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Wright et al.

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[45] **May 20, 1975**

[54] **SOLVENT REFINED COAL PROCESS WITH ZONES OF INCREASING HYDROGEN PRESSURE**

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[73] Assignee: **The United States of America as represented by the Secretary of the Interior,** Washington, D.C.

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[52] **U.S. Cl.** **208/8**

[51] **Int. Cl.** **C10g 1/00**

[58] **Field of Search** 208/8

[56] **References Cited**

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[57] **ABSTRACT**

A solvation process for producing deashed solid and liquid hydrocarbonaceous fuel from coal. Raw coal is slurried with a solvent comprising hydroaromatic compounds in contact with hydrogen in a first zone operating at a low residence time, a relatively high temperature and a relatively low hydrogen pressure to dissolve hydrocarbonaceous fuel from coal minerals by transfer of hydrogen from hydroaromatic solvent compounds to hydrocarbonaceous material in the coal. The solvent is then treated with hydrogen in a second zone at a longer residence time, a relatively low temperature and a relatively high hydrogen pressure to replenish the solvent with hydrogen.

15 Claims, 7 Drawing Figures

FIG. 2

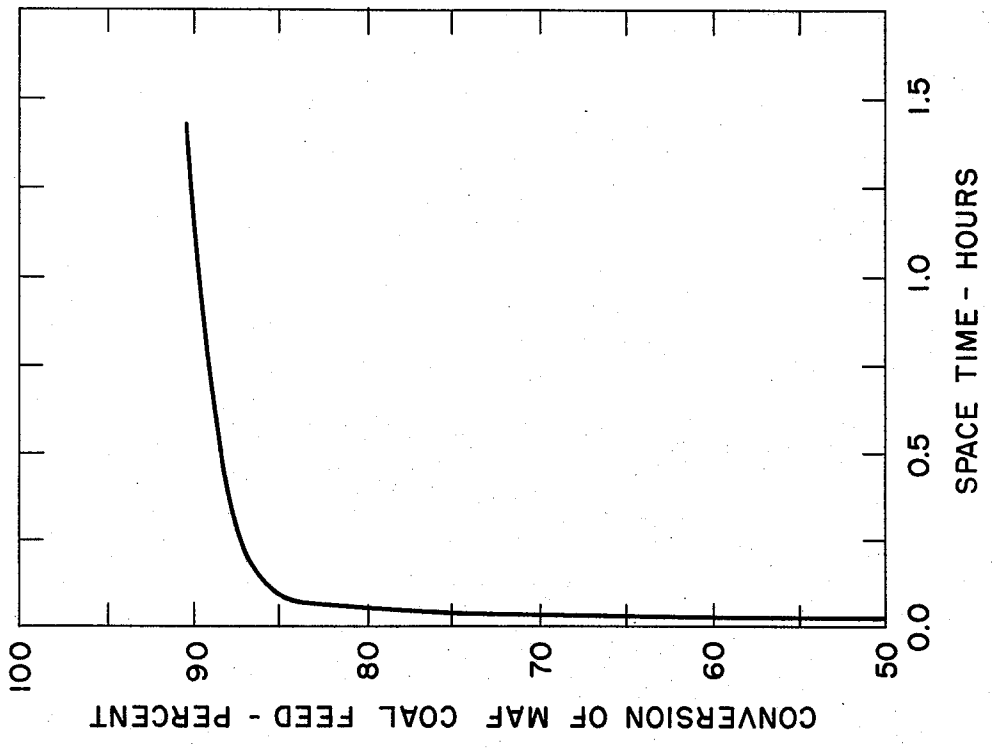

CONVERSION OF MAF COAL FEED - PERCENT
100
90
80
70
60
50
0.0
0.5
1.0
1.5
SPACE TIME - HOURS

FIG. 1

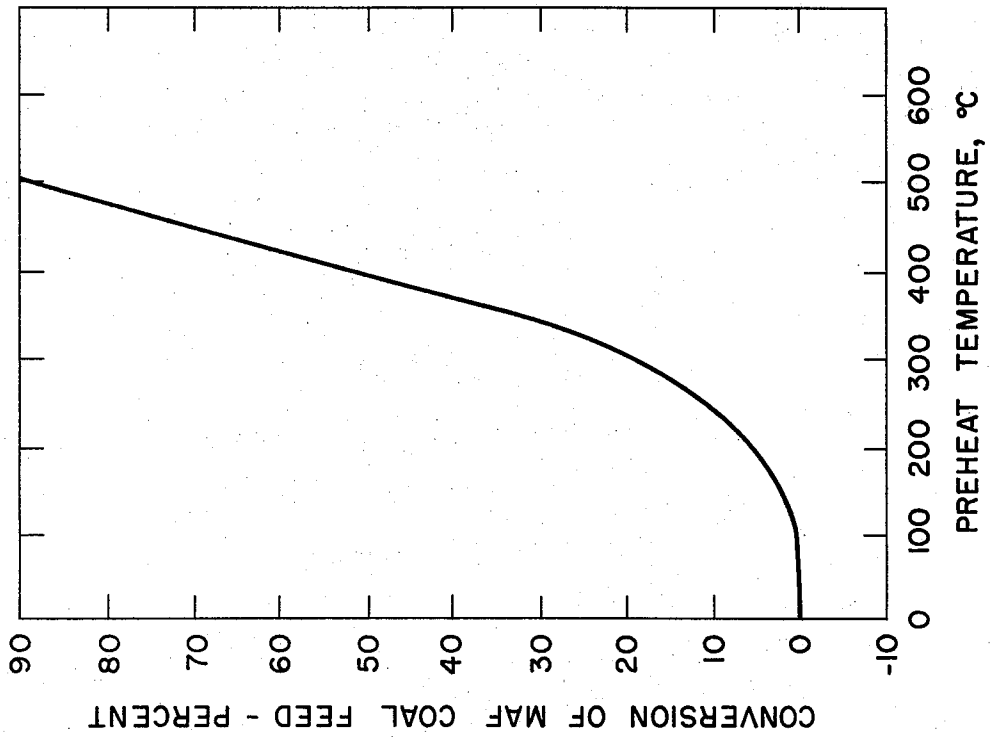

CONVERSION OF MAF COAL FEED - PERCENT
90
80
70
60
50
40
30
20
10
0
-10
0
100
200
300
400
500
600
PREHEAT TEMPERATURE, °C

FIG. 4

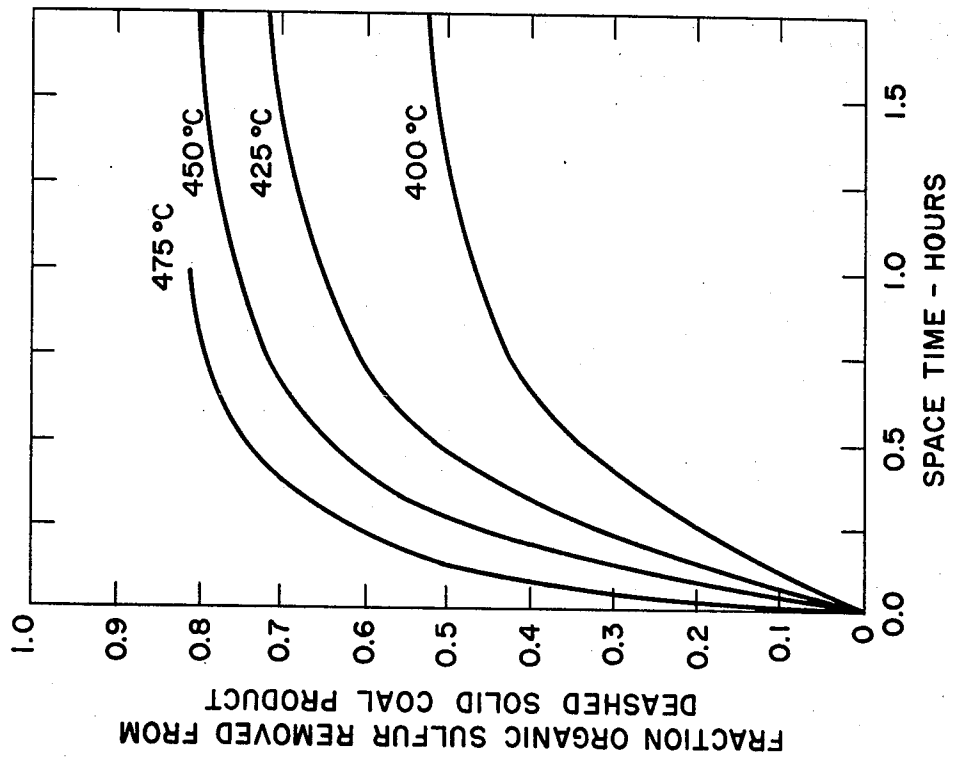

475 °C
450 °C
425 °C
400 °C
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.0
0.5
1.0
1.5
SPACE TIME - HOURS
FRACTION ORGANIC SULFUR REMOVED FROM DEASHED SOLID COAL PRODUCT

FIG. 3

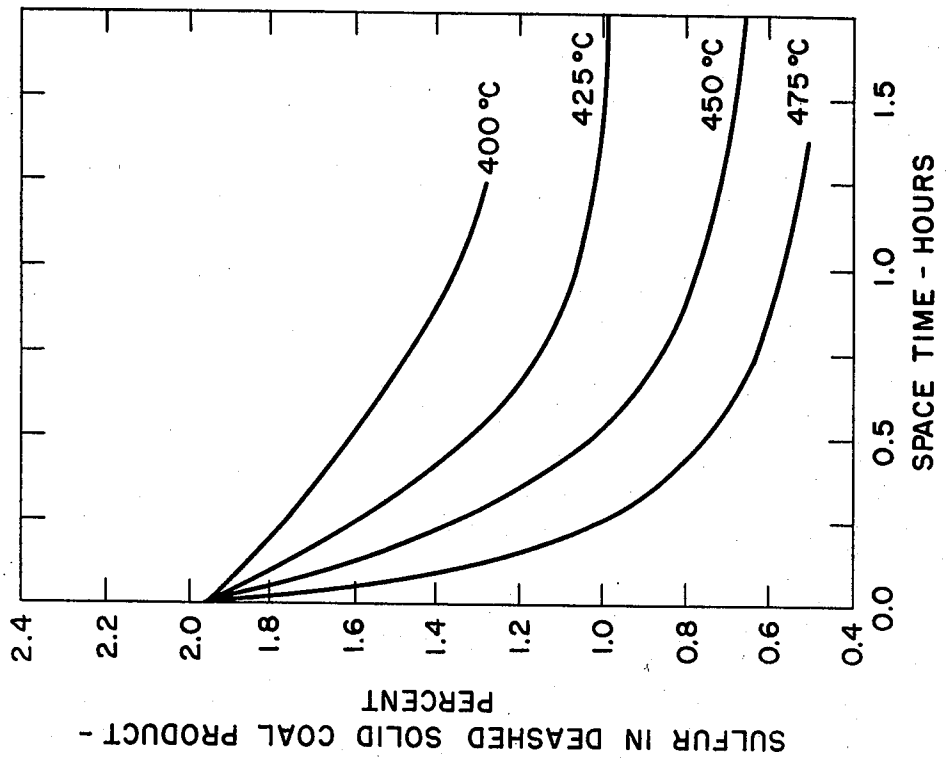

400 °C
425 °C
450 °C
475 °C
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.0
0.5
1.0
1.5
SPACE TIME - HOURS
SULFUR IN DEASHED SOLID COAL PRODUCT - PERCENT

FIG. 6

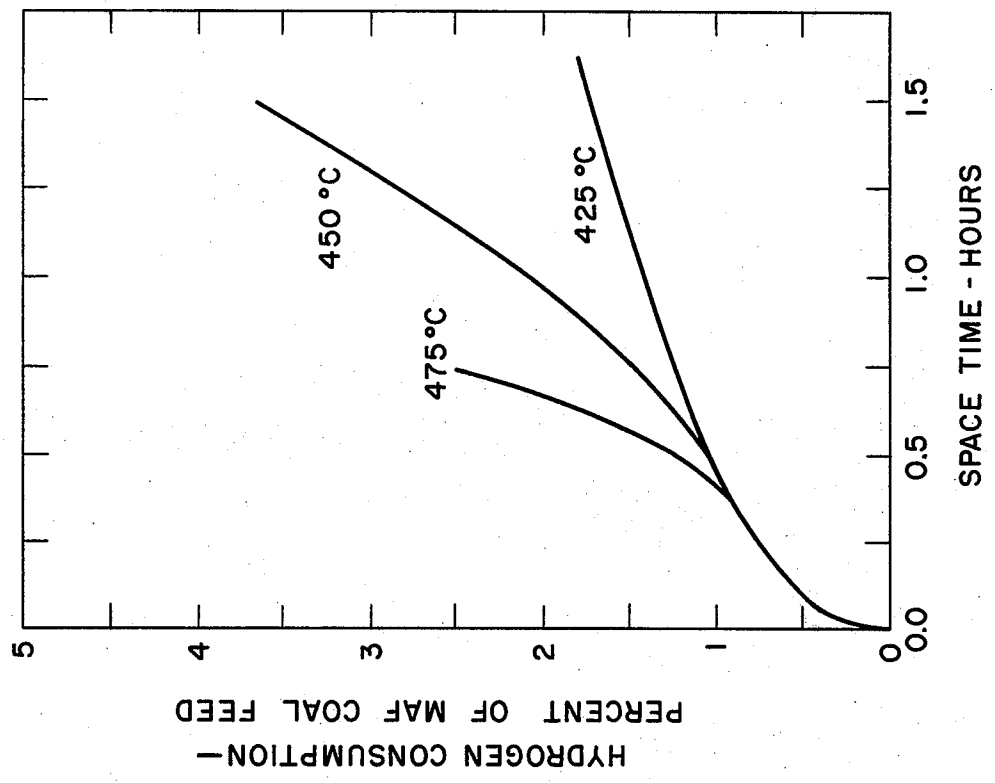

450 °C
425 °C
475°C
0.0
0.5
1.0
1.5
SPACE TIME - HOURS
0
1
2
3
4
5
HYDROGEN CONSUMPTION—
PERCENT OF MAF COAL FEED

FIG. 5

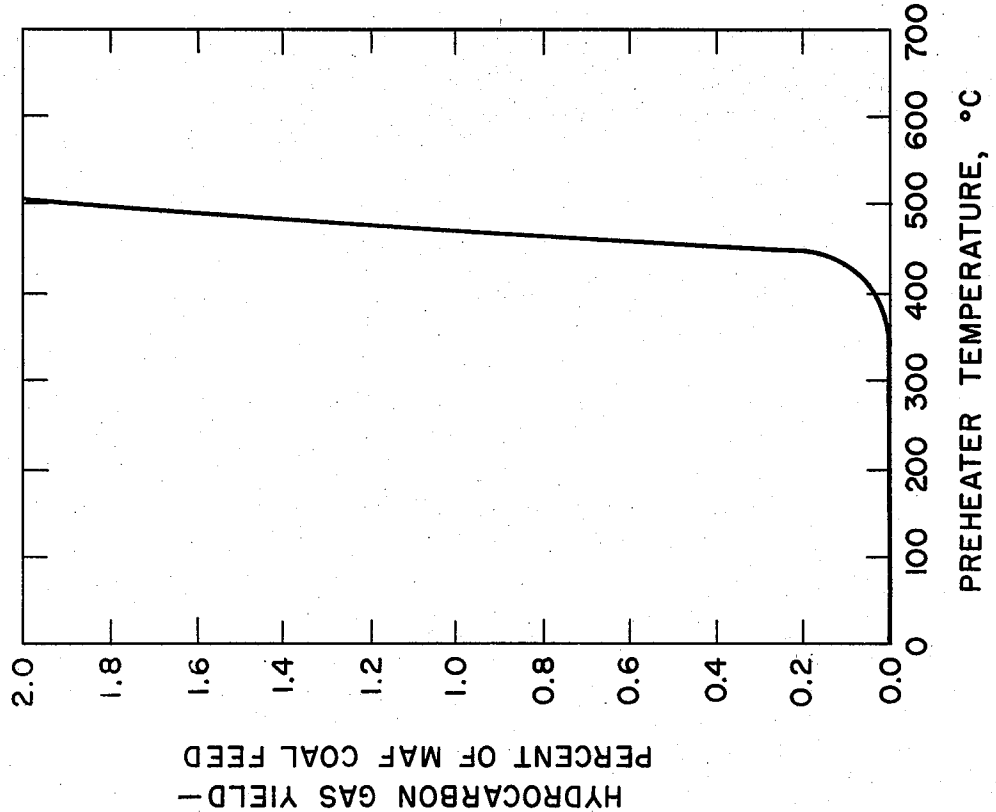
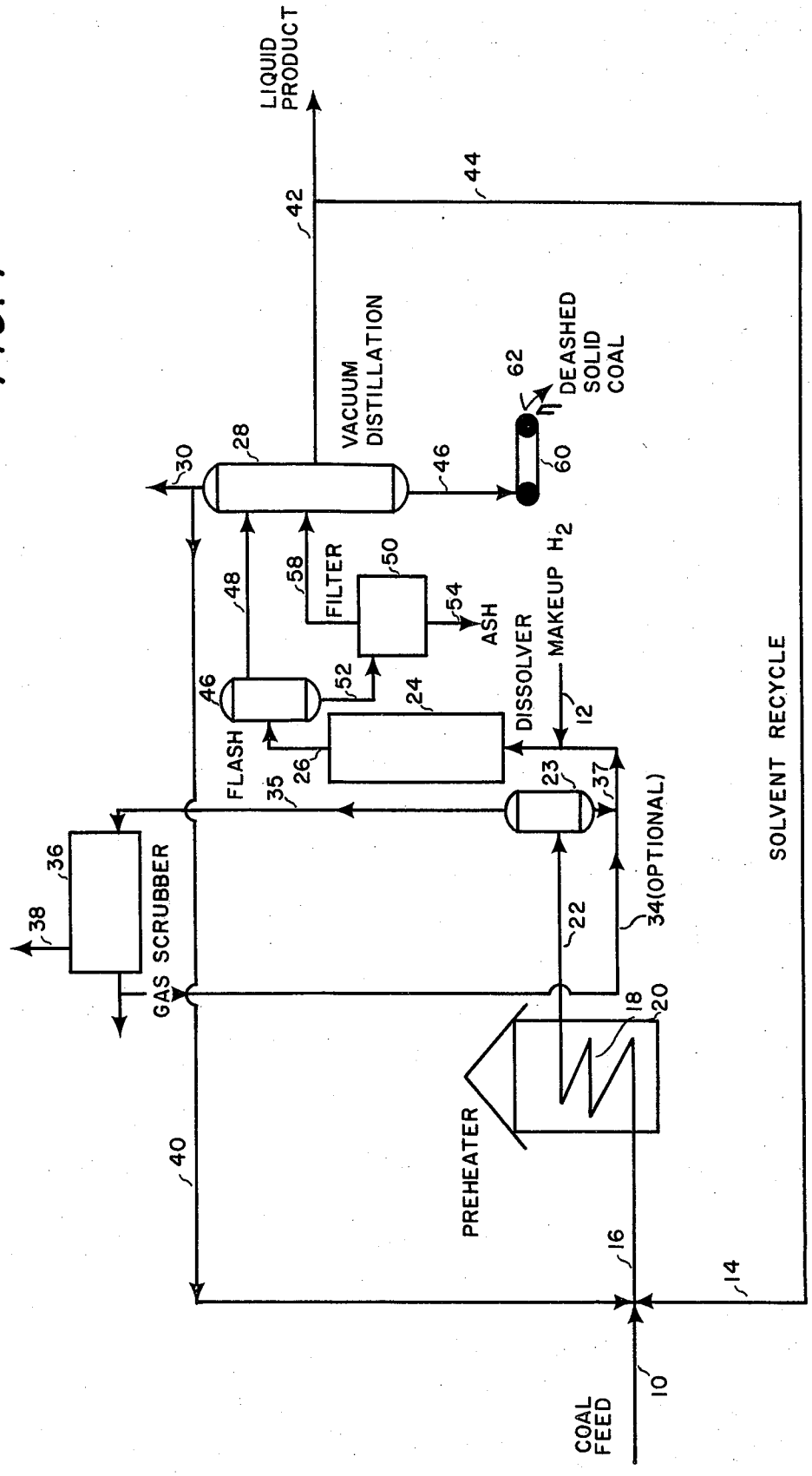

0
100
200
300
400
500
600
700
PREHEATER TEMPERATURE, °C
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
HYDROCARBON GAS YIELD—
PERCENT OF MAF COAL FEED

FIG. 7


LIQUID PRODUCT
42
44
VACUUM DISTILLATION
28
30
46
62
DEASHED SOLID COAL
60
FILTER
58
50
54
ASH
48
MAKEUP H_2
DISSOLVER
24
12
46
52
FLASH
26
35
23
37
SOLVENT RECYCLE
36
38
GAS SCRUBBER
22
34(OPTIONAL)
18
20
PREHEATER
40
16
14
COAL FEED
10

SOLVENT REFINED COAL PROCESS WITH ZONES OF INCREASING HYDROGEN PRESSURE

This invention resulted from work performed under Contract No. 14-01-0001-496 between The Pittsburg and Midway Coal Mining Co., a subsidiary of Gulf Oil Corporation, and the Office of Coal Research of the Department of the Interior, entered into pursuant to the Coal Research Act, 30 U.S.C. 661 to 668.

This invention relates to a non-catalytic liquid solvent dissolving process for producing reduced or low ash hydrocarbonaceous solid fuel and hydrocarbonaceous distillate liquid fuel, from ash-containing raw coal. The process produces deashed solid fuel (dissolved coal) together with as much coal derived liquid as possible, with an increase in liquid fuel product being accompanied by a decrease in solid fuel product. Liquid fuel is the more valuable product but the production of liquid fuel is generally accompanied by excess production of undesired by-product hydrocarbon gases. Although liquid fuel is of greater economic value than deashed solid fuel, hydrocarbon gases are of smaller economic value than either deashed solid fuel or liquid fuel and have a greater hydrogen to carbon ratio than either solid or liquid fuel so that their production is not only wasteful of other fuel product but is also wasteful of hydrogen.

Hydrocarbon gases are produced primarily by hydrocracking, and since their production is undesired in this process no external catalyst is employed, since catalysts generally impart hydrocracking activity in a coal solvation process.

In the process of this invention, the solvent extraction of coal occurs in at least two separate zones of increasing hydrogen pressure. If desired, carbon monoxide can be charged to the process to produce hydrogen in situ by reaction with steam. Steam is present from water in the feed coal or from independently added water. Preferred coal feeds contain hydrogen, such as bituminous and sub-bituminous coals, and lignites.

In accordance with the present invention, a raw coal containing ash is treated in a first zone, referred to as a preheater zone, in which progressive heating in an elongated tubular reactor to a relatively high discharge temperature occurs in the presence of a solvent which extracts carbonaceous fuel from the coal. In the high temperature preheating zone, extracted substantially ash-free carbonaceous fuel also undergoes reactions wherein sulfur, oxygen and some nitrogen are removed. The preheater temperature also induces some hydrocracking so that the gaseous effluent from the preheater contains in addition to hydrogen gas, which is charged to the preheater, hydrogen sulfide, carbon dioxide, carbon monoxide, nitrogen, methane, ethane and other gaseous hydrocarbons. These gases produced in the preheater result in a significant reduction in hydrogen partial pressure in the preheater. However, the dissolving and sulfur, oxygen and nitrogen removal reactions occurring in the preheater are primarily temperature dependent rather than hydrogen partial pressure dependent. The reactions occurring in the preheater do not depend primarily upon hydrogen pressure because the preheater reactions are primarily hydrogen donor reactions wherein hydrogen is released by the partially saturated condensed aromatic rings in the solvent to the carbonaceous material extracted from the coal.

Since the hydrogen donor reactions in the preheater involve transfer of hydrogen from partially saturated condensed aromatic ring compounds in the process solvent during passage through the preheater, the solvent tends to become depleted in hydrogen so that its hydrogen transfer capabilities tend to become exhausted. Thereupon, it becomes necessary to replenish the hydrogen lost from the solvent. In accordance with this invention, the replenishment of hydrogen in the solvent is most advantageously performed in a separate reactor operating under different conditions than prevail in the preheater. The replenishment of hydrogen in the solvent is a solvent hydrogenation or partial saturation reaction wherein solvent aromatic ring compounds are partially saturated by gaseous hydrogen. Elevated hydrogen partial pressure is more critical in the hydrogen acceptance reaction occurring in the dissolver than in the hydrogen donation reaction occurring in the preheater. Because the reaction of the solvent in the dissolver is of a different nature than the reaction of the solvent in the preheater, it also requires different temperature conditions. In accordance with this invention, the dissolver reactions, which involve solvent partial saturation with hydrogen, are advantageously performed at a lower temperature than prevails at the preheater outlet even though they are more advantageously performed at a higher hydrogen partial pressure than prevails in the preheater.

High hydrogen pressure favors an equilibrium in favor of increased hydrogen to carbon ratio in the hydroaromatic solvent, thereby encouraging addition of hydrogen to the solvent. Lower hydrogen pressure favors an equilibrium in favor of reduced hydrogen to carbon ratio in the hydroaromatic solvent, thereby encouraging hydrogen transfer from the solvent to the coal. Therefore, the preheater is operated at a relatively low hydrogen pressure and the dissolver is operated at a relatively high hydrogen pressure, whereby the specialized solvent reactions in each stage are respectively encouraged.

In accordance with the present invention a relatively high hydrogen partial pressure is employed in the dissolver zone wherein it is desired to add hydrogen to the hydrogen donor solvent material in order to increase the hydrogen to carbon ratio in the solvent and to form a hydroaromatic having a high energy for hydrogen transfer in the subsequent pass through the preheater. A relatively low hydrogen partial pressure is employed in the preheater zone wherein it is desired to encourage hydrogen to be transferred from the hydrogen donor solvent and to decrease the hydrogen to carbon ratio in the solvent. The equilibrium ratio of hydrogen to carbon in the hydroaromatic solvent varies with hydrogen pressure. The equilibrium ratio increases at a high hydrogen pressure decreases at a low hydrogen pressure. Therefore, if the hydroaromatic solvent employed in the preheater is prepared at a higher hydrogen pressure, its excess hydrogen content under equilibrium preheater conditions will constitute a high potential capacity for hydrogen donation.

A feature of this invention is that the preheater reaches a temperature which is higher than the dissolver temperature. Since the preheater operates at a higher temperature than the dissolver, preheater reactions are conducive to the production of light gases, such as hydrogen sulfide, carbon dioxide, carbon monoxide and gaseous hydrocarbons. These light gases di-

lute the hydrogen atmosphere in the preheater and reduce the hydrogen partial pressure in the preheater. On the other hand, the dissolver operates at a lower temperature than the preheater so that the tendency to produce these diluent gases in the hydrogen atmosphere of the dissolver is much lower. Only one hydrogen compressor need be employed whereby the hydrogen is available to the dissolver stage at a relatively higher hydrogen partial pressure than prevails in the preheater stage. In this manner, process conditions are established in the combination preheater and dissolver operation so that the preheater and dissolver each are provided with temperature and hydrogen pressure conditions best adapted to perform its respective type of reactions.

Furthermore, the low hydrogen partial pressure in the preheater zone is especially important to inhibit hydrocracking in the combination process. Since the preheater outlet reaches the highest temperature occurring anywhere in the two zones, use of a relatively low hydrogen pressure at the preheater outlet tends to inhibit hydrocracking thereat. It is an important feature of the present invention that the region of highest temperature in the overall process (the preheater outlet) is the region of lowest hydrogen pressure in the overall process. In this manner, hydrocracking is most inhibited by hydrogen pressure control at the most critical temperature region of the process.

FIGS. 1 through 6 illustrate the effects of varying certain parameters in the process of this invention. FIG. 7 presents a schematic diagram of the present process.

The present invention is advantageously performed by passing the hydrogen and coal-solvent slurry through the process countercurrently with respect to each other in regard to the stages, but the flow can be concurrent in each stage. This represents an advantageous mode of insuring that the highest solvation temperatures occur in the presence of the lowest hydrogen partial pressures. Since low hydrogen partial pressures inhibit hydrocracking, the process tends to accomplish the high liquid fuel yields and low sulfur levels obtainable through elevated temperatures while still tending to depress production of hydrocarbon gases and to conserve hydrogen.

As indicated above, the chemical energy of the hydroaromatic solvent to perform hydrogen donor reactions in the present process is dependent upon its hydrogen content, which in turn is dependent upon hydrogen pressure in the dissolver and preheater. At 70 kg/cm^2, the solvent becomes adjusted to a hydrogen content of about 6.1 weight percent. If the solvent hydrogen content is above this level, transfer of hydroaromatic hydrogen to dissolved coal takes place to convert solid fuel product to liquid fuel product. If the solvent hydrogen content is below 6.1 weight percent, the solvent appears to gain hydrogen at a faster rate than the dissolved coal product. Once the hydrogen content of the solvent is roughly adjusted, conversion of dissolved deashed solid (at room temperature) fuel to liquid fuel depends on the catalytic effect of FeS, derived from the coal mineral. Minor deviations from this basic situation are observed in response to temperature and time variables. Higher temperatures tend to lower the hydroaromatic content of the system while rapid feed rates (insufficient residence time) may preclude attainment of equilibrium values. In addition, higher pressures may favor more rapid equilibrium and will tend to increase the hydroaromatic character of the system.

Conversion of solvent aromatics with hydrogen to form hydroaromatics is reversible since hydrogen can be removed from the hydroaromatics by hydrogen transfer. The rate of hydrogen replenishment is affected by the FeS (from the coal mineral) catalyst concentration and the partial pressure of the hydrogen available. Hydrogenation of deashed solid fuel product probably occurs due to both hydrogen donation and direct hydrogenation. Both mechanisms may operate and produce similar contributions to the conversion rate. Ultimately, the final hydrogen content depends on time and temperature. At high temperatures, hydrogen transfer seems to be driven far toward completion, leaving the solvent highly aromatic. The solvent then tends to gain hydrogen rapidly, and this seems to have precedence over further liquefaction of deashed solid fuel product. Generally, the solvent composition then tends to move to an equilibrium which is pressure dependent, although temperature has an effect on the time needed to reach the limiting values. Under process dynamics, deviations from the equilibrium value is the rule, with higher temperatures tending to produce the more aromatic system.

The relative process conditions of the preheater and dissolver are established so that the temperature at the outlet of the elongated preheater is higher than the dissolver temperature. This temperature differential may be imparted by a flashing step between the preheater and the dissolver wherein gases, including light hydrocarbons and hydrogen, are removed from deashed fuel liquid and coal ash followed by addition of fresh and/or purified recycle hydrogen to the stream before it is charged to the dissolver. The temperature adjustment via flashing and hydrogen addition interdependently tends to increase hydrogen partial pressure in the dissolver. The addition of make-up and/or scrubbed recycle hydrogen to the interstage slurry following the flashing step enables the hydrogen to account for a high proportion of the total pressure in the dissolver. The temperature of the liquid slurry charged to the dissolver is sufficiently low to inhibit cracking reactions of the type which produce light gases and reduce the hydrogen partial pressure in the dissolver. The make-up and/or purified recycle hydrogen gas charged to the dissolver can be compressed to the desired hydrogen pressure and thereupon undergo only little reduction in hydrogen partial pressure in the dissolver. This permits the dissolver to experience a hydrogen pressure relatively close to the pressure produced by the compressor. After the hydrogen passes through the dissolver, it is charged without scrubbing to remove contaminants to the preheater wherein it undergoes a pressure drop and become diluted with light gases produced by the reactions occurring at the higher preheater temperature, so that the hydrogen partial pressure in the preheater is lower than the hydrogen partial pressure in the dissolver. In this manner the dissolver experiences the relatively high hydrogen pressure which it requires for hydrogen saturation of the solvent whereas the preheater experiences a lower hydrogen partial pressure since the hydrogen donation reactions occurring in the preheater are encouraged at lower hydrogen partial pressures.

The preheater zone and the dissolver zone experience a high degree of time interdependence as well as

temperature and hydrogen pressure interdependence. The reactions occurring in the preheater must be carefully timed so that they are terminated before the advantageous effect of the preheater is lost. Therefore, the liquid coal slurry must be removed from the preheater at a highly critical time during preheater operation and then subjected to different conditions of temperature and pressure in the dissolver so that the type of reaction occurring in the preheater is terminated and a different type of reaction becomes initiated in the dissolver. The two types of reactions having time-temperature-hydrogen pressure interdependency are now explained more fully in the following process description.

When raw coal is subjected to solvation at a relatively low temperature, the dissolved product comprises in major proportion a high molecular weight fuel which is solid at room temperature. When the mixture of solvent and dissolved coal is subsequently filtered to remove ash and undissolved coal and the filtrate is then subjected to vacuum distillation, this high boiling solid fuel product is recovered as the vacuum bottoms. This vacuum bottoms, referred to herein as either vacuum bottoms or deashed solid fuel product, is cooled to room temperature on a conveyor belt and is scraped from the belt as fragmented deashed hydrocarbonaceous solid fuel.

As the temperature of the solvation process is progressively increased, the vacuum bottoms (deashed solid fuel at room temperature), which is a high molecular weight polymer, is converted to lower molecular weight hydrocarbonaceous liquid fuel which is chemically similar to the process solvent and which has a similar boiling range. The liquid fuel product is in part recycled as process solvent for the subsequent pass and is referred to herein as either liquid fuel product or excess solvent. Production of liquid fuel occurs by depolymerization of solid fuel through various reactions, such as removal therefrom of heteroatoms, including sulfur and oxygen. As a result of the depolymerization reactions, the liquid fuel has a somewhat higher hydrogen to carbon ratio than the solid fuel and therefore exhibits a correspondingly higher heat content upon combustion. It is desirable in the process to convert as much of the vacuum bottoms (solid fuel) product to solvent boiling range (liquid fuel), since liquid fuel is economically more valuable than solid fuel. As the temperature of solvation continues to be increased, an increasing proportion of vacuum bottoms fuel is converted to solvent boiling range fuel until a temperature is reached at which conversion of vacuum bottoms to liquid fuel occurs only at the price of excessive production of relatively hydrogen-rich by-product hydrocarbon gases due to the onset of excessive thermal hydrocracking. The present invention produces 20 or 40 to 80 weight percent of deashed solid fuel on an MAF (moisture and ash free) basis, the remaining product being primarily liquid fuel. It is a feature of the present invention that the amount of thermal hydrocracking is inhibited by a combination of factors whereby the residence time of maximum process temperature is minimized by operating the preheater in a tube with plug flow with progressively increasing temperatures along the tube length and by conjoining the occurrence of maximum process temperature at the preheater tube outlet with the lowest hydrogen partial pressure in the process. In this manner, a segment of the process is isolated so that maximum process temperature is conjoined with minimum process hydrogen partial pressure at a low residence time whereby overall process hydrocracking is inhibited.

It is the purpose of the present invention to avoid thermal hydrocracking as much as possible and at least to the extent of avoiding excessive production of hydrocarbon gases since production of gases diminishes the yield of desired deashed solid fuel and liquid fuel products. This purpose requires performance of the solvation process in two separate stages, each stage employing a different temperature and hydrogen partial pressure. In a preferred embodiment of this invention, less than 6 weight percent of hydrocarbon gases, based on MAF coal feed, is produced. The production limit of hydrocarbon gases establishes the production limit of liquid fuel product and therefore also the production limit of solid fuel product.

A further and very important advantage of the dual stage method of this invention is that a high temperature stage is made possible whereby product sulfur level can be reduced. Relatively high temperatures are required for sulfur removal whereas temperatures below the required level are not as effective for sulfur removal. The high temperatures required for effective sulfur removal also induce hydrocracking but the hydrocracking reaction is more time dependent and by rapid reduction of the high process temperatures reduction of sulfur level is achieved with a minimum of hydrocracking.

