 91. A suitable wash solution of aqueous zinc iodide is removed through line 92, combined with the zinc iodide filtrate in line 91, and the mixture pumped by pump 94 to provide absorbent in absorber 76; excess thereof is transferred by lines 95 and 96 to recycle pump 99.

The stripped molten zinc iodide from stripper 67 is withdrawn through line 80 and transferred to line 96 for recycle through pump 99. As desired, if necessary, a portion of the stripped molten zinc iodide is passed through valved line 81 and heat exchanger 82 to line 79 for use in the iodine absorber.

Thus, this invention provides an efficient integrated combination process for recovering the zinc and iodide values otherwise lost from the molten zinc iodide medium due to the presence in the coal of sulfur and nitrogen and their conversion under hydrocracking conditions to materials which convert a portion of the zinc iodide to undesirable contaminants.

What is claimed is:

1. In a continuous process of hydrocracking coal wherein coal is slurried in a major proportion of a molten salt mixture predominating in zinc iodide and containing a

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melting point depressing amount of an alkali or alkaline earth metal iodide, and wherein said slurry is contacted with hydrogen at a pressure of about 200 to 3000 p.s.i.g. and a temperature of from about 300° C. to about 500° C. whereby hydrocracking products are obtained, and wherein said hydrocracking products are separated from the molten salt mixture which also contains coal residue, ammonium iodide and zinc sulfide, the latter resulting from nitrogen and sulfur impurities in the coal, the improvement which comprises recovering the zinc and iodide values of the zinc sulfide and ammonium iodide in said resulting molten salt mixture for further use in the hydrocracking process by the combined steps of:

- (1) separating the zinc sulfide from a portion of the molten salt mixture containing zinc sulfide and ammonium iodide,
 - (2) reacting a portion of the molten salt mixture with oxygen in an amount stoichiometrically equivalent to the separated zinc sulfide to convert a stoichiometric portion of the zinc iodide to zinc oxide and iodine, and separately recovering the same,
 - (3) reacting the recovered iodine with the separated zinc sulfide to form zinc iodide and sulfur, and recycling the zinc iodide to the hydrocracking process, and
 - (4) reacting the zinc oxide recovered in step (2) with a portion of the molten salt mixture containing ammonium iodide to liberate ammonia and form zinc iodide, and recycling the formed zinc iodide to the hydrocracking process.
2. The process of claim 1 wherein the portion of molten salt mixture from which the zinc sulfide is separated is

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first extracted while in a molten state with an aromatic hydrocarbon solvent.

3. The process of claim 2 wherein the extracted molten salt mixture is stripped with an inert gas at a temperature of about 300–500° C. to remove any volatile materials present.

4. The process of claim 1 wherein the portion of the molten salt mixture reacted with oxygen is extracted with an aromatic hydrocarbon solvent and stripped with an inert gas prior to reaction with oxygen.

5. The process of claim 4 wherein the reaction of the molten salt mixture with air is conducted at a temperature of from 300–500° C. and the iodine is recovered by absorption in aqueous zinc iodide.

6. The process of claim 4 wherein the recovered iodine is reacted with zinc sulfide at a temperature of from about 130–170° C.

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PAUL M. COUGHLAN, JR., Primary Examiner

V. O'KEEFE, Assistant Examiner

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