

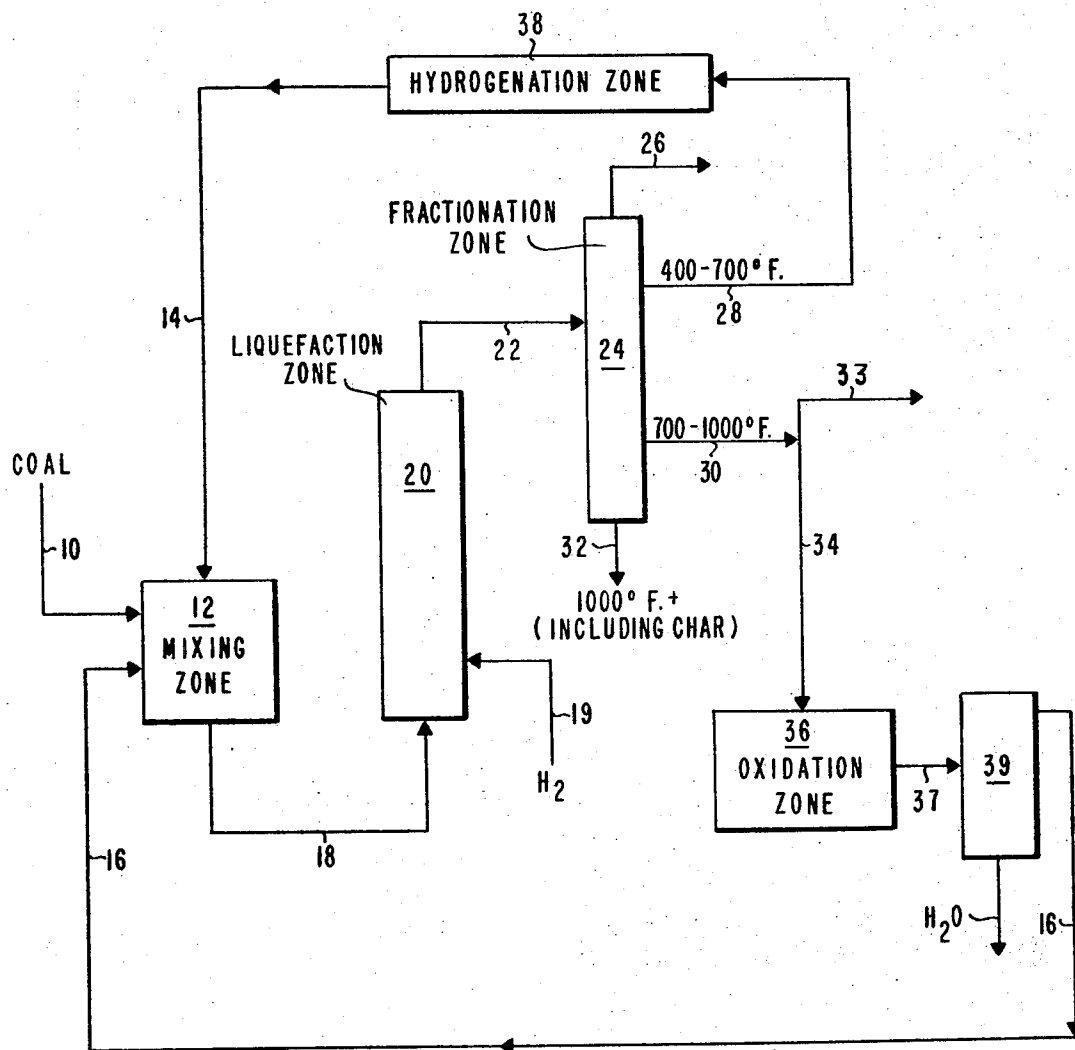
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J. E. SALAMONY ET AL

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COAL LIQUEFACTION USING CARBON RADICAL SCAVENGERS

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JAMES E. SALAMONY,
WILLIAM H. STARNES,
INVENTORS.

BY

Frederick L. Burgess
ATTORNEY.

1

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COAL LIQUEFACTION USING CARBON RADICAL SCAVENGERS

James E. Salamony, Summerville, S.C., and William H. Starnes, Jr., Baytown, Tex., assignors to Esso Research and Engineering Company

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10 Claims

ABSTRACT OF THE DISCLOSURE

Coal liquefaction yields are increased by liquefying the coal in a liquefaction zone as a slurry in a hydrogen-donor solvent in the presence of a carbon radical scavenger selected from quinones and the halogens iodine, bromine and chlorine, and the hydrogen halides thereof. Preferably a coal liquids stream which boils within the range from about 500° F. to about 1000° F. is oxidized to generate quinones, and the oxidized stream is recycled to the liquefaction zone.

BACKGROUND OF THE INVENTION

This invention relates to the production of coal liquids from solid coal, and more particularly, to the liquefaction of coal slurried in a hydrogen-donor solvent in the presence of a carbon radical scavenger.

Of recoverable fossil fuels, coal reserves are vastly greater than petroleum and natural gas reserves. Accordingly, there has been much investigation into the transformation of coal solids into liquid products that can be upgraded for petroleum-like uses. One method of converting the coal into a liquid product involves heating the coal as a slurry in a selected solvent in a high-temperature reactor. The solvent is usually an oil derived from the coal and contains partially hydrogenated polynuclear aromatics which have the ability to donate hydrogen to the liquids being made from the coal. Liquids are made from the coal when weaker chemical bonds in the very large coal molecules are thermally cracked, producing carbon free radicals. If hydrogen is available to react with the free radicals, desirable lower molecular weight hydrocarbons soluble in benzene are produced. On the other hand, if hydrogen is not available, the carbon free radicals combine with one another through carbon-to-carbon bonds, producing high molecular weight molecules that are more stable and intractable than the parent coal molecules. These higher molecular weight molecules, many of which are benzene-insoluble, are essentially unconvertible in the liquefaction reaction and require a considerable expenditure of energy in further processing in order to reduce them to a suitable low molecular weight range.

It is desirable, however, to reduce the formation of these high molecular weight molecules to below the levels occurring in solvents having high hydrogen-donor concentrations. In addition, the yield of benzene-soluble liquid products sought to be produced are desirably increased.

The most pertinent patents considered in connection with the preparation of this application are U.S. Pats. 2,100,354; 3,158,561; and 3,453,202.

2

SUMMARY OF THE INVENTION

More benzene-soluble liquid product and less intractable and essentially unconvertible coal residues are obtained, in accordance with our invention, by liquefying coal slurried in a hydrogen-donor solvent in the presence of a carbon radical scavenger selected from quinones, the halogens iodine, bromine and chlorine, and the hydrogen halides thereof.

Of the halogens iodine, bromine and chlorine and hydrogen halides thereof, iodine is preferred, since it is more reactive and at the same time is more easily recoverable and less corrosive than bromine or chlorine. For example, iodine may be recovered from the liquid product removed from a liquefaction zone by separating it in a vapor state from liquids in the liquid product, condensing the vapor state and recovering crystallized iodine from the condensate. The order of preference for the halogens employed is generally iodine>bromine>chlorine, whereas the order of preference for the hydrogen halides is generally hydrogen iodide>hydrogen bromide>hydrogen chloride. These orders depend on the relative reactivities of the halogens and hydrogen halides toward free radicals, in that the most reactive scavengers of this type generally give higher yields of the desired liquid products.

Quinone carbon-radical scavengers are preferably quinone derivatives of mono- and/or polynuclear aromatic compounds present in the benzene-soluble coal liquid product obtained from the liquefaction zone. Most polynuclear aromatic compounds in the coal liquid product boil above about 500° F. Quinone derivatives suitably are formed from such mono- and/or polynuclear aromatic compounds by passing a coal liquid stream boiling within the range from about 500° F. to about 1000° F. into an oxidation zone where conditions are regulated to oxidize at least a portion of the constituents in the coal liquids to quinones, including one or more of benzoquinones, naphthoquinones, anthraquinones, phenanthrenequinones, and the like. The preferred quinones are those which have relatively low molecular weights and do not contain bulky substituents attached to the quinoid rings, since such quinones generally give higher yields of benzene-soluble liquids products.

Ordinarily, only small quantities of a carbon radical scavenger selected from one of the aforesaid quinones, halogens or halogen halides need to be incorporated in the liquefaction zone during the liquefaction process, and for that matter, small quantities provide very beneficial results. Amounts of the aforesaid carbon radical scavengers ranging from about 0.01 to about 5 weight percent, based upon the total weight of the slurry, are suitably incorporated in the liquefaction zone. Preferably, smaller quantities than 2 weight percent are used, since large amounts, although enhancing benzene-soluble yields, may cause side reactions leading to undesirable products. Preferably from about 0.05 to about 1 weight percent of the quinone, halogen or hydrogen halide is introduced into the liquefaction zone, based on the total weight of the slurry.

The coal which is liquefied in the process is a solid, particulate coal such as a bituminous coal, a sub-bituminous coal, lignite, brown coal, and the like. Although it is desirable to grind the coal to a particle size distribution of about 8 mesh (Tyler) or smaller, it has been found that the coal suitably liquefies even if particles as large as ¼ inch on a major dimension are in the slurry. A

3

typical proximate and ultimate analysis of a suitable high-volatile bituminous coal is set forth in Table I, which follows:

TABLE I

Chemical analysis of coal wt. percent dry analysis

Illinois #6 coal (with 95% confidence limit)	
Carbon	68.77±0.22
Hydrogen	5.01±0.03
Organic oxygen	9.80
Nitrogen	1.13±0.03
Organic sulfur	3.13±.78
Total sulfur	4.51±0.1
Ash	10.23±0.13
Mineral matter	11.7±0.1
Volatile matter	46.63±0.47

Preferably the coal is dried to remove excess water, either by conventional techniques or preferably by mixing the wet coal with a hot hydrogen-donor solvent so to volatilize water vapor therefrom. Moisture in the resultant slurry preferably is less than about 2 weight percent.

The hydrogen-donor solvent is suitably mixed with the particulate coal in a solvent-to-coal ratio of from about 0.8:1 to about 2:1, preferably about 1.2:1.

The hydrogen-donor solvent will boil within the range from about 350° F. to about 1000° F., preferably from about 375° F. to about 800° F., so as to remain in the liquid phase after the slurry is formed. The solvent contains at least 30 weight percent, preferably at least about 50 weight percent, of compounds which are known to be hydrogen donors under the liquefaction conditions hereinbefore set out. Hydrocarbon streams containing one or more of the hydrogen-donor compounds, in admixture with nondonor compounds or with each other, are suitable. Preferred hydrogen-donor compounds include indane, C₁₀-C₁₂ tetrahydronaphthalenes, C₁₂ and C₁₃ acenaphthenes, particularly tetrahydroacenaphthene, the di-, tetra-, and octahydroanthracenes, as well as other derivatives of partially saturated aromatic compounds.

The hydrogen-donor solvent stream preferably is a hydrogenated recycle solvent fraction. The composition of the equilibrium solvent will vary somewhat, depending upon the source of the coal used as a feedstock to the system and further depending upon the operating conditions in the liquefaction and subsequent solid hydrogenation solvents. However, a hydrogenated recycle solvent fraction will typically have a description similar to that shown in Table II.

TABLE II.—SOLVENT PROPERTIES
[Typical solvent distillation]

Weight average boiling point	Weight percent vaporized	Specific gravity of fraction
400	3.35	.9120
442	8.61	.9592
463	9.09	.9729
488	9.09	.9813
518	9.57	.9933
549	9.57	1.0115
568	10.05	1.0473
596	10.05	1.0643
622	10.05	1.0613
674	10.04	1.0774
733	7.18	1.0942
775	3.35	1.1069

Overall specific gravity=1.0229.

Solvent elemental composition (weight percent): Carbon, 90.42; hydrogen, 8.46; oxygen, .68; nitrogen, .36; sulfur, .075.

In the liquefaction zone, liquefaction conditions include a temperature within the range from about 700° F. to about 950° F., preferably from about 800° F. to about 850° F., and a pressure from about 300 p.s.i.g. to about 3000 p.s.i.g., preferably from about 800 p.s.i.g. to about 2000 p.s.i.g. Hydrogen preferably also is added to the liquefaction zone at a rate from about 1 to about 6 weight percent (MAF coal basis). Liquid residence time

4

in the liquefaction zone is from about 5 to about 60 minutes. The concentration of quinone, the halogen selected from iodine, bromine and chlorine, or the hydrogen halide thereof, in the liquefaction zone is from about 0.01 to about 5 weight percent on the slurry, preferably from about 0.05 to about 1 weight percent. Conditions are correlated in the liquefaction zone so as to provide a benzene conversion of the coal within the range from about 50 to 90 weight percent. The conversion is expressed as a percent of MAF coal that is converted to materials which are soluble in benzene. It is calculated by the equation:

$$\text{Percent conversion} = \frac{100(S_t - S_p)}{S_t(1 - 0.1a)}$$

wherein

a=percent ash in moisture free coal

S_t=percent solids in coal feed slurry

S_p=percent solids in product slurry

Before measuring S_p, benzene is added to the product slurry as a solvent, in the ratio of 1 volume of benzene for each volume of product slurry. The results so obtained are referred to as "benzene conversion."

The product removed from the liquefaction zone includes a gaseous phase product as well as the liquid slurry. An example of the composition of the gaseous product and liquid slurry product (without separation of solids from the slurry) is given below in Table III.

TABLE III.—EXEMPLARY GAS AND LIQUID PRODUCTS

Gas product		Liquid product		
Comp.	Wt. percent	Temp. ° F.	Cum. wt. percent	Sp. gr. 60/60° F.
CO	1.2	337	(1)	
CO ₂	21.8	437	7.4	0.9014
H ₂ S	17.7	485	14.7	0.9496
CH ₃ SH	5.2	549	22.6	0.9667
H ₂	4.7	595	31.4	1.0089
C ₁	20.1	658	40.2	1.0370
C ₂	15.8	732	49.0	1.0560
C ₃	0.4	785	53.4	1.0791
C ₄	7.3	835	59.1	(2)
C ₅	0.5	(2)	30.9	(2)
C ₆	2.9		100.0	
C ₇	1.1			
C ₈	1.3			
Total	100.0			

1 IBP.
2 Solid.
3 Bottoms.

The invention will be better understood from a detailed description of a preferred embodiment of it, taken with the attached drawing.

DESCRIPTION OF THE DRAWING

The drawing is a schematic flow diagram of a process for liquefying coal utilizing quinone carbon-radical scavengers produced from liquid streams derived from the coal.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawing, particulate coal is introduced by way of line 10 into a mixing zone 12, where it is combined with a hydrogenated recycle oil stream, introduced by way of line 14, to form a paste. Also introduced into mixing zone 12 by line 16 is an oxidized recycle oil stream containing quinones. From about 0.05 to about 0.2 part by weight of the oxidized recycle oil stream are introduced in the mixing zone 12 per part by weight of the hydrogenated recycle oil from line 14. The solvent/coal ratio in mixing zone 12 may suitably be about 1.2 parts of solvent per part of coal by weight.

The slurry from the mixing zone 12 is conducted by way of line 18 into a liquefaction zone 20, which is maintained under liquefaction conditions including a temperature of about 800° F. and a pressure of about

1500° p.s.i.g. Hydrogen also may be introduced, in the gaseous form, by way of line 19 in amounts of, e.g. 2 weight percent, based on MAF coal, if desired, although it is not necessary for the basic hydrogen-donor liquefaction process. Within the liquefaction zone 20, hydrogen is transferred from the hydrogen-donor solvent to the coal, causing a depolymerization of the coal along with the solvation effect of the solvent. The quinones present in the slurry inhibit the recombination of carbon free radicals. Thus, within the liquefaction zone 20 a mixture of undepleted hydrogen-donor solvent, depleted hydrogen-donor solvent, reduced quinones, unreduced quinones, dissolved coal, undissolved coal and mineral matter is obtained. This mixture remains in the liquid phase, and a vapor phase of lighter hydrocarbons and gases is maintained above the liquid phase.

The liquid mixture is removed by way of line 22 and transported into a fractionating zone 24, where light fractions boiling below 400° F. are recovered by way of line 26 as fuel gas, and intermediate fractions boiling from 400° F. to 700° F. are recovered by way of line 28 for hydrogenation. Heavier fractions boiling from 700° F. to 1000° F. are recovered by way of line 30, and bottoms fractions boiling above 1000° F., including char, are withdrawn by way of line 32 for use in gasification process or for coking, as desired. The 700–1000° F. fraction in line 30 is carried to line 33 for subsequent refining, as by hydrocracking, to generate fuel products, and a portion of such fraction is carried by way of line 34 into oxidation zone 36. In oxidation zone 36, the quinones used as carbon radical scavengers in the liquefaction zone are produced by mixing the vaporized 700–1000° F. fraction with air and allowing the mixture to pass over a solid oxidation catalyst. The volume ratio of air to vaporized 700–1000° F. fraction may range from about 1:1 to about 200:1, with the preferred ratio being about 20:1. The oxidation catalyst is an oxide of antimony, bismuth, chromium, tungsten, uranium, molybdenum, or vanadium, and it may be suspended on a solid support. A preferred catalyst is V₂O₅ suspended on silica gel. Pressures in zone 36 may range from about 0.5 to 20 atmospheres, and the temperature of this zone may range from about 800° F. to 1000° F. However, the preferred pressure and temperature are generally about 1 atmosphere and 900° F., respectively. The flow rate in zone 36 is regulated so as to cause the vapor mixture to come in contact with the catalyst for about 0.5 to 10 sec., with the preferred contact time generally being about 5 sec. After oxidation, the 700–1000° F. stream is condensed, withdrawn as a liquid from zone 36 by line 37, separated in oil-water separator 39 from water produced in oxidation zone 36 as oxidation product, and recycled by line 16 to mixing zone 12. The 400–700° F. fraction withdrawn from fractionator 24 by line 28 is introduced into a catalytic hydrogenation zone 38 to upgrade the hydrogen content of that fraction. Hydrogenation conditions maintained in hydrogenation zone 38 include a nondestructive (i.e., non-cracking) temperature within the range from about 650° F. to about 850° F., preferably about 700° F., and pressures suitably within the range from about 650 p.s.i.g. to about 2000 p.s.i.g., preferably about 1300 p.s.i.g. The hydrogen treat rate in hydrogenation zone 38 is within the range from about 1000 to about 10,000 s.c.f./b., preferably up to about 5000 s.c.f./b. Hydrogenation catalysts employed in zone 38 are of conventional nature. Without being limited to any particular catalyst, these catalysts will typically comprise an alumina or silica-alumina support carrying one or more iron group metals and one or more metals of Group VI–B of the Periodic Table in the form of the oxides or sulfides. In particular, combination of one or more Group VI–B metal oxides or sulfides with one or more Group VIII metal oxides or sulfides are preferred. For example, typical catalyst metal combinations contemplated are oxides and/or sulfides of cobalt-molybdenum, nickel-tungsten, nickel-

molybdenum-tungsten, cobalt-nickel-molybdenum, nickel-molybdenum, etc. As a typical example, one catalyst will comprise a high metal-content sulfided cobalt-molybdenum-alumina catalyst containing about 1 to 10 weight percent cobalt oxide and about 5 to 40 weight percent molybdenum oxide, especially about 2 to 5 weight percent cobalt and about 10 to 30 weight percent molybdenum. It will be understood that other oxides and sulfides will be useful, such as those of iron, nickel, chromium, tungsten, etc. The preparation of these catalysts is now well known in the art. The active metals can be added to the relatively inert carrier by impregnation from aqueous solutions followed by drying and calcining to activate the composition. Suitable carriers include, for example, activated alumina, activated alumina-silica, zirconia, titania, etc., and mixtures thereof. Activated clays, such as bauxite, bentonite and montmorillonite, may also be employed.

A hydrogenated recycle solvent stream is recovered from hydrogenation zone 38 and recycled to mixing zone 12 for slurring of more coal from line 10, as heretofore described.

The following examples illustrate the increase in yield obtained on liquefying the coal slurries in accordance with this invention.

Example 1

Base case: coal liquefaction without halogen or quinone carbon radical scavenger.—Three 20-ml. stainless steel tubing bombs were charged with a slurry of Illinois No. 6 coal in Tetralin at a solvent-to-coal ratio of 1.2:1. The bombs were agitated at 2 c.p.s. for 5 hours in a fluidized sandbath heated to 750° F. The liquid product recovered from the bombs had benzene conversions of 81.0, 82.0 and 82.7 weight percent (MAF coal), the average conversion value being 81.9 weight percent.

Coal liquefaction with a halogen or quinone carbon radical scavenger present.—Under the same reaction conditions as those used in the Base case, two of the bombs were charged with slurries of Illinois No. 6 coal in Tetralin at a 1.2:1 solvent-to-coal ratio. One charge contained, in addition, 1 weight percent iodine, based on the total slurry weight; the other charge included 1 weight percent, on the total slurry, of *p*-benzoquinone. After reacting the charge for 5 hours at 750° F., the liquid recovered from the bomb containing iodine had a benzene conversion of 86.9 weight percent (MAF coal) and that from the bomb containing *p*-benzoquinone had a benzene conversion of 88.8 weight percent (MAF coal). The comparative results are set forth in Table IV.

TABLE IV

Run:	Benzene conversion, wt. percent MAF coal
No inhibitor	81.9
Iodine	86.9
<i>p</i> -Benzoquinone	88.8

Quite clearly, liquid yields measured by benzene conversion were notably increased either by inclusion of the halogen, iodine, or by inclusion of the quinone, *p*-benzoquinone, in the slurried coal.

Additional runs were conducted to study the efficacy of these carbon radical scavengers at a higher liquefaction temperature. The results of these runs are set out in Example 2.

Example 2

Run 1: Iodine.—Two of the bombs used in Example 1 were charged with the base slurry used in Example 1, the slurry in one bomb also containing 0.5 weight percent of iodine on the total slurry. The bombs were agitated for 1 hour at 2 c.p.s. in a fluidized sandbath at a temperature of 875° F. On analysis, the liquid from the base case bomb had a benzene conversion of 79.4 weight percent (MAF coal), while that from the bomb having the iodine

7

had a benzene conversion of 88.2 weight percent (MAF coal), evidencing an increased yield of 8.8 weight percent benzene soluble liquids.

Run 2: *p*-Benzoquinone.—The base slurry was charged to two bombs, one of the slurries containing 0.1 weight percent of *p*-benzoquinone, on the total slurry. After reacting the slurries in the bombs for 1 hour at 875° F., the base case slurry was found to have a benzene conversion of 80.2 weight percent (MAF coal) but the slurry with the *p*-benzoquinone had a benzene conversion of 90.6 weight percent (MAF coal), an increase in conversion of 10.4 weight percent.

Run 3: *p*-Benzoquinone.—Run 2 was repeated except that 0.05 weight percent on the total slurry *p*-benzoquinone was used, instead of 0.1 weight percent, and the reaction was carried out for one-half hour instead of 1 hour. The liquid from the base case bomb showed a benzene conversion of 73.4 weight percent (MAF coal) while that from the other bomb had a 80.9 weight percent (MAF coal) slurry.

The results of Runs 1–3 are summarized in Table V.

TABLE V

Run No.	Inhibitor	Wt. percent inhibitor	Time, hours	Temp., (° F.)	benzene conv. (wt. percent)	Yield, increase
1a	Iodine	0.5	1	875	88.2	8.8
1b			1	875	79.4	
2a	<i>p</i> -Benzoquinone	0.1	1	875	90.6	10.4
2b			1	875	80.2	
3a	<i>p</i> -Benzoquinone	0.05	0.5	875	80.9	7.5
3b			0.5	875	73.4	

At the higher liquefaction temperatures in Runs 1–3, cracking of coal particles is more rapid, but at the same time more of the Tetralin solvent is in the vapor state, which depletes the liquid phase hydrogen donors available to prevent carbon radical repolymerization. In addition, the reaction times for Runs 1–3 were much shorter than in Example 1. Consequently, as seen from Table V, base case conversions are lower than in the base case of Example 1. However, even under these conditions, when the iodine or quinone carbon-radical scavengers were present, liquid yields were very good indeed, especially in view of the lower concentrations of these scavengers used in Runs 1–3 relative to the scavenger concentrations employed in Example 1.

Having now set forth in detailed description of our invention for using quinone and the halogens iodine, bromine and chlorine, and the hydrohalide derivatives thereof, as carbon radical scavengers in the hydrogen-donor solvent liquefaction process, we anticipate the various modifications and variations in the invention will now become apparent to those skilled in the art. Insofar as these changes and modifications are essentially the same way of accomplishing the same result within the spirit and scope of the appended claims, they are within our invention.

We claim:

1. A process for producing coal liquids, which comprises: liquefying a slurry of coal in a hydrogen-donor solvent in the presence of a carbon radical scavenger selected from quinones and the halogens iodine, bromine and chlorine, and the hydrogen halides thereof.

2. A process for producing coal liquids, which comprises: liquefying a slurry of coal in a hydrogen-donor solvent in the presence of a carbon radical scavenger, selected from quinones and the halogens iodine, bromine and chlorine, and the hydrogen halides thereof, present in an amount effective to increase the yield of liquids produced from said coal.

8

3. The process of claim 2 in which said carbon radical scavenger is present in amounts of from about 0.01 to about 5 weight percent based on said slurry.

4. The process of claim 2 in which said quinone is selected from quinone derivatives of a mono- or a polynuclear aromatic compound, or a mixture thereof, present in said coal liquids.

5. The process of claim 2 in which said quinone is selected from *p*-benzoquinone, naphthoquinones, anthraquinones, phenanthrenequinones, and mixtures of two or more thereof.

6. The process of claim 2 in which said quinone is introduced into said liquefaction zone in oxidized coal liquids boiling within the range from about 500° F. to about 1000° F.

7. The process of claim 6 in which said oxidized coal liquids boil from about 700° F. to about 1000° F.

8. A process for liquefying coal, which comprises: passing a slurry of coal in a hydrogen-donor solvent at a solvent-to-coal ratio of from about 0.8:1 to about 2:1 through a liquefaction zone at a temperature of from

about 700° F. to about 950° F. and a pressure of from about 300 p.s.i.g. to about 3000 p.s.i.g. in the presence of from 0.01 to about 5 weight percent, based on the slurry of a carbon radical scavenger selected from quinones and the halogens iodine, bromine and chlorine and the hydrohalide derivatives thereof, said scavenger being present in an amount effective to increase the yield of coal liquids recovered from said zone.

9. The process of claim 8 in which the slurry of coal is contacted with hydrogen in said liquefaction zone at a treat rate of from about 1 to about 6 weight percent (MAF coal basis).

10. A process for liquefying coal, which comprises: passing a coal liquids stream boiling within the range from about 500° F. to about 1000° F. through an oxidation zone under conditions effective to oxidize at least a portion of the constituents in such stream to quinones.

passing the oxidized liquid coal stream and a slurry stream of coal in a hydrogen-donor solvent through a liquefaction zone under predetermined liquefaction conditions, the feed rates of said streams to said liquefaction zone being correlated with the amount of quinones in said oxidized liquid coal stream so as to effect an increased yield of liquid product from said liquefaction zone.

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