The first reactor stage of the present process is a tubular preheater having a relatively short residence time in which a slurry of feed coal and solvent in essentially plug flow is progressively increased in temperature as it flows through the tube. The tubular preheater has a length to diameter ratio of at least 100, generally, and at least 1,000, preferably. A series of different reactions occur within a flowing stream increment as the temperature of the increment increases from a low inlet temperature to a maximum or exit temperature, at which it remains for only a short time and at which the process hydrogen partial pressure is minimized. The second reactor stage employs a relatively longer residence time in a larger vessel maintained at a substantially uniform temperature throughout. An important feature of this invention is that a regulated amount of forced cooling occurs between the stages so that the second stage temperature is lower than the maximum preheater temperature. Cooling can be accomplished at least in part by an interstage flashing step with injection of a relatively cool make-up hydrogen stream following the flashing step so that cooling is conjoined with an increase in hydrogen partial pressure. Although the preheater stage is operated with plug flow without significant backmixing, full solution mixing with a uniform reactor temperature occurs in the dissolver stage.

Data presented below show that dual temperature operation results in high conversion of raw coal to deashed solid fuel and liquid fuel with an enhanced proportion of liquid to solid fuel product while avoiding excessive production of by-product hydrocarbon gases. It is shown below that these results are better accomplished by employing a split temperature process than by employing a process having a uniform temperature in the two stages, even when the uniform temperature is the same as either temperature of a split temperature operation.

The coal solvent for the present process comprises liquid hydroaromatic compounds. The coal is slurried with the solvent for charging to the first or preheater stage. In the first stage, hydrogen transfer from the solvent hydroaromatic compounds to coal hydrocarbonaceous material occurs resulting in swelling of the coal and in breaking away of hydrocarbon polymers from coal minerals. The range of maximum temperatures suitable in the first (preheater) stage is generally 400° to 525°C., or preferably 425° to 500°C. If there are inadequate facilities to handle hydrocarbon gaseous by-products, the upper temperature limit should be 470°C., or below, since production of gaseous products is minimized at low temperatures. The residence time in the preheater stage is generally 0.01 to 0.25 hours, or preferably 0.01 to 0.15 hours.

In the second (dissolver) stage of the process of this invention, the solvent compounds, which have been depleted of hydrogen and converted to their precursor aromatics by hydrogen donation to the coal in the first stage, are reacted wtih gaseous hydrogen and reconverted to hydroaromatics for recycle to the first stage. The temperature in the dissolver stage is 350° to 475°C., generally, and 400° to 450°C., preferably. The residence time in the dissolver stage is 0.1 to 3.0 hours, generally, and 0.15 to 1.0 hours, preferably. The temperature in the dissolver stage is lower than the maximum temperature in the preheater stage. Whatever the total pressure in the dissolver stage the hydrogen partial pressure in the dissolver is higher than the hydrogen partial pressure in the preheater. Any suitable forced cooling step can be employed to reduce stream temperature between the preheater and the dissolver. The preferred method is to employ an interstage flash and to inject purified, cool hydrogen to the flash after the flashing step. Also, a heat exchanger can be employed. It is important for the residence time in the preheater to be lower than the residence time in the dissolver.

The liquid space velocity for the process (volume of slurry per hour per volume of reactor) ranges from 0.2 to 8.0, generally, and 0.5 to 3.0, preferably. The ratio of hydrogen to slurry ranges from 200 to 10,000 standard cubic feet per barrel, generally, and 500 to 5,000 standard cubic feet per barrel, preferably, (3.6 to 180, generally, and 9 to 90, preferably SCM/100L). The weight ratio of recycled solvent product to coal in the feed slurry ranges from 0.5:1 to 5:1, generally, and from 1.0:1 to 2.5:1, preferably.

The reactions in both stages occur in contact with gaseous hydrogen and in both stages heteroatom sulfur and oxygen are removed from solvated deashed coal polymer, resulting in depolymerization and conversion of dissolved coal polymers to desulfurized and deoxygenated free radicals of reduced molecular weight. These free radicals have a tendency to repolymerize at the high temperatures reached in the preheater stage, but at the reduced temperature of the dissolver stage of this invention these free radicals tend to be stabilized against repolymerization by accepting hydrogen at the free radical site. This acceptance of hydrogen is encouraged by the relatively high hydrogen partial pressure in the dissolver. The reaction of hydrogen at the free radical site occurs more readily at the relatively low dissolver temperature than at the higher preheater exit temperature. Therefore, there is a significant advantage in conjoining reduced process temperatures and increased hydrogen partial pressures in the dissolver stage.

The solvent used at process start-up is advantageously derived from coal. Its composition will vary, depending on the properties of the coal from which it is derived. In general, the solvent is a highly aromatic liquid obtained from previous processing of fuel, and generally boils within the range of about 150° to 450°C. Other generalized characteristics include a density of about 1.1 and a carbon to hydrogen mole ratio in the range from about 1.0 to 0.9 to about 1.0 to 0.3. Any organic solvent for coal can be used as the start-up solvent in the process. A solvent found particularly useful as a start-up solvent is anthracene oil or creosote oil having a boiling range of about 220° to 400°C. However, the start-up solvent is only a temporary process component since during the process dissolved fractions of the raw coal constitute additional solvent which, when added to start-up solvent, provides a total amount of solvent exceeding the amount of start-up solvent. Thus, the original solvent gradually loses its identity and approaches the constitution of the solvent formed by solution and depolymerization of the coal in the process. Therefore, in each pass of the process after start-up, the solvent can be considered to be a portion of the liquid product produced in previous extraction of the raw coal.

The residence time for the dissolving step in the preheater stage is critical in the process of this invention. Although the duration of the solvation process can vary for each particular coal treated, viscosity changes as the slurry flows along the length of the preheater tube provide a parameter to define slurry residence time in the preheater stage. The viscosity of an increment of feed solution flowing through the preheater initially increases with increasing increment time in the preheater, followed by a decrease in viscosity as the solubilizing of the slurry is continued. The viscosity would rise again at the preheater temperature, but preheater residence time is terminated before a second relatively large increase in viscosity is permitted to occur. An advantageous means for defining proper time for completion of the preheater step is use of the "Relative Viscosity" of the solution formed in the preheater, which is the ratio of the viscosity of the solution formed to the viscosity of the solvent, as fed to the process, both viscosities being measured at 99°C. Accordingly, the term Relative Viscosity as used herein is defined as the viscosity at 99°C., of an increment of solution, divided by the viscosity of the solvent alone fed to the system measured at 99°C., i.e.

$$\text{Relative Viscosity} = \frac{\text{Viscosity of Solution at 99°C}}{\text{Viscosity of Solvent at 99°C.}}$$

The Relative Viscosity can be employed as an indication of the residence time for the solution in the preheater. As the solubilizing of an increment of slurry proceeds during flow through the preheater, the Relative Viscosity of the solution first rises above a value of 20 to a point at which the solution is extremely viscous and in a gel-like condition. In fact, if low solvent to coal ratios are used, for example, 0.5:1, the slurry would set up into a gel. After reaching the maximum Relative Viscosity, well above the value of 20, the Relative Viscosity of the increment begins to decrease to a minimum, after which it has a tendency to again rise to

higher values. The solubilization proceeds until the decrease in Relative Viscosity (following the initial rise in Relative Viscosity) falls to a value at least below 10, whereupon the preheater residence time is terminated and the solution is cooled and passed to the dissolver stage which is maintained at a lower temperature to prevent the Relative Viscosity from again rising above 10. Normally, the decrease in Relative Viscosity will be allowed to proceed to a value less than 5 and preferably to the range of 1.5 to 2. The conditions in the preheater are such that the Relative Viscosity will again increase to a value above 10, absent abrupt termination of preheater exit conditions, such as a forced lowering of temperature.

When a slug of hydroaromatic solvent and coal first experience heating in the preheater, the first reaction product is a gel which is formed in the temperature range 200° to 300°C. Formation of the gel accounts for the first increase in Relative Viscosity. The gel forms due to bonding of the hydroaromatic compounds of the solvent with the hydrocarbonaceous material in the coal and is evidenced by a swelling of the coal. The bonding is probably a sharing of the solvent hydroaromatic hydrogen atoms between the solvent and the coal as an early stage in transfer of hydrogen from the solvent to the coal. The bonding is so tight that in the gel stage the solvent cannot be removed from the coal by distillation. Further heating of a slug in the preheater to 350°C. causes the gel to decompose, evidencing completion of hydrogen transfer, producing a deashed solid fuel, liquid fuel and gaseous products and causing a decrease in Relative Viscosity.

A decrease of Relative Viscosity in the preheater is also caused by depolymerization of solvated coal polymers to produce free radicals therefrom. The depolymerization is caused by removal of sulfur and oxygen heteroatoms from hydrocarbonaceous coal polymers and by rupture of carbon—carbon bonds by hydrocracking to convert deashed solid fuel to liquid fuel and gases. The depolymerization is accompanied by the evolution of hydrogen sulfide, water, carbon dioxide, methane, propane, butane, and other hydrocarbons.

At the high temperatures of the preheater outlet zone, repolymerization of free radicals is a reaction which is favored over hydrogenation of free radical sites and accounts for the final tendency towards increase in Relative Viscosity in the preheater to a value above 10. This second increase in Relative Viscosity is avoided in accordance with the present invention. The elimination of sulfur and oxygen from the solvated deashed solid fuel is probably caused by stripping out of these materials by thermal rupture of bonds leaving free radical molecular fragments which have a tendency towards subsequent repolymerization at elevated temperature conditions. The drop in stream temperature by forced cooling following the preheater step tends to inhibit polymer formation. The observed low level of sulfur in the liquid fuel product, which for one coal feed is about 0.3 weight percent, as compared to 0.7 weight percent in the vacuum bottoms (solid fuel) product, indicates that sulfur is being stripped out of the solid fuel product in the formation of low sulfur smaller molecular fragments as free radicals.

As indicated above, maximum or exit preheater temperatures should be in the range of 400° to 525°C. The residence time in the preheater for a feed increment to achieve this maximum temperature is about 0.01 to 0.25 hours. At this combination of temperature and residence time, and with a lower hydrogen partial pressure in the preheater than in the dissolver, coke formation is not a problem unless flow is stopped, that is, unless the residence time is increased beyond the stated duration. The hydrocarbon gas yield under these conditions is generally less than about 6 weight percent while excess solvent (liquid fuel) yield is above 10 or 15 weight percent, based on MAF coal feed, while the solid fuel product is above 20 weight percent. High production of gases is to be avoided because such production involves high consumption of hydrogen and because special facilities are required. However, a gaseous yield above 6 weight percent can be tolerated if facilities to store and/or transport the gas are available.

The relatively low sulfur content in the vacuum bottoms (deashed solid fuel) product of the present process is an indication that the reaction proceeds to a high degree of completion. It is also an indication that the vacuum bottoms product has been chemically released from the ash so that it can be filtered therefrom.

The hydrogen pressure in the present process is 35 to 300 kg/cm², generally, and 50 to 200 kg/cm², preferably. Whatever hydrogen pressure is employed within these ranges, the hydrogen is circulated through the stages so that the hydrogen pressure is higher in the dissolver stage than in the preheater stage.

In the dissolver stage of the present process, aromatic compounds which have surrendered hydrogen in the preheater under a relatively low hydrogen pressure are reacted with hydrogen under a relatively higher hydrogen pressure to again form hydroaromatic compounds. Hydroaromatic compounds are partially (not completely) saturated aromatics. The chemical potential (temperature and hydrogen pressure levels) in the dissolver is too low for full saturation of aromatics to be a significant reaction. This is important because while hydroaromatics are capable of hydrogen transfer, saturated aromatics are not. Most of the saturates observed in the dissolver tend to be light products derived from ring opening of liquid product or solvent, or derived from aliphatic side chain removal. Solid fuel product aromatic species tend to remain aromatic or hydroaromatic.

This invention is based upon the use of the effect of time in conjunction with the effects of temperature and hydrogen pressure in the preheater stage. The desired temperature effect in the preheater stage is substantially a short time effect while the desired temperature effect in the dissolver requires a relatively longer residence time. The desired low preheater residence times are accomplished by utilizing an elongated tubular reactor having a high length to diameter ratio of at least 100, generally, and at least 1,000, preferably, so that rapidly upon reaching the desired maximum preheater temperature the preheater stream is discharged and the elevated temperature is terminated by forced cooling. It is important that the highest preheater temperature is accompanied by the lowest process hydrogen pressure to inhibit hydrocracking.

Free radicals formed in the preheater by coal solvation and heteroatom removal from solvated coal tend to polymerize at the elevated temperature at the preheater exit to produce high molecular weight polymers, as evidenced by the fact that the viscosity of the preheater solution tends to rise at the preheater outlet causing the Relative Viscosity to tend to increase again

to a value greater than 10. It is important to the present process that the stream be removed from the preheater before the Relative Viscosity again increases to a value above 10. Therefore, the temperature is dropped by flashing and/or hydrogen injection to a level which is sufficiently low to inhibit repolymerization. In the dissolver the temperature is maintained at a sufficiently low level that a much longer residence time is permissible without danger of incurring repolymerization. Make-up and/or scrubbed and newly compressed recycle hydrogen is charged directly to the dissolver slurry and reacts with the hydrogen depleted aromatic solvent at a relatively higher hydrogen partial pressure as compared to the hydrogen partial pressure in the preheater to replenish the hydrogen removed from the aromatic solvent in the preheater. This replenishment of aromatics with hydrogen requires the extended residence times of the dissolver.

It is seen that the time at which reactions in the preheater are terminated is established so that the termination occurs when a viscosity increase is incipient. This requires that the maximum temperature reached in the preheater near the outlet thereof is not so high that extensive hydrocracking occurs. If extensive hydrocracking were to occur at the preheater outlet, this would itself defeat the onset of viscosity increase because viscosity increase is evidence of increasing molecular weight whereas hydrocracing causes a decrease in molecular weight. Therefore, the preheater operation is terminated when the temperature is only sufficiently high to induce repolymerization and molecular weight increase but not so high as to permit extensive hydrocracking and molecular weight decrease. Because the preheater residence time is restricted in this manner, a considerable proportion of the carbonaceous fuel recovered from th coal is a solid at room temperature and is produced without excessive hydrogen consumption. Extensive hydrocracking would consume hydrogen and produce a higher hydrogen content, lower molecular weight non-solid fuel product. The process of the present invention produces a deashed solid coal without excessive hydrogen requirements and therefore at low hydrogen cost.

It is a feature of the present invention that the differentials in temperature and in hydrogen pressure between the preheater and the dissolver cooperate to inhibit hydrocracking and thereby reduce hydrogen consumption to produce a substantial quantity of solid, low hydrogen fuel without producing an excessive quantity of liquid fuel of higher hydrogen content which would cause the process to be more costly to operate. The lack of extensive hydrocracking is evidenced by the fact that the viscosity tends to increase at the time the stream leaves the preheater. If extensive hydrocracking were occurring the viscosity would be decreasing rather than increasing due to cracking at the high temperature at the preheater outlet.

The data in Table 1 show that there is an adverse effect in employing excessively high preheater temperatures.

TABLE 1

TEST NUMBER	1	2	3	4	5
H_2 Pressure, kg/cm²	70	70	70	70	70
Max. Preheater Temp., °C.	450	500	450	450	475
Dissolver Temp., °C.	450	450	425	425	425
1/LHSV: Hr.	0.52	0.98	1.79	1.89	1.79
GHSV	304	239	342	342	342
Solvent/MAF Coal/H_2O (wt)	2.50/1/0.08	2.49/1/0.06	2.49/1/0.05	2.49/1/.05	2.49/1/00
% Ash in Feed Slurry	5.0	5.0	5.285	7.42	10.65
% Coal Derived Feed	33.3	33.3	34.8	48.7	69.9
YIELDS ON MAF COAL BASIS — %					
CO	0.23	0.42	0.51	0.27	0.28
CO_2	1.12	1.20	0.64	0.68	0.28
H_2S	2.32	2.12	2.04	1.62	1.95
Hydrocarbon Gas	5.28	8.89	5.73	5.80	7.11
Gas Not Identified	—	—	—	—	12.87
H_2O	3.60	4.10	3.82	1.22	1.81
Excess Solvent	5.36	15.10	31.98	62.08	49.37
Vacuum Bottoms	68.12	56.81	48.66	30.36	21.06
Insol. Organic Matter	14.91	13.83	11.59	4.99	9.07
TOTAL	100.94	102.47	104.97	107.92	103.20
DATA					
Recovery, weight %	97.94	96.59	95.91	92.63	93.35
MAF Conversion, weight %	85.09	86.17	88.41	95.01	90.93
COMPOSITION OF LIQUID AND VACUUM BOTTOM FUEL PRODUCT					
Carbon, weight %	89.68	—	89.40	89.72	90.65
Hydrogen, weight %	5.94	—	5.93	6.20	6.54
Nitrogen, weight %	0.979	—	1.06	1.15	1.31
Sulfur, weight %	0.46	—	0.410	0.420	0.438
Oxygen, weight %	4.13	—	5.00	2.51	1.062
VACUUM BOTTOMS FUEL PRODUCT COMPOSITION					
Carbon, weight %	87.32	89.03	88.54	88.71	91.12
Hydrogen, weight %	5.11	5.12	4.74	5.35	5.10
Nitrogen, weight %	1.91	2.02	2.22	2.10	2.22
Sulfur, weight %	0.944	0.719	0.676	0.606	0.488
Oxygen, weight %	4.58	3.04	3.619	3.156	1.00
Ash, weight %	0.133	0.067	0.205	0.078	0.075

As shown in Table 1, an increase in maximum preheater temperature from 450° to 475° or 500°C., results in an increased yield of hydrocarbon gases to a level about 6 weight percent based on MAF coal feed. A 6 weight percent hydrocarbon gas yield on a MAF basis is a suitable upper limit for gas production unless gas handling facilities are available. Not only are hydrocarbon gases of considerably lower economic value than liquid and deashed solid fuel product, but they contain a considerably higher ratio of hydrogen to carbon than either liquid or deashed solid fuel product. Therefore, excessive production of hydrocarbon gases not only signifies a depressed yield of liquid and solid fuel product but also constitutes an unnecessary consumption of valuable process hydrogen due to hydrocracking of higher molecular weight fuel to produce the by-product hydrocarbon gases. Table 1 shows that preheater temperatures of 475° and 500°C. both result in a hydrocarbon gas yield above 6 weight percent, while a 450°C. preheater temperature results in a hydrocarbon gas yield below 6 weight percent.

The data of Table 1 show that by far the best results are obtained when the maximum temperature in the preheater is higher than the temperature in the dissolver, and furthermore yield of hydrocarbon gases are low providing that the maximum preheater temperature is below 475°C. (i.e. 450°C.). Table 1 shows that the use of a preheater temperature of 450°C. and a dissolver temperature of 425°C., rather than a temperature of 450°C. in both stages, results in an increase in the ratio of excess solvent (liquid fuel product) yield to vacuum bottoms (solid fuel product) yield, an increase in conversion of MAF coal, and a reduction in the sulfur content of the excess solvent plus vacuum bottoms product and of the vacuum bottoms product itself. These data clearly show the considerable advantages realized by employing a higher temperature at the preheater exit than in the dissolver, as compared to employing a uniform temperature at the preheater exit and in the dissolver, even though the split temperature results in an overall lower average temperature in the process.

The data of Table 1 show that when employing a maximum preheater temperature of 475°C. and a lower dissolver temperature, the ratio of solvent to vacuum bottoms yield, the percent MAF conversion, the total liquid and vacuum bottoms sulfur content and the vacuum bottoms sulfur content all improved when compared to a test employing a uniform maximum preheater temperature and dissolver temperature, but the improvement is achieved by increasing hydrocarbon gas yield above 6 weight percent. If hydrocarbon has yields above 6 weight percent are not desired the preheater temperature should not extend up to 475°C., and preferably should be lower than 460° or 470°C. The temperature of the preheater effluent should be quenched at least about 25° or 50 ° or 100°C., or more, before entering the dissolver. In some cases a smaller extent of cooling, such as at least 10°, 15° or 20°C. can be effective.

Test 4 of Table 1 shows an especially advantageous split temperature test of the present invention because the liquid product yield (excess solvent) is greater than the vacuum bottoms yield (solid deashed fuel product), while the yield of hydrocarbon gases is low.

Higher temperatures can be advantageously employed in the preheater than in the dissolver only in conjunction with a lower residence time in the preheater than in the dissolver. Most of the residence time in the preheater is employed in heating the coal-solvent slurry mixture to the maximum preheater temperature, which is the exit preheater temperature. Preheater reactions are rapid and tend to occur at the required maximum temperature with a low residence time. On the other hand, the reactions which occur in the dissolver are slower reactions. Therefore, the dissolver not only operates at a lower temperature than the maximum preheater temperature but also at a longer residence time. Although the preheater substantially avoids backmixing, considerable backmixing occurs in the dissolver which contributes to a uniform temperature throughout the dissolver.

In the dissolver, the reactions occurring require a temperature lower than the maximum preheater temperature. Rehydrogenation of the aromatics in the solvent to replenish hydrogen lost from the solvent by hydrogen donation reactions in the preheater requires a longer residence time than is required in the preheater, but procedes at a temperature lower than the preheater temperature. After the solvent is hydrogenated in the dissolver to reconvert aromatics to hydroaromatics, it is in condition to be recycled to the next preheater pass for hydrogen donation reactions. A coincident reaction which occurs in the dissolver in addition to formation of hydroaromatics is the removal of additional sulfur from the extracted coal. The relatively higher preheater temperatures are more effective for sulfur removal than the lower dissolver temperatures. However, some of the sulfur cannot be removed at the low residence time of the preheater, but requires an extended residence time. Therefore, additional sulfur in the coal product is removed during the extended residence time utilized in the dissolver. A third and highly important reaction occurring in the dissolver is the addition of hydrogen to free radicals formed in both the preheater and the dissolver to arrest polymerization of molecular fragments to high molecