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ABSTRACT: Coal liquefaction products are separated into a plurality of fractions of varying softening points and molecular complexity in a solvent mixture containing a heavy organic coal liquefaction solvent and a light organic fractionating solvent having a critical temperature below 800° F. under elevated temperature and pressure conditions. In one variant, coal is liquefied with a heavy organic coal liquefaction solvent, the light organic fractionating solvent is added to the solution thus produced, and thereafter the coal liquefaction products are separated into a plurality of fractions at elevated temperature and pressure. Preferred heavy organic solvents include anthracene oil, tetralin, catalytic cracker recycle stocks, thermally cracked stocks and lubricating oil aromatic extracts, and preferred light organic solvents include pyridine, benzene and hexane. In a preferred variant, a mixture of the light and heavy organic solvents is recovered directly from the final fractionating stage, the solvent mixture is separated in a solvent separating vessel directly into a heavy organic solvent phase and a light organic solvent phase, and the two solvent phases are passed in heat exchange relationship with incoming solvent-rich streams to preceding fractionating stages to recover the heat content and produce cooled liquid heavy and light organic solvent streams for recycle. The invention further provides a method of separating finely divided insoluble material from products of coal liquefaction present in a solvent comprising a heavy organic coal liquefaction solvent.

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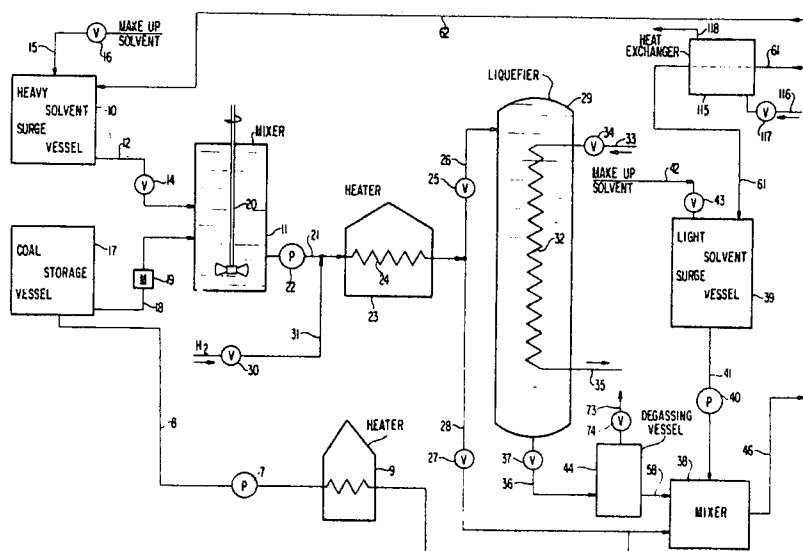


FIGURE - 1B

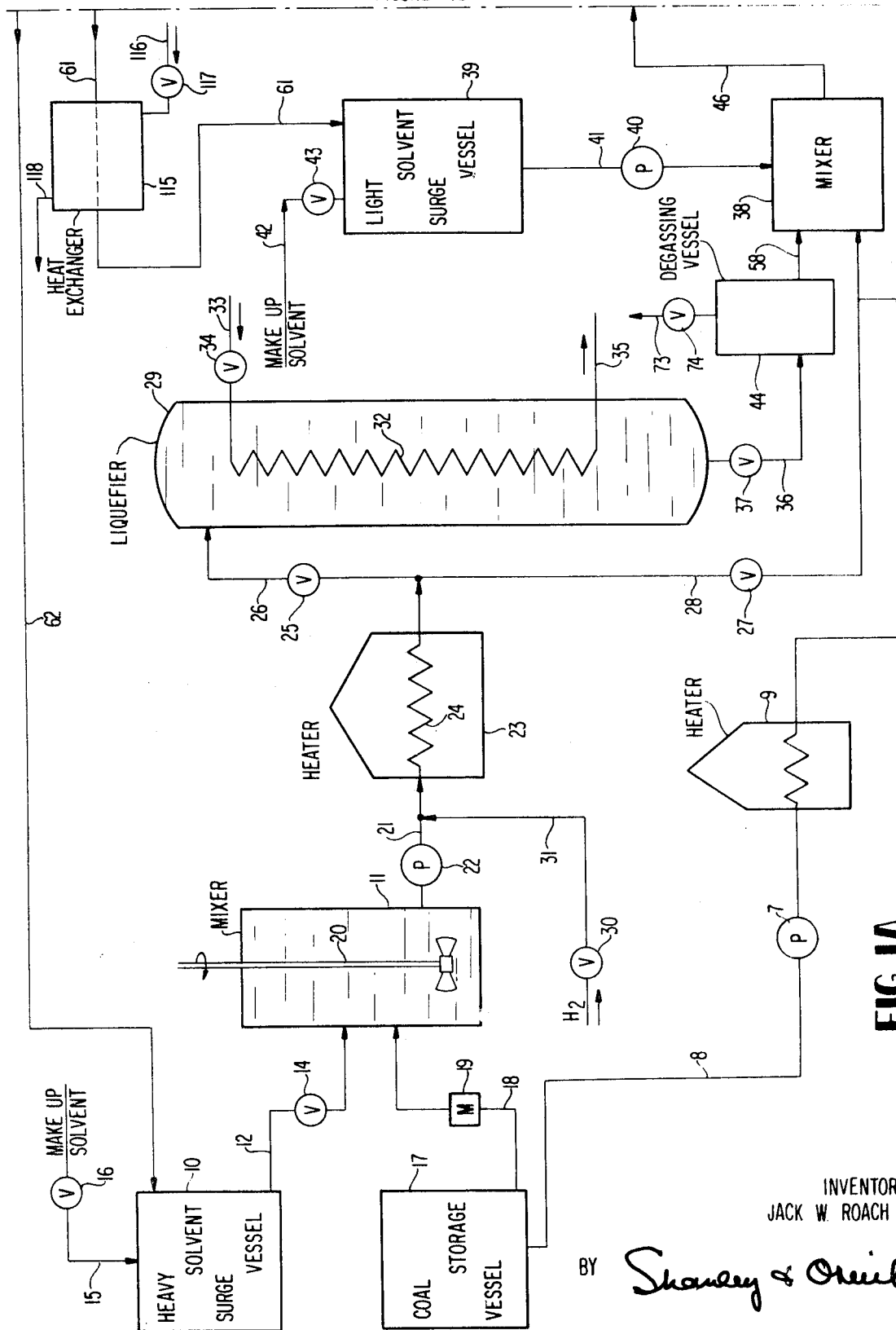


FIG. 1A

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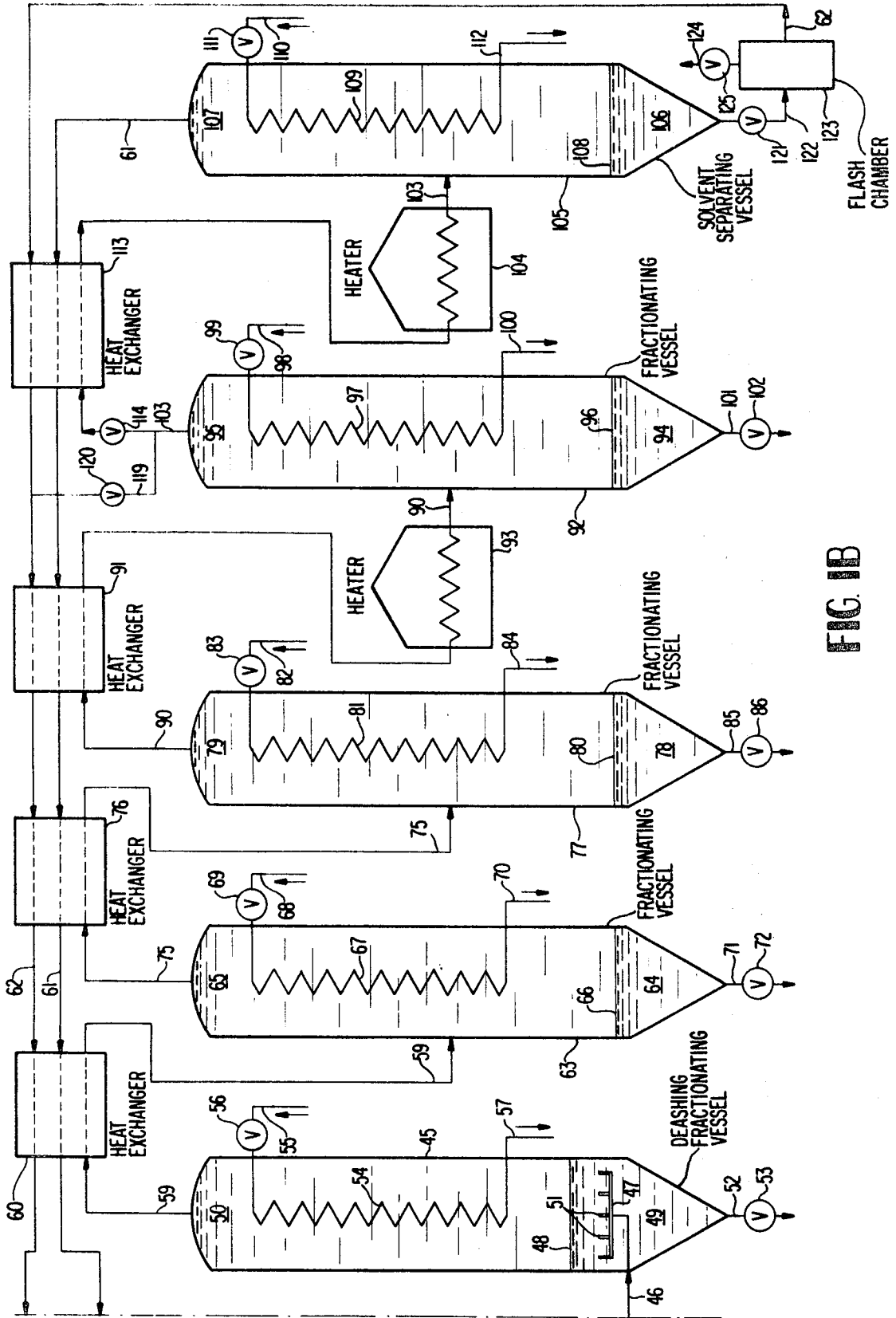


FIG. 1B

FIGURE - 1A

FRACTIONATION OF COAL LIQUEFACTION PRODUCTS IN A MIXTURE OF HEAVY AND LIGHT ORGANIC SOLVENTS

BACKGROUND OF THE INVENTION

This invention broadly relates to a method of separating coal liquefaction products into a plurality of fractions in a solvent mixture containing heavy and light organic solvents under elevated temperature and pressure conditions. The invention further relates to a novel process for liquefying coal with heavy organic solvents and thereafter fractionating the resultant products with light organic solvents, and a method of separating finely divided insoluble material from a solution of coal liquefaction products in a solvent comprising a heavy organic solvent.

The potentially soluble substances in fossilized carbonaceous materials such as coal are composed largely of high molecular weight three-dimensional cyclic structures which contain predominantly six-membered rings. For example, coal contains bitumen and humin, which have large, flat, aromatic lamellar structures that differ in molecular weight, degree of aromaticity, oxygen content, nitrogen content and cross-linking, volatile matter, fusain, mineral matter, sulfur and moisture. The sulfur content may be present as pyritic sulfur, inorganic sulfates, and/or organic sulfur compounds.

The mineral matter remains behind as ash when the coal is burned and fusain, which is a mineral charcoal, is consumed during burning at high temperatures in the presence of sufficient oxygen for complete combustion. The presence of sulfur in the coal in substantial quantities results in contamination of the atmosphere with oxides of sulfur upon combustion, and highly corrosive sulfurous acid and/or sulfuric acid is produced therefrom upon reaction with atmospheric moisture. As a result, air pollution regulations in metropolitan areas often require that the sulfur content of fuels be reduced so as to control atmospheric pollution. The mineral content of the coal may be 10–15 per cent by weight or higher in some instances, and this reduces the B.t.u. value of the raw coal per unit weight and increases transportation costs. There is an additional cost when the coal is burned as the ash residue must be removed and disposed of in some manner.

The presence of mineral matter, fusain and sulfur in substantial quantities also reduces the value of the coal for specialized uses. For example, if these substances are removed prior to coking, the deashed coal thus produced may be used for preparing high purity anode coke which has a substantially higher value than the usual impure coke produced from raw coal.

For the above and other reasons, it is desirable to reduce the mineral matter, fusain and sulfur contents of coal. One process presently used for removing these substances involves solvation or liquefaction of desirable coal constituents such as bitumen and humin in a heavy organic solvent to produce a solution of coal liquefaction products containing suspended finely divided insoluble material. Thereafter, the undesirable insoluble constituents such as mineral matter, fusain and inorganic sulfur are separated from the solution prior to recovery of the deashed coal liquefaction products.

The methods available heretofore for separating finely divided insoluble material from a solution of coal liquefaction products in a heavy organic solvent have left much to be desired. For example, gravity settling has a number of disadvantages due in part to the low settling rates encountered under ambient conditions of temperature and pressure, and especially in instances where the solution is somewhat viscous in nature. Filtration methods also have disadvantages as the solution is often viscous at room temperature and must be heated to obtain sufficiently fast filtration rates. Plugging of the filter pores with finely divided insoluble constituents is an additional problem. In instances where the viscosity of the solution is sufficiently low, centrifuging is usually satisfactory insofar as the physical separation of the solids from the solution is concerned. However, centrifuging equipment is costly

and it is difficult to remove the lighter micron-sized particles. As a result of the above and other deficiencies, there has not been an entirely satisfactory method available heretofore for separating suspended finely divided insoluble materials from a heavy organic solvent solution of coal liquefaction products.

As a general rule, heavy organic solvents are much more efficient coal liquefaction solvents than light organic solvents. The solvation of coal in a heavy organic solvent produces a mixture of coal liquefaction products which differ greatly with respect to their chemical and physical properties. For example, the liquefaction products may vary from low-boiling liquids to solids which are soluble in the organic solvent and have softening points of 300°–400° F. and higher. The low-boiling liquid products may be recovered by distillation, but a method has not been available heretofore for separating normally solid coal liquefaction products into a plurality of fractions having desired softening points or other physical and/or chemical characteristics. A satisfactory fractionating method would be very useful as coal liquefaction products with widely differing properties could be produced for specific end uses.

The present invention provides an efficient method of separating ash constituents from previously prepared coal liquefaction products, and/or fractionating previously prepared deashed coal liquefaction products into a plurality of fractions. Additionally, it is also possible to liquefy coal employing heavy organic solvents which are very efficient coal liquefaction solvents, and to thereafter deash and/or fractionate the coal liquefaction products with a light organic solvent which is much less efficient as a coal-liquefying solvent. Heretofore it has been necessary to recover the solvents used by flashing, condensation of the vapor, and fractional distillation. This prior art method of solvent recovery involves the use of expensive equipment with high operating costs as the utility requirements are excessive. The present invention overcomes this disadvantage by providing for the direct recovery of each solvent, whereby each solvent may be heat exchanged with incoming solvent rich streams to recover heat and produce separate cooled streams of liquid light and heavy solvents for recycle.

It is an object of the present invention to provide a novel method of separating products of coal liquefaction into a plurality of fractions in a solvent mixture containing a heavy organic coal liquefaction solvent and a light organic fractionating solvent under elevated temperature and pressure conditions.

It is a further object to provide a novel method of fractionating coal liquefaction products in a mixture of light and heavy organic solvents wherein a mixture of the light and heavy organic solvents is obtained from the final fractionating stage, and the solvent mixture is separated directly into light and heavy organic solvent phases which are recovered and passed in heat exchange relationship with incoming solvent-rich streams to recover the heat content thereof prior to recycle.

It is a further object to provide a novel process for liquefying coal with a heavy organic coal liquefaction solvent, and then separating the coal liquefaction products in the solution thus produced into a plurality of fractions employing selected light organic fractionating solvents at elevated temperature and pressure.

It is a further object to provide a novel method of separating suspended finely divided insoluble material from coal liquefaction products present in a solvent comprising a heavy coal liquefaction solvent.

Still other objects and advantages of the invention will be apparent to those skilled in the art upon reference to the following detailed description and the examples.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B of the drawings illustrate one presently preferred arrangement of apparatus for use in practicing the invention. FIG. 1B is a continuation of FIG. 1A.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED VARIANTS THEREOF

The process of the present invention provides a method whereby liquefied coal dissolved in a mixture of heavy dissolving solvent and light fractionating solvent is introduced into a deashing-fractionating vessel under temperature and pressure conditions such that the solvent density of the light fractionating solvent is about 0.40–0.65 g./cc. and sufficiently low to cause the rejection or separation of a small amount of the heavy liquefied coal constituents. The lighter mixed solvent-rich liquefied coal solution exiting from the deashing-fractionating vessel may then be introduced into at least one vessel, in the last of which the temperature and pressure of the solution are adjusted to give a light solvent density of about 0.10–0.20 g./cc. to yield a fluid bottom fraction comprising the heavy solvent and any residual dissolved coal, as well as a light fractionating solvent phase which may be withdrawn and recycled for heat recovery and reuse in the method. In those instances where more than one vessel is employed, the light solvent densities prevailing in such intermediate vessels are decreased progressively from that existing in the deashing-fractionating vessel to that existing in the final vessel to thereby provide a succession of heavy coal fractions of decreasing softening point and a succession of correspondingly lighter mixed solvent rich phases. In one variant of the invention, the deashing-fractionating vessel and all subsequent vessels may be operated at a pressure which is at or below the critical pressure of the light fractionating solvent provided that the pressure, temperature and enthalpy are controlled whereby the light solvent densities set forth herein are maintained.

Referring now to the drawings, a heavy organic coal liquefaction solvent to be defined more fully hereinafter is passed from solvent surge vessel 10 to mixer 11 via conduit 12 at a rate controlled by valve 14. Makeup solvent is supplied to heavy solvent surge vessel 10 via conduit 15 upon opening valve 16. In the variant to be presently described, which includes liquefying the coal in heavy organic solvent and thereafter fractionating the liquefaction products in the presence of selected light organic solvents, finely divided raw coal in storage vessel 17 is introduced into mixer 11 via conduit 18 at a rate determined by meter 19. The relative feed rates of heavy solvent and coal may be controlled so that the weight ratio of solvent to coal in mixer 11 is between about 1:1 and 20:1, and preferably between about 2:1 and 5:1. The best results are usually obtained when the weight ratio of solvent to coal is approximately 3:1.

The coal and solvent in mixer 11 are agitated with agitator 20, and the slurry thus prepared is withdrawn via conduit 21 and transferred by pump 22 to gas fired heater 23 where the slurry flowing in coil 24 is heated to an elevated temperature which preferably closely approximates the desired initial temperature of solvation or liquefaction. In the variant presently described, valve 25 in conduit 26 is open and valve 27 in conduit 28 is closed, and the heated slurry is passed to liquefier 29 via conduit 26. While it is not essential, it is usually preferred to carry out the liquefaction in the presence of added gaseous hydrogen. When gaseous hydrogen is added, it may be passed into the slurry flowing in conduit 21 upon opening valve 30 in conduit 31.

The liquefier 29 preferably operates under a superatmospheric pressure which is determined by the overpressure of gaseous hydrogen when present, the vapor pressure of the solvent at the operating temperature, and/or the hydraulic pressure applied by pump 22. The liquefaction temperature is determined by the initial temperature of the slurry flowing in conduit 26 and by the temperature control fluid which is supplied to coil 32 via conduit 33 at a rate controlled by valve 34 and withdrawn via conduit 35. The solvent is contacted with the coal under the temperature and pressure conditions existing in the liquefier 29 for a sufficient period of time to solubilize extractable carbonaceous constituents therefrom and

produce a solution of coal liquefaction products which contains suspended finely divided fusain, mineral ash and other insoluble constituents. The resultant solution usually contains relatively large amounts of dissolved normally solid liquefaction products of widely varying softening points, and in many instances little or no low boiling normally liquid products. The solution is preferably but not necessarily substantially saturated with respect to the dissolved coal liquefaction products under the temperature and pressure conditions existing in liquefier 29, i.e., at the solvent density in the liquefier 29.

The solution of coal liquefaction products containing insoluble constituents and gases is withdrawn from liquefier 29 via conduit 36 and after passing through reducing valve 37, is introduced into degassing vessel 44 where it is degassed and then introduced into mixer 38 via conduit 58. The excess hydrogen and other gases are withdrawn from vessel 44 via conduit 73 upon opening valve 74. Light organic solvent is withdrawn from surge vessel 39 and transferred by pump 40 via conduit 41 to mixer 38 where it is admixed with the solution flowing in conduit 58 to form a solution of coal liquefaction products in the resultant mixed light and heavy organic solvents. Makeup solvent is supplied to vessel 39 via conduit 42 upon opening valve 43. The light organic solvent is supplied to mixer 38 in an amount to provide a weight ratio of light organic solvent to the solution of coal liquefaction products between about 2:1 and 20:1, and preferably between about 2:1 and 10:1. The best results are usually obtained when the weight ratio of light solvent to the solution is between about 3:1 and 4:1. The light solvent in vessel 39 is normally below the operating temperature of liquefier 29 and has a temperature whereby the solution flowing in conduit 58 is cooled to approximately the operating temperature of vessel 45.

The pressure on the solution flowing in conduit 36 is reduced while passing through reducing valve 37 to approximately the desired pressure of operation of deashing fractionating vessel 45. The temperature and pressure conditions selected for operation of vessel 45 are such that the density of the light solvent is sufficiently low to cause the rejection or precipitation of a small amount of the heavy coal liquefaction products. While the mechanism is not fully understood, it is believed that the coal liquefaction products thus rejected tend to coat or encompass the particles of insoluble material, and this causes the surfaces of the particles to be tacky so that they are much easier to agglomerate. The amount of coal liquefaction products rejected as a heavy phase from the solution in vessel 45 should be sufficient to coat and, with the attendant solvent, aid in fluxing the insoluble particles, and usually is no more than about one–two times the weight of insoluble material. However, substantially larger amounts may be rejected such as three–five times the weight of insoluble material.

The solution of coal liquefaction products in the mixed light and heavy organic solvents is withdrawn from mixer 38 via conduit 46 and introduced into vessel 45 through header 47. The header 47 is positioned a substantial distance beneath the liquid-to-liquid bulk interface 48 which is formed under the existing temperature and pressure conditions between the body of relatively heavy fluidlike slurry 49 in the bottom portion of vessel 45 and the lighter clarified solution of coal liquefaction products 50. The header 47 is provided with a plurality of spaced outlets 51 and the solution is injected into the slurry 49 therethrough. The slurry 49 contains suspended mineral ash, fusain, and other insoluble material in finely divided form fluxed with solvent and coal liquefaction products, and has a viscosity whereby it may be readily withdrawn via conduit 52 at a rate controlled by valve 53, or by the operation of a pump which controls the volume withdrawn. The slurry 49 is withdrawn at a rate to maintain the interface 48 substantially above the outlets 51 on header 47. The vessel 45 may be maintained at the desired operating temperature by passing a heat exchange fluid to coil 54 via conduit 55 at a rate controlled by valve 56 and withdrawing it via conduit 57.

The solution introduced into vessel 45 is at an elevated temperature and has a low viscosity, and the particles of coated insoluble material settle out rapidly. Unexpectedly, injecting the solution into the relatively heavy slurry 49 and passing the solution therethrough aids in coating the individual particles of micron-sized solids and in the agglomeration thereof to produce much heavier and faster settling particles. As a result, the clarified solution 50 in the upper portion of vessel 45 is substantially free of insoluble material and it does not require filtering or centrifuging to remove the last traces of solids.

The clarified solution 50 containing coal liquefaction products substantially free of insoluble material is withdrawn from the top of vessel 45 at a rate to provide a sufficient residence time to assure adequate settling of the insoluble material, such as 1-30 minutes and preferably 5-15 minutes. The clarified solution 50 is passed through heat exchanger 60 in heat exchange relationship with a relatively warm stream of light organic solvent recycled through conduit 61 to storage vessel 39, and a relatively warm stream of heavy organic coal liquefaction solvent recycled through conduit 62 to surge vessel 10. The solution 50 is withdrawn from heat exchanger 60 at a substantially higher temperature and preferably at a temperature closely approximating the desired operating temperature for equilibrium vessel 63, and is then introduced into vessel 63 via conduit 59. The light solvent density existing in vessel 63 is substantially less than that existing in vessel 45 due to the higher operating temperature and the slightly lower pressure resulting from the drop in line and heat exchanger pressure. The differential in the solvent density is sufficiently large to cause a fluidlike fraction 64 of heavy coal liquefaction products to separate from the solvent-rich lighter phase 65 of residual coal liquefaction products. The vessel 63 is maintained at a uniform operating temperature which is sufficiently elevated to permit a liquid-to-liquid bulk interface 66 to form between the heavy fraction of coal liquefaction products 64 and solvent-rich phase 65. The temperature is maintained at the desired level by means of a heat exchange fluid fed to coil 67 via conduit 68 at a rate controlled by valve 69 and withdrawn via conduit 70. The temperature and pressure conditions existing within vessel 63 are selected to provide a light solvent density whereby a desired percentage of the heavier material dissolved in the solution 50 is rejected in the form of a fluidlike heavy fraction 64. The heavy fraction 64 contains sufficient solvent to lower the viscosity and allow it to be withdrawn via conduit 71 upon opening valve 72 without plugging the same. The light and heavy solvent contents of the withdrawn heavy fraction 64 may be recovered for recycling in the process by flashing, condensation of the vapor to produce liquid mixed solvent and fractionating into light and heavy solvent streams. The residue remaining after flashing the solvent is a hard friable deashed coal fraction having a softening point of about 400° F. or higher.

The solvent-rich phase 65 containing residual liquefied coal products is withdrawn from the top of vessel 63 via conduit 75 and passed through heat exchanger 76 in heat exchange relationship with the relatively warm light and heavy solvents flowing in conduits 61 and 62, respectively. The solvent-rich phase 65 is withdrawn from heat exchanger 76 at a substantially higher temperature and preferably at a temperature closely approximating the desired operating temperature for fractionating vessel 77, and is introduced into vessel 77 via conduit 75. The light solvent density existing in vessel 77 is substantially less than that existing in vessel 63 due to the higher operating temperature and the slightly lower pressure level resulting from the drop in line and heat exchanger pressure. The differential in light solvent density between vessels 63 and 77 is sufficiently large to cause a fluidlike fraction 78 of residual liquefied coal products to be rejected from the solvent-rich phase 79. The vessel 77 is maintained at a uniform operating temperature which is sufficiently elevated to permit a liquid-to-liquid bulk interface 80 to form between heavy fraction 78 and the solvent rich phase 79. The temperature is maintained at the desired level by means of heat exchange

fluid fed to coil 81 via conduit 82 at a rate controlled by valve 83 and withdrawn via conduit 84. The temperature and pressure conditions existing within vessel 77 are selected so that a desired percentage of residual liquefied coal products of intermediate softening point are rejected from the incoming solvent-rich phase 65. The heavy phase 78 contains some solvent and has a sufficiently low viscosity to be withdrawable via conduit 85 upon opening valve 86 without plugging the same. The solvent content may be recovered for recycle by flashing, condensing the vapor, and fractionating the resultant mixed solvent to produce liquid light solvent and liquid heavy solvent. The residue is a normally solid deashed coal product having an intermediate softening point such as about 100°-400° F. in most instances.

The solvent rich phase 79 containing dissolved light liquefied coal products is withdrawn from the top of vessel 77 via conduit 90 and passed through heat exchanger 91 in heat exchange relationship with the relatively warm light and heavy solvent streams being recycled through conduits 61 and 62, respectively. The solvent rich phase 79 is withdrawn from heat exchanger 91 at a substantially higher temperature, passed to gas-fired heater 93 where it is heated to a temperature closely approximating the desired operating temperature for fractionating vessel 92, and is then introduced into vessel 92 via conduit 90. The light solvent density existing in vessel 92 is substantially less than that existing in vessel 77 due to the higher operating temperature and the slightly lower pressure level resulting from the drop in line, heat exchanger and heater pressure. The light solvent density differential between vessels 77 and 92 is sufficient to cause a fluidlike fraction of the remaining liquefied coal products 94 to be rejected from the incoming solvent rich phase 79, and to form a lighter phase 95 which contains a mixture of the light and heavy solvents. The operating temperature is sufficiently elevated to permit a liquid-to-liquid bulk interface 96 to form between the rejected fraction 94 and the solvent phase 95. A uniform operating temperature is maintained by means of a heat exchange fluid fed to coil 97 via conduit 98 at a rate controlled by valve 99 and withdrawn via conduit 100. The separated fraction 94 contains sufficient solvent to lower the viscosity whereby it is withdrawable via conduit 101 upon opening valve 102 without plugging the same. The solvent content of the withdrawn fraction 94 may be recovered by flashing, condensing the vapor to produce liquid mixed solvent, and fractionally distilling the mixed solvent to produce liquid light organic solvent and liquid heavy organic solvent for recycling. The residue is a deashed coal fraction which is usually semisolid to liquid at room temperature.

Upon closing valve 120 in conduit 119 and opening valve 114, the mixed solvent phase 95 is withdrawn from the top of vessel 92 via conduit 103, passed through heat exchanger 113 in heat exchange relationship with relatively warm light and heavy solvent streams flowing in conduits 61 and 62, respectively, passed to gas fired heater 104 where it is heated to a temperature closely approximating the desired operating temperature for solvent-separating vessel 105, and then introduced into vessel 105 via conduit 103. The density of the light organic solvent in vessel 105 is substantially less than that existing in vessel 92 due to the higher operating temperature and the slightly lower pressure level resulting from the drop line, heat exchanger and heater pressure. The light solvent density differential between vessels 92 and 105 is sufficient to cause a heavy organic solvent phase 106 to separate from the light organic solvent phase 107. The vessel 105 is maintained at an operating temperature which is sufficiently elevated to permit a liquid-to-liquid bulk interface 108 to form between the heavy organic solvent phase 106 and the light organic solvent phase 107. Such operating temperature is maintained in vessel 105 by means of a heat exchange fluid fed to coil 109 via conduit 110 at a rate controlled by valve 111 and withdrawn via conduit 112.

The heavy organic solvent phase 106 is withdrawn from the bottom of vessel 105 via conduit 122 and, after flashing

through valve 121 to a lower pressure, is introduced into flash chamber 123 where substantially all of its contained light organic solvent is vaporized and withdrawn via conduit 124 and normally open valve 125. The vapor flowing in conduit 124 is passed to light organic solvent recovery, and the heavy organic solvent is withdrawn via conduit 62 and passed successively through heat exchangers 113, 91, 76 and 60 in heat exchange relationship with the relatively cool solvent-rich phases flowing in conduits 103, 90, 75 and 59, respectively. The solvent rich phases are heated and the heavy organic solvent is cooled to below its flash point and introduced into surge vessel 10 awaiting recycle. This method of operation allows cool liquid heavy organic solvent to be recovered directly from the solution of liquefied coal products flowing in conduit 103. As a result, the cost of heavy organic solvent recovery for recycle is much lower.

The hot light organic solvent phase 107 is withdrawn from the top of vessel 105 via conduit 61 and passed successively through heat exchangers 113, 91, 76 and 60 in heat exchange relationship with the relatively cool solvent-rich phases flowing in conduits 103, 90, 75 and 59, respectively. The solvent-rich phases are heated and the light organic solvent phase 107 is cooled. The solvent flowing in conduit 61 downstream of heat exchanger 60 is further cooled in heat exchanger 115 by means of a coolant supplied by conduit 116 at a rate controlled by valve 117 and withdrawn via conduit 118. This method of operation allows cool light organic solvent to be recovered directly from the solution of liquefied coal products flowing in conduit 103 without flashing and condensing solvent vapor. As a result, the cost of recovery of the light organic solvent for recycle is much lower.

In instances where the heavy organic solvent has a high solvent capacity for the liquefied coal products, a mixed light and heavy organic solvent may be employed for both liquefaction of the raw coal and fractionation of the resultant liquefied coal products. Examples of solvent mixtures for liquefaction and fractionation include anthracene oil, tetralin, catalytic cracker recycle oil and/or lubricating oil extracts as the heavy organic solvent in admixture with a light organic solvent such as pyridine, benzene, and hexane. The light and heavy organic solvents may be present in the solvent mixture in the same ratios as exist in the mixture in mixer 38. In instances where a small amount of light organic solvent is contained in the heavy organic solvent used for liquefaction, such mixture may be the heavy phase 106 in vessel 105, recycled through heat exchanger 113, 91, 76 and 60, but without any pressure reduction through valve 121 for light solvent flashing and removal.

In instances where a mixed light and heavy organic solvent is used for liquefaction and fractionation, valve 114 in conduit 103 is closed, and valve 120 in conduit 119 is opened, and the mixed solvent phase 95 is withdrawn from vessel 92 via conduit 103, passed via conduit 119 to conduit 62, and then passed successively through heat exchangers 91, 76 and 60 in heat exchange relationship with the relatively cool solvent-rich phases flowing in conduits 90, 75 and 59, respectively. The cooled mixed solvent is then introduced into solvent surge vessel 10 for recycle in the process. The recovery of liquid mixed solvent in this manner has all of the advantages noted above in recovering the light and heavy organic solvents as separate liquid streams for recycle. In instances where the mixed solvent is used, then light solvent need not be introduced into mixer 38 via conduit 41 unless required to achieve the desired ratio of light to heavy solvents. In general, the remaining steps in the liquefying and fractionating steps remain the same as previously described with the exception of substituting the mixed solvent for the solvent previously used.

Referring again to FIGS. 1A and 1B of the drawings, previously prepared coal liquefaction products dissolved in a heavy organic liquefying solvent are withdrawn from vessel 17, and passed into mixer 38 via conduit 8 and heater 9 at a rate determined by pump 7. In mixer 38, it is admixed with light organic fractionating solvent in the manner and ratio previously described. The solution of coal liquefaction products in the

mixed solvent is withdrawn via conduit 46, passed to header 47, and introduced into equilibrium vessel 45 through outlets 51.

The vessel 45 may be operated as previously described to remove insoluble constituents which are withdrawn as a fluidlike phase via conduit 52. In instances where the coal liquefaction products have been previously deashed, very little if any insoluble material is removed but passing the solution through vessel 45 assures that a small amount of insoluble material is not present in the heavy coal fraction produced in vessel 63. The coal liquefaction products contained in the clarified solution 50 withdrawn via conduit 59 are fractionated in vessels 63, 77 and 92 to produce heavy, intermediate and light fractions which are withdrawn via conduits 71, 85 and 101, respectively, in the manner previously discussed. The heavy and light organic solvents are also recovered for recycle as previously discussed.

The carbonaceous material fed to mixer 11 and liquefied in liquefier 29 may be coal, which preferably is of a rank lower than anthracite, such as subanthracite, bituminous, subbituminous, and lignite or brown coal. Peat also may be used in some instances. The particle size of the coal may vary over wide ranges and in general the particles only need be sufficiently small to be slurried in the solvent and pumped. For example, the coal may have an average particle size of one-fourth inch in diameter or larger in some instances, and as small as -200 mesh (Tyler screen) or smaller. The most practical particle size is usually between -30 mesh and -100 mesh as less energy is required for grinding and yet the particles are sufficiently small to achieve an optimum rate of liquefaction. The particle size is not of great importance, provided extremely large particles are not present as the solvent penetrates the coal particles and the extractable constituents are liquefied rapidly.

The heavy organic coal-liquefying solvent has a critical temperature above 800° F. and preferably above 850° F. and prior art coal-liquefying solvents falling within this classification may be used. Examples of suitable liquefying solvents include cyclic hydrocarbons having normal boiling points of about 400°-1,000° F., and preferably polycyclic hydrocarbons containing at least two condensed benzene rings. Polycyclic hydrocarbons having an aromatic-naphthenic fused ring structure wherein a benzenoid ring and a nonbenzenoid or a naphthenic ring adjacent thereto are fused are especially useful. Specific examples of solvents include fused ring aromatic hydrocarbons containing two, three and four fused benzene rings such as tetralin, decalin, diphenyl, methylnaphthalene, dimethylnaphthalene, fluorene, anthracene, phenanthrene, pyrene and chrysene. Commercially available mixtures including one or more of the above mentioned compounds may be derived from petroleum refining operations and from other sources, such as the destructive distillation of coal, coal tar and oils. Examples of preferred mixtures include anthracene oil, catalytic cracker recycle stocks such as light recycle catalytic cracker oil, heavy recycle catalytic cracker oil, and clarified catalytic cracker slurry oil, thermally cracked petroleum stocks, and lubricating oil aromatic extracts such as bright stock phenol extracts. The boiling range of the mixtures may be, for example, about 500°-1,000° F. and preferably about 700°-900° F. Refractory highly aromatic streams wherein the aromatic constituents contain two or more fused benzene rings per molecule and make up at least 50 percent by weight of the stream are preferred, and for better results the aromatic constituents should be present in an amount of at least 80-95 percent by weight. Clarified catalytic cracker slurry oil is especially useful.

Light organic solvents having critical temperatures below 800° F., and preferably below 750° F., are employed as fractionating solvents. Light organic fractionating solvents comprise one or more substances selected from the following groups:

1. Cyclic hydrocarbons:

- a. Aromatic hydrocarbons having a single benzene nucleus and preferably six to nine carbon atoms, such as benzene, toluene, *o*-, *m*-, and *p*-xylene, ethyl benzene, *n*-propyl or isopropyl benzene, and monocyclic aromatic hydrocarbons in general having normal boiling points below about 310° F., and
- b. Cycloparaffin hydrocarbons which preferably contain four to nine carbon atoms, such as cyclobutane, cyclopentane, cyclohexane, cycloheptane, and nonaromatic monocyclic hydrocarbons in general having normal boiling points below about 310° F.
2. Open chain hydrocarbons:
 - a. Open chain mono-olefin hydrocarbons having normal boiling points below about 310° F. and preferably containing about four to seven carbon atoms, such as butene, pentene, hexene, and heptene, and
 - b. Open chain saturated hydrocarbons having normal boiling points below about 310° F. and preferably containing about five to eight carbon atoms such as pentane, hexane, heptane, and octane.
3. Amines, including the following:
 - a. Mono-, di-, and tri-open chain amines which preferably contain about two to eight carbon atoms such as ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl amines;
 - b. Carbocyclic amines having a monocyclic structure and preferably containing approximately six to nine carbon atoms, such as aniline and its lower alkyl homologs wherein the alkyl groups contain about one to three carbon atoms and up to three alkyl groups are present on each monocarbocyclic structure; and
 - c. Heterocyclic amines preferably those amines containing about five to nine carbon atoms such as pyridine and its lower alkyl homologs wherein the alkyl groups contain approximately one to four carbon atoms and up to three alkyl groups are present on each heterocyclic structure.
4. Phenol and its lower alkyl homologs, and preferably phenols having six to nine carbon atoms. The alkyl groups may contain, for example, one to three carbon atoms and up to three alkyl groups may be present on each phenolic nucleus.

Pyridine, benzene and hexane are usually the preferred fractionating solvents. Other preferred fractionating solvents include light aromatic extracts of reformat obtained by extracting a catalytic reformat by a number of commercial processes including the UDEX process and aromatic or phenolic cuts in general which have critical temperatures below 800° F., including those derived from the destructive distillation of coal or coal tar and light oils. Still other commercially available mixtures including one or more of the foregoing classes of compounds may be employed, and in many instances the mixture need not be purified prior to use.

The presence of added elemental hydrogen during the coal liquefaction step is not necessary, but it is usually beneficial. When hydrogen is added, the feed to the liquefier 29 may include 0.1–2 percent and preferably about 0.25–1 percent by weight of hydrogen based upon the weight of the coal. The excess hydrogen which does not enter into the liquefaction reaction may be recovered from the coal liquefaction products and recycled if desired, and thus higher percentages than 2 percent by weight of the coal may be used such as up to 5 percent by weight or more. The hydrogen content of the vapor phase in contact with the liquid solvent phase may be about 5–50 percent and preferably is about 10–35 percent by volume, but it may be higher or lower as desired in a given instance. As a general rule, the higher the partial pressure of hydrogen, the faster the liquefaction reaction, as more hydrogen is available in the solvent for transfer to the active sites produced on the decomposing or depolymerizing coal.

The temperature employed in operating liquefier 29 should be sufficiently high to result in a fast solvation rate. The upper limit is the temperature at which the carbonaceous material is coked and/or the organic solvent is decomposed substantially during the period of treatment. The temperature of liquefaction may be 550°–1,000° F. for the most liquefying solvents

and coals, and preferably is at least 650° F. to 700° F. In most instances, the temperature should be about 650°–900° F., and about 700°–850° F. for best results. The solvation temperature should not be sufficiently high to result in substantial coking within the period of treatment. The coking temperature varies from coal to coal, and coals having a higher rank usually have a higher decomposition or coking temperature. Oklahoma bituminous coal cokes at about 800°–840° F., and the more volatile Wyoming coals at a lower temperature such as 700°–800° F. In instances where a tubular reactor is employed and a slurry of coal is passed through the tubes on a continuous basis, then somewhat higher solvation temperatures are suitable due to the dynamic nature of the system. Also, the flow rates through the tubes may be sufficiently fast to reduce coking on the tube surfaces.

The liquefying solvent is contacted with the coal in liquefier 29 for a sufficient period of time to solubilize a substantial amount of the extractable constituents, such as about 0.2–2 hours. For economic reasons, the contact period should not be more than about 1 hour, and preferably no more than 0.25–0.5 hour. Usually more than 50 percent by weight of the coal is liquefied, and often up to 80–90 percent.

The minimum weight ratio of light organic fractionating solvent to the solution of coal liquefaction products is about 2:1 by weight, and the upper limit is practical in nature and may be as high as 20:1. There is little improvement in the sharpness of fractionation beyond weight ratios of 5:1 and 10:1, and the lowest weight ratio necessary to give a desired degree of sharpness of fractionation is preferred as the cost of handling the solvent increases with the amount used. Usually a weight ratio between about 3:1 and 5:1 is preferred.

The pressure in liquefier 29 may be between about 400 and 10,000 pounds per square inch absolute (p.s.i.a.), and preferably is about 500–3,000 p.s.i.a. for most heavy organic coal liquefaction solvents. The pressure should be sufficient to provide a solvent density of at least 0.5 g./cc. and preferably at least 0.6 g./cc. at the existing temperature. There is no upper limit on the solvent density during liquefaction as the highest that can be achieved under practical operating conditions gives improved results due to the increased solubility of the coal liquefaction products. The liquefying solvents defined herein have a solvent density of about 0.5–0.9 g./cc., and preferably about 0.6–0.8 g./cc. under practical temperature and pressure conditions for operating liquefier 29. If the liquefying solvent density is too low, then it is necessary to resort to pressure to increase the density. Usually pressurized hydrogen is preferred as a pressurizing medium, but inert gases or gaseous mixtures may be employed such as nitrogen, argon and helium. Also, the pressure existing in liquefier 29 may be imposed by suitable hydrostatic means such as a high pressure pump.

In instances where the solution flowing in conduit 46 contains low boiling normally liquid liquefaction products, as well as insoluble constituents and/or dissolved liquefaction products which are semisolid to solid at room temperature, then the low-boiling products may be removed by fractional distillation prior to removal of the insoluble constituents and/or fractionating the semisolid to solid coal liquefaction products. As a general rule, the average molecular weight and complexity of the coal liquefaction products increase with the boiling points of the normally liquid products and with the softening points of the semisolid to solid products, and products having a similar boiling point or softening point also tend to have similar physical and/or chemical characteristics.

It is possible to separate one or more distillate fractions of normally liquid products by a prior art fractionating step which is not shown in the drawings in the interest of clarity, and thereafter separate the heavy oils, semisolid, and solid products into a plurality of fractions by the method of the invention. While the fractions may differ markedly in chemical and/or physical characteristics, the products within a fraction may have similar chemical and/or physical characteristics and it is possible to produce fractions which are suitable for

specific end uses. For example, low boiling normally liquid fractions may be used as fuels, and liquid fractions of higher boiling point may be catalytically or thermally cracked to produce low boiling distillates suitable for use as fuels. The slurry 49 withdrawn from vessel 45 contains a high concentration of sulfur, mineral ash and other undesirable constituents, but it is possible to use the residue remaining after flashing off the solvent as a fuel for firing boilers and the like in areas where air pollution is not a problem. The heavy fraction of coal liquefaction products 64 withdrawn from vessel 63, after flashing off the solvent, is useful as a solid fuel in metropolitan areas where air pollution regulations require the use of low sulfur fuels. The fraction 78 of coal liquefaction products of intermediate softening point withdrawn from vessel 77 has a low sulfur content and it is useful as a solid fuel in metropolitan areas. Additionally, vessel 77 may be operated in many instances at a sufficiently elevated temperature and low solvent density to separate a fraction having a softening point below 200° F. and preferably below 150° F. which may be hydrofined and/or hydrocatalytically cracked to produce liquid fuels. The fraction 94 of light coal liquefaction products withdrawn from vessel 92 is normally semisolid to liquid upon flashing off the mixed solvent, and it likewise may be fed to a conventional catalytic hydrofining unit and/or catalytic or hydrocatalytic cracker to produce low boiling distillate fractions useful as fuels.

It is possible to bypass up to two of the vessels 45, 63 and 77 in instances where the desired end products will permit it. For example, when the solution flowing in conduit 46 contains an unobjectionable amount of insoluble constituents, vessel 45 may be bypassed and the solution flowing in conduit 46 may be introduced directly into vessel 63. If insoluble constituents are not objectionable in the heavy fraction 64, then vessel 45 may be operated under the conditions described for vessel 63 to thereby cause the separation of heavy fraction 64 and slurry phase 49 simultaneously in vessel 45, vessel 63 may be bypassed, and the solution flowing in conduit 59 may be introduced directly into vessel 77. Similarly, the heavy fractions 64 and 78 may be rejected along with slurry 49 by operating vessel 45 under conditions described for vessel 77, and the solution flowing in conduit 59 may be introduced directly into vessel 92. It is also possible to bypass vessel 63 and introduce the solution flowing in conduit 59 directly into vessel 77, and thereby separate the insoluble materials in slurry phase 49 in vessel 45 and reject heavy phases 64 and 78 in vessel 77. Still other modifications may be made in the fractionating scheme illustrated in the drawings and described herein.

The vessels 45, 63, 77 and 92 are operated at a sufficiently elevated temperature to form a liquid-to-liquid bulk interface between the separated fluidlike heavy fractions 49, 64, 78 and 94 and the lighter mixed solvent-rich fractions 50, 65, 79 and 95; respectively. The minimum temperature sufficient to form the liquid-to-liquid bulk interface will vary somewhat with the mixed solvent and the chemical and physical nature of the separated heavy fractions and the lighter mixed solvent-rich fractions. For example, the minimum temperature is at least 400° F. and sufficiently high to form the necessary liquid-to-liquid bulk interface, which may be as high as 500°-650° F. with some mixed solvents when separating heavy fractions. At lower fractionating temperatures, a fraction may be precipitated, but the fraction has a viscosity whereby it is not fluidlike and freely flowable from the treating zone. The fractions precipitated at lower temperatures are semisolids or solids which tend to plug the apparatus as they are withdrawn and thus continuous operation is very difficult or impossible.

The maximum temperature for operating vessel 63 at practical pressures to separate a fraction containing coal solubilization products having a softening point above 400° F. is approximately the critical temperature of the light organic fractionating solvent, the pressure being adjusted simultaneously to provide a light solvent density of about 0.05 g./cc. less than that prevailing in vessel 45. At temperatures above this level, the density change in the fractionating solvent is very

rapid and coal liquefaction products having lower softening points than about 400° F. separate along with the higher softening point materials, and this lowers the softening point of fraction 64. By operating vessel 63 near the minimum fractionating temperature, it is possible to separate a heavy fraction having a softening point in excess of about 400° F.

The selection of a specific fractionating temperature between 400° F. and about the critical temperature of the fractionating solvent provides a convenient means of separating varying yields of heavy fractions of coal liquefaction products having high softening points and a high degree of molecular complexity. Inasmuch as some of the heavy constituents often have objectionable characteristics for certain end uses, the invention provides a convenient means for removing the objectionable heavy fraction prior to recovery of the remaining lighter fractions. It is also possible to operate vessel 45 at a temperature closely approximating the minimum level for forming a liquid-to-liquid bulk interface, and reject a small amount of heavy tarry coal liquefaction products along with the insoluble constituents to flux the same. Thereafter, the temperature may be raised in one or more stages to a level approaching the maximum for separating fractions having softening points of 400° F. or higher, and additional fractions having softening points above 400° F. may be separated at successively lower solvent densities.

In instances, for example, where the heavy fraction 64 has a softening point of 400° F. or above, then vessel 77 may be operated at a temperature higher than about the critical temperature at a solvent density of about 0.05 g./cc. less than that prevailing in vessel 63 to separate a fraction having a softening point below about 400° F. Surprisingly, the critical temperature of the fractionating solvent is not the maximum temperature at which a fraction of coal liquefaction products may be recovered. Under the proper pressure conditions, the upper temperature limit is the decomposition temperature of the fractionating solvent and/or the solution of coal liquefaction products. In instances where the temperature is significantly higher than the critical temperature of the fractionating solvent, then the fraction of liquefaction products usually has a lower softening point, such as below 100° F.

The vessel 92 is preferably operated above the critical temperature of the light fractionating solvent to separate the remaining dissolved coal liquefaction products as a heavy phase 94 from the lighter phase 95 of mixed solvent. Vessel 92 may be operated at essentially the same pressure as vessel 77, and the temperature may be increased to a value such that the density of the light fractionating solvent is about 0.2 g./cc. at the prevailing pressure. Similarly, vessel 105 may be operated at about the same pressure as vessel 92, and the temperature may be increased to a value such that the density of the light fractionating solvent is reduced to about 0.10-0.20 g./cc.

The following specific examples further illustrate the invention.

EXAMPLE I

One hundred pounds per hour of Oklahoma Stigler seam coal having a particle size of -65 mesh, a volatile matter content of 25.8 weight percent, a fixed carbon content of 63.0 weight percent, and an ash content of 12.1 weight percent is transferred from vessel 17 to mixer 11 and admixed therein with 300 pounds per hour of anthracene oil transferred from vessel 10. The mixture is slurried and transferred by pump 22 to heater 23 via conduit 21, into which 4 pounds per hour of hydrogen is introduced immediately upstream of heater 23. The heated slurry is withdrawn via conduit 26 and introduced into liquefier 29. The residence time in liquefier 29 is one hour, the temperature is 750° F., and the pressure is 1,200 p.s.i.g. Under these conditions, the density of the anthracene oil is 0.82 g./cc. and 85 weight percent of the coal is dissolved.

The solution of liquefied coal products in anthracene oil containing insoluble constituents is withdrawn from the bottom of liquefier 29 via conduit 36 and passed through pressure

reducing valve 37 where the pressure is reduced to approximately 1,000 p.s.i.g. The mixture is introduced into degassing vessel 44, and hydrogen, light hydrocarbons and other gaseous constituents are separated therefrom and withdrawn via conduit 73. The degassed solution is withdrawn from vessel 44 via conduit 58 and passed into mixer 38 where it is admixed with a stream of pyridine flowing from surge vessel 39 via conduit 41 at the rate of 1,500 pounds per hour. The temperature of the pyridine stream is adjusted by means of heat exchanger 115 to a value such that, upon admixture with the deashed coal solution flowing in conduit 58, the resultant temperature in mixer 38 is 560° F. Under the prevailing temperature and pressure conditions of 560° F. and 1,000 p.s.i.g. respectively, the density of the pyridine is 0.62 g./cc.

The solution of coal liquefaction products in the mixed solvent is withdrawn from mixer 38 via conduit 46 and introduced into deashing-fractionating vessel 45 by means of header 47 and outlets 51 as illustrated in the drawing. Under the conditions prevailing in vessel 45, a small amount of the coal liquefaction products previously in solution are separated out, and a slurry phase 49 is formed in the bottom of vessel 45. The heavy slurry phase 49 is withdrawn as a fluid phase from vessel 45 at a rate of 50 pounds per hour. It consists of 25 pounds per hour of pyridine and 25 pounds per hour of a mixture of the ash mineral content of the coal and separated coal liquefaction products to flux the same.

The deashed solution of coal liquefaction products in the mixed solvent phase 50 is withdrawn from vessel 45 via conduit 59, heated to a temperature of 620° F. by passing through heat exchanger 60, and then introduced into vessel 63. At the existing temperature and pressure of 620° F. and 975 p.s.i.g. respectively, the density of pyridine is 0.57 g./cc. Two fluid phases form in vessel 63, the heavy phase 64 of which is withdrawn via conduit 71 at a rate of 60 pounds per hour, of which 30 pounds per hour is pyridine and the remainder is a heavy deashed coal fraction which has a softening point in excess of 400° F. upon flashing off the pyridine solvent. The heavy deashed coal fraction has a volatile matter content of 29.6 weight percent and a fixed carbon content of 66.2 weight percent.

The lighter solvent-rich phase 65 remaining in vessel 63 is withdrawn via conduit 75, heated to a temperature of 700° F. by passing through heat exchanger 76, and then introduced into vessel 77. The density of the pyridine in vessel 77 is 0.23 g./cc. A heavy phase 78 separates in vessel 77 and is withdrawn as a fluid phase via conduit 85, at a rate of 40 pounds per hour, and containing 20 pounds per hour of pyridine and approximately 20 pounds per hour of liquefied coal product. Upon flashing off the pyridine solvent, this intermediate coal liquefaction product has a softening point of 250° F., a volatile matter content of 77.8 weight percent, and a fixed carbon content of 20.2 weight percent.

The solution of coal liquefaction products 79 is withdrawn from the top of fractionating vessel 77 via conduit 90, heated to a temperature of 755° F. by passing through heat exchanger 91 and heater 93, and the heated solution is introduced into vessel 92. The pyridine density is 0.17 g./cc. in vessel 92. The heavy phase 94 settling in the bottom of vessel 92 is withdrawn therefrom as a fluid phase via conduit 101 at the rate of 50 pounds per hour, and it consists of equal parts by weight of pyridine and a light coal liquefaction product fraction. Upon flashing off the pyridine, the light coal liquefaction product remains liquid at room temperature, and it has a volatile matter content of 83.9 weight percent, an ash content of less than 0.1 weight percent, and a fixed carbon content of 16.1 weight percent.

The light phase 95 in vessel 92 contains mixed anthracene oil and light pyridine solvents. The light phase 95 is withdrawn via conduit 103, further heated in heat exchanger 113 and heater 104 to a temperature of 820° F., and then introduced into solvent separating vessel 105 in which the pyridine density is 0.14 g./cc. The anthracene oil separates as a heavy phase 106, and it is withdrawn as a fluid phase via conduit 122 at a

rate of 300 pounds per hour in admixture with an equal weight of pyridine and introduced into flash chamber 123. Upon flashing off the pyridine content, the anthracene oil has a volatile matter content of 99.3 weight percent, an ash content of less than 0.01 weight percent, and a fixed carbon content of 0.53 weight percent. The light phase 107 withdrawn via conduit 61 consists essentially of pyridine, and it is passed in succession through heat exchangers 113, 91, 76, 60 and 115, the first four being in heat exchange relationship with the incoming streams to vessels 105, 92, 77, and 63, respectively, and is then introduced into surge vessel 39 for recycle. After flashing off the pyridine content in flash chamber 123, the relatively pure anthracene oil flowing in conduit 62 is passed in heat exchange relationship successively through heat exchangers 113, 91, 76 and 60, and is then introduced into anthracene oil surge vessel 10 for recycle.

EXAMPLE II

A batch of several thousand pounds of Oklahoma Stigler seam coal having a volatile matter content of 25.8 weight percent, a fixed carbon content of 63.0 weight percent, an ash content of 12.1 weight percent, and a particle size of -65mesh was treated in facilities not shown in the drawing with 3 times its weight of catalytic cracker slurry oil. The slurry oil had an API gravity of 2.2° and a boiling range of 700°-900°F., and was contacted with the coal at a temperature of 700°-740° F. in the presence of hydrogen and at a pressure of 1,500 p.s.i.g. for 1 hour. Under these conditions 87 weight percent of the coal was dissolved. Upon cooling and depressurization, the mixture was filtered to remove the insoluble ash mineral. A sample of the deashed coal remaining in solution contained 31.8 weight percent of volatile matter, 1.08 weight percent of ash, and 67.1 weight percent of fixed carbon.

The filtered solution is transferred to coal storage vessel 17 for fractionating into a plurality of fractions. Five hundred pounds per hour of deashed coal solution is withdrawn from vessel 17 via conduit 8 by means of pump 7 which raises the pressure to 1,200 p.s.i.g., and the solution is then passed to heater 9 where the temperature is raised to approximately 500° F. The heated solution is introduced into mixer 38 and admixed with 2,500 pounds per hour of hexane introduced via conduit 41 from light solvent surge vessel 39. The temperature of the hexane is adjusted by heat exchanger 115 to give a composite temperature in mixer 38 of 480° F.

The solution is passed from mixer 38 to deashing-fractionating vessel 45 in which the hexane density is 0.42 g./cc. The heavy fluid phase 49 settling in vessel 45 is withdrawn at a rate of 10 pounds per hour and consists of 5 pounds per hour of hexane, 1.5 pounds per hour of ash mineral, and 3.5 pounds per hour of coal liquefaction product.

The light phase 50 in vessel 45, consisting of a solution of the remaining coal liquefaction products in the mixed slurry oil and hexane solvent, is withdrawn via conduit 59 and passed to heat exchanger 60 where its temperature is raised to 505° F. The heated solution is then introduced into vessel 63 wherein the hexane density is 0.39 g./cc. A heavy fluid phase separates in vessel 63, and is withdrawn at the rate of 180 pounds per hour. Upon flashing off the hexane solvent, 90 pounds per hour of heavy coal liquefaction product is obtained having a softening point of about 400° F., about 50 weight percent of volatile matter, less than 0.1 weight percent of ash, and about 50 weight percent of fixed carbon. The light phase 65 remaining in vessel 63 is withdrawn and passed successively through heat exchangers 76 and 91 and heater 93. The heated solution is then introduced into vessel 92, thus bypassing vessel 77. Vessel 92 is operated at a temperature of 560° F., a pressure of 1,175 p.s.i.g., and a hexane density of 0.33 g./cc. A fluid heavy phase 94 consisting of equal parts by weight of hexane and light coal liquefaction product separates in the bottom of vessel 92 and is withdrawn therefrom at the rate of 30 pounds per hour. Upon flashing off the hexane solvent, the light coal liquefaction product is fluid at room temperature, and has a

volatile matter content of 75 weight percent, an ash content of less than 0.1 weight percent, and a fixed carbon content of 25 weight percent.

The mixed solvent phase 95 is withdrawn via conduit 103, passed through heat exchanger 113 and heater 104, and then introduced into solvent separating vessel 105. The vessel 105 is operated at a temperature of 800° F., a pressure of 1,150 p.s.i.g., and a hexane solvent density of 0.18 g./cc. The slurry oil forms a heavy fluid phase 106 containing some hexane which is withdrawn via conduit 122, the hexane is flashed off in flash chamber 123, and the slurry oil is passed through heat exchangers 113, 91, 76 and 60 in succession to transfer its heat to the countercurrently flowing solution of coal liquefaction products. The cool slurry oil then leaves the system for reuse in dissolving more coal. The hexane phase 107 leaving the top of vessel 105 is also passed successively through heat exchangers 113, 91, 76 and 60 to transfer its heat to the countercurrently flowing solution of coal liquefaction products. The hexane is then given a final cooling in heat exchanger 115 and returned to vessel 39 for reuse.

EXAMPLE III

One thousand grams of the filtered slurry oil solution of Stigler seam coal of example II is refiltered and introduced into a pressure vessel along with 5,000 grams of benzene. The vessel is maintained at a pressure of 1,000 p.s.i.g. and the temperature is raised in increments. The initial temperature level is 550° F., at which the density of the benzene is 0.52 g./cc. A fluidlike heavy phase forms and is withdrawn from the bottom of the vessel which phase consists of one part by weight of benzene and one part by weight of heavy coal liquefaction products and ash mineral.

The temperature is raised to 600° F., at which temperature the density of the benzene is 0.34 g./cc. A fluidlike heavy phase forms and is withdrawn. Upon flashing off the benzene, this heavy phase has a volatile matter content of 32.1 weight percent, an ash content of less than 0.1 weight percent, and a fixed carbon content of 67.9 weight percent.

The temperature is raised to 655° F., at which temperature the benzene density is 0.20 g./cc. The heavy fluidlike phase which forms is withdrawn from the bottom of the vessel and the benzene is flashed off. This product has a volatile matter content of 66.2 weight percent and a fixed carbon content of 33.4 weight percent.

The temperature is raised to 705° F., at which temperature the density of benzene is 0.16 g./cc. The heavy fluidlike phase which forms is withdrawn from the vessel and is freed of solvent. This product has a volatile matter content of 79.2 weight percent and a fixed carbon content of 20.3 weight percent.

The temperature is raised to 785° F., to provide a benzene density of 0.13 g./cc. The fluidlike heavy phase which forms is withdrawn and desolvated. This product has a volatile matter content of 93.1 weight percent, a negligible ash content, and a fixed carbon content of 6.9 weight percent.

When desired, the various heavy organic coal liquefying solvents disclosed on pages 26 and 27 of the specification may be substituted for anthracene oil in example I and for slurry oil in examples II and III to thereby obtain comparable results. Similarly, the various light organic solvents disclosed on pages 27-30 of the specification may be substituted for pyridine in example I, for hexane in example II, and for benzene in example III to thereby obtain comparable results.

I CLAIM:

1. A method of fractionating products of coal liquefaction into a plurality of fractions comprising

treating an organic solvent solution of products of coal liquefaction in a treating zone at an elevated temperature and pressure to separate a fluidlike first heavy fraction of coal liquefaction products from a lighter first solvent-rich phase containing dissolved coal liquefaction products, the organic solvent consisting essentially of a mixture of at least one heavy organic coal-liquefying solvent having a

critical temperature above about 800° F. and at least one light organic fractionating solvent having a critical temperature below about 800° F.,

the light organic fractionating solvent being selected from the group consisting of aromatic hydrocarbons having a single benzene nucleus and normal boiling points below about 310° F., cycloparaffin hydrocarbons having normal boiling points below about 310° F., open chain monoolefin hydrocarbons having normal boiling points below about 310° F., open chain saturated hydrocarbons having normal boiling points below about 310° F., mono-, di-, and tri-open chain amines, carbocyclic amines having a monocyclic structure, heterocyclic amines, and phenol and its homologs,

the organic solvent solution containing the heavy organic coal-liquefying solvent in an amount to dissolve the coal liquefaction products,

the organic solvent solution containing at least two parts by weight of the light organic fractionating solvent for each part by weight of the heavy organic coal-liquefying solvent and the dissolved coal liquefaction products,

the organic solvent solution of coal liquefaction products being treated at a temperature of at least 400° F. and the temperature being sufficiently elevated to form a liquid-to-liquid bulk interface between the first heavy fraction and the first solvent-rich phase,

the temperature and pressure being adjusted to provide a light organic fractionating solvent density in the treating zone of less than about 0.65 g./cc., the solvent density being sufficiently low to separate the first heavy fraction from the first solvent-rich phase and sufficiently high to retain the remaining coal liquefaction products in solution in the first solvent-rich phase,

the first heavy fraction having a viscosity under the temperature and pressure conditions existing in the treating zone whereby it is flowable from the treating zone, and withdrawing the first heavy fraction from the treating zone.

2. The method of claim 1 wherein said light organic fractionating solvent is selected from the group consisting of pyridine, benzene and hexane.

3. The method of claim 1 wherein said organic solvent solution contains initially finely divided insoluble material derived from coal during liquefaction, the temperature and pressure are adjusted to provide a light organic fractionating solvent density in the treating zone of about 0.40-0.65 g./cc. when separating the first heavy fraction,

a body of slurry containing the insoluble material and the first heavy fraction is separated in a lower portion of the treating zone, the body of slurry contains the first heavy fraction in an amount to flux the insoluble material present therein under the temperature and pressure conditions existing in the treating zone, and the slurry is withdrawn from the treating zone.

4. The method of claim 1 wherein said heavy organic coal liquefying solvent is selected from the group consisting of anthracene oil, tetralin, catalytic cracker recycle stocks, thermally cracked stocks, and lubricating oil aromatic extracts.

5. The method of claim 1 wherein said heavy organic coal-liquefying solvent is catalytic cracker slurry oil.

6. The method of claim 1 wherein said light organic fractionating solvent is selected from the group consisting of pyridine, benzene and hexane, and said heavy organic coal-liquefying solvent is selected from the group consisting of anthracene oil, tetralin, catalytic cracker recycle stocks, thermally cracked stocks and lubricating oil aromatic extracts.

7. The method of claim 6 wherein said heavy organic coal-liquefying solvent is catalytic cracker slurry oil.

8. The method of claim 1 wherein the first solvent-rich phase is further treated in a treating zone under elevated temperature and pressure conditions to separate at least one additional fluidlike heavy fraction of coal liquefaction products including a fluidlike final

heavy fraction of residual coal liquefaction products which is separated from a lighter organic solvent phase containing mixed heavy organic coal liquefying solvent and light organic fractionating solvent,

the temperature and pressure are adjusted to provide a light organic fractionating solvent density in the treating zone during separation of the final heavy fraction not greater than about 0.35 g./cc. and sufficiently low to separate the residual coal liquefaction products from the organic solvent phase,

the final heavy fraction having a viscosity under the temperature and pressure conditions existing in the treating zone during separation thereof whereby it is flowable from the treating zone, and

withdrawing the final heavy fraction of residual coal liquefaction products from the treating zone.

9. The method of claim 8 wherein the pressure in the treating zone during separation of the first heavy fraction and at least one additional heavy fraction including the final heavy fraction is approximately the same, and the temperature of the organic solvent is adjusted to provide the desired light organic fractionating solvent density for separation of at least one additional heavy fraction including the final heavy fraction.

10. The method of claim 8 wherein

the temperature and pressure of said organic solvent phase are adjusted in a treating zone to provide a light organic fractionating solvent density not greater than about 0.10–0.20 g/cc. and sufficiently low to form a light organic fractionating solvent phase and a heavy organic coal-liquefying solvent phase.

said heavy organic coal-liquefying solvent phase having a viscosity whereby it is flowable from the treating zone, and

withdrawing said heavy organic coal-liquefying solvent phase from the treating zone.

11. The method of claim 10 wherein

said light organic fractionating solvent phase is withdrawn from the treating zone, and

at least one of said withdrawn solvent phases is passed in heat exchange relationship with a coolant comprising at least one relatively cool solvent-rich phase whereby heat is recovered.

12. The method of claim 8 wherein

at least one fluidlike intermediate heavy fraction of coal liquefaction products is obtained by treating the first solvent-rich phase in at least one treating zone under elevated temperature and pressure conditions providing a light organic fractionating solvent density therein which is less than that existing in the treating zone when separating the first heavy fraction and greater than 0.2 g./cc.,

at least one intermediate heavy fraction separate by this treatment having a viscosity under the temperature and pressure conditions existing in the treating zone whereby it is freely flowable therefrom, and

withdrawing at least one intermediate heavy fraction from at least one treating zone.

13. The method of claim 12 wherein

said organic solvent solution contains initially finely divided insoluble material derived from coal during liquefaction,

the temperature and pressure are adjusted to provide a light organic fractionating solvent density in the treating zone of about 0.40–0.65 g./cc. when separating the first heavy fraction,

a body of slurry containing the insoluble material and the first heavy fraction is separated in a lower portion of the treating zone, the body of slurry contains the first heavy fraction in an amount to flux the insoluble material present therein under the temperature and pressure conditions existing in the treating zone, and

the slurry is withdrawn from the treating zone.

14. The method of claim 13 wherein the pressure in the treating zone during separation of the first heavy fraction and

at least one additional heavy fraction including the final heavy fraction is approximately the same, and the temperature of the organic solvent is adjusted to provide the desired light organic fractionating solvent density for separation of at least one additional heavy fraction including the final heavy fraction.

15. The method of claim 14 wherein

the temperature and pressure of said organic solvent phase are adjusted in a treating zone to provide a light organic fractionating solvent density not greater than about 0.10–0.20 g./cc. and sufficiently low to form a light organic fractionating solvent phase and a heavy organic coal-liquefying solvent phase,

said heavy organic coal-liquefying solvent phase having a viscosity whereby it is flowable from the treating zone, and

withdrawing said heavy organic coal-liquefying solvent phase from the treating zone.

16. The method of claim 15 wherein

said light organic fractionating solvent phase is withdrawn from the treating zone, and

at least one of said withdrawn solvent phases is passed in heat exchange relationship with a coolant comprising at least one relatively cool solvent-rich phase whereby heat is recovered.

17. A method of liquefying and fractionating coal comprising

intimately contacting each part by weight of coal in particulate form with at least two parts by weight of a heavy organic solvent consisting essentially of an organic coal liquefaction solvent having a critical temperature above about 800° F. to produce a heavy organic solvent solution containing coal liquefaction products and finely divided insoluble material,

the coal being contacted with the solvent in a liquefaction zone at a temperature of about 550°–1,000° F. and under a pressure providing a solvent density of at least 0.5 g./cc.

the temperature in the liquefaction zone being below the solvent decomposition temperature and the solution thus produced containing at least two parts by weight of the heavy organic solvent for each part by weight of the coal liquefaction products,

withdrawing the heavy organic solvent solution of coal liquefaction products from the liquefaction zone,

admixing at least two parts by weight of light organic fractionating solvent with each part by weight of the organic solvent solution of coal liquefaction products to produce a mixed organic solvent solution of coal liquefaction products,

the light organic fractionating solvent consisting essentially of at least one substance having a critical temperature below about 800° F. selected from the group consisting of aromatic hydrocarbons having a single benzene nucleus and normal boiling points below about 310° F., cycloparaffin hydrocarbons having normal boiling points below about 310° F., open chain mono-olefin hydrocarbons having normal boiling points below about 310° F., open chain saturated hydrocarbons having normal boiling points below about 310° F., mono-, di-, and tri-open chain amines, carbocyclic amines having a monocyclic structure, heterocyclic amines, and phenol and its homologs,

treating said organic solvent solution of coal liquefaction products at an elevated temperature and pressure in a first treating zone to separate a fluidlike first heavy fraction containing coal liquefaction products and said finely divided insoluble material and a first solvent-rich phase containing dissolved coal liquefaction products,

the organic solvent solution of coal liquefaction products being treated in the first treating zone at a temperature of at least 400° F. and the temperature being sufficiently elevated to form a liquid-to-liquid bulk interface between the first heavy fraction and the first solvent-rich phase,

the temperature and pressure being adjusted to provide a light organic fractionating solvent density in the treating

zone of less than about 0.65 g./cc., the solvent density being sufficiently low to separate the first heavy fraction from the first solvent-rich phase and sufficiently high to retain the remaining coal liquefaction products in solution in the first solvent-rich phase,

the first heavy fraction having a viscosity under the temperature and pressure conditions existing in the treating zone whereby it is flowable from the treating zone, and withdrawing the first heavy fraction from the treating zone.

18. The method of claim 17 wherein said light organic fractionating solvent is selected from the group consisting of pyridine, benzene and hexane.

19. The method of claim 17 wherein said organic solvent solution contains initially finely divided insoluble material derived from coal during liquefaction, the temperature and pressure are adjusted to provide a light organic fractionating solvent density in the treating zone of about 0.40–0.65 g./cc. when separating the first heavy fraction,

a body of slurry containing the insoluble material and the first heavy fraction is separated in a lower portion of the treating zone, the body of slurry contains the first heavy fraction in an amount to flux the insoluble material present therein under the temperature and pressure conditions existing in the treating zone, and the slurry is withdrawn from the treating zone.

20. The method of claim 17 wherein said heavy organic coal liquefying solvent is selected from the group consisting of anthracene oil, tetralin, catalytic cracker recycle stocks, thermally cracked stocks, and lubricating oil aromatic extracts.

21. The method of claim 17 wherein said heavy organic coal-liquefying solvent is catalytic cracker slurry oil.

22. The method of claim 17 wherein said light organic fractionating solvent is selected from the group consisting of pyridine, benzene and hexane, and said heavy organic coal-liquefying solvent is selected from the group consisting of anthracene oil, tetralin, catalytic cracker recycle stocks, thermally cracked stocks and lubricating oil aromatic extracts.

23. The method of claim 22 wherein said heavy organic coal-liquefying solvent is catalytic cracker slurry oil.

24. The method of claim 17 wherein said first solvent-rich phase is withdrawn from the first treating zone and is introduced into at least one additional treating zone including a final treating zone,

the first solvent-rich phase is further treated under elevated temperature and pressure conditions to separate at least one additional fluidlike heavy fraction of coal liquefaction products including a fluidlike heavy fraction of residual coal liquefaction products which is separated in the final treating zone from a lighter organic solvent phase containing mixed heavy organic coal-liquefying solvent and light organic fractionating solvent,

the temperature and pressure are adjusted to provide a light organic fractionating solvent density in the final treating zone during separation of the final heavy fraction not greater than about 0.35 g./cc. and sufficiently low to separate the residual coal liquefaction products from the organic solvent phase.

the final heavy fraction has a viscosity under the temperature and pressure conditions existing in the final treating zone during the separation thereof whereby it is flowable from the treating zone, and

the final heavy fraction of residual coal liquefaction products is withdrawn from the final treating zone.

25. The method of claim 24 wherein the pressure in the treating zone during separation of the first heavy fraction and

at least one additional heavy fraction including the final heavy fraction is approximately the same, and the temperature of the organic solvent is adjusted to provide the desired light organic fractionating solvent density for separation of at least one additional heavy fraction including the final heavy fraction.

26. The method of claim 24 wherein the temperature and pressure of said organic solvent phase are adjusted in a treating zone to provide a light organic fractionating solvent density not greater than about 0.10–0.20 g./cc. and sufficiently low to form a light organic fractionating solvent phase and a heavy organic coal-liquefying solvent phase,

said heavy organic coal-liquefying solvent phase having a viscosity whereby it is flowable from the treating zone, and

withdrawing said heavy organic coal-liquefying solvent phase from the treating zone.

27. The method of claim 26 wherein said light organic fractionating solvent phase is withdrawn from the treating zone, and

at least one of said withdrawn solvent phases is passed in heat exchange relationship with a coolant comprising at least one relatively cool solvent-rich phase whereby heat is recovered.

28. The method of claim 24 wherein at least one fluidlike intermediate heavy fraction of coal liquefaction products is obtained by treating the first solvent-rich phase in at least one treating zone under elevated temperature and pressure conditions providing a light organic fractionating solvent density therein which is less than that existing in the first treating zone when separating the first heavy fraction and greater than about 0.2 g./cc.,

at least one intermediate heavy fraction separated by this treatment having a viscosity under the temperature and pressure conditions existing in the treating zone whereby it is freely flowable therefrom, and

withdrawing at least one intermediate heavy fraction from at least one treating zone.

29. The method of claim 28 wherein the pressure in the treating zone during separation of the first heavy fraction and at least one additional heavy fraction including the final heavy fraction is approximately the same, and the temperature of the organic solvent is adjusted to provide the desired light organic fractionating solvent density for separation of at least one additional heavy fraction including the final heavy fraction.

30. The method of claim 29 wherein the temperature and pressure of said organic solvent phase are adjusted in a treating zone to provide a light organic fractionating solvent density not greater than about 0.10–0.20 g./cc. and sufficiently low to form a light organic fractionating solvent phase and a heavy organic coal-liquefying solvent phase,

said heavy organic coal-liquefying solvent phase having a viscosity whereby it is flowable from the treating zone, and

withdrawing said heavy organic coal-liquefying solvent phase from the treating zone.

31. The method of claim 30 wherein said light organic fractionating solvent phase is withdrawn from the treating zone, and

at least one of said withdrawn solvent phases is passed in heat exchange relationship with a coolant comprising at least one relatively cool solvent-rich phase whereby heat is recovered.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607,716

Dated September 21, 1971

Inventor(s) Jack W. Roach

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 62, after "drop" please insert -- in --.

Column 9, line 3, "oe" should be -- o- --.

Column 14, line 26, after "and" (second occurrence)
insert -- it --.

Column 17, line 53, "separate" should read -- separated --.

Signed and sealed this 18th day of April 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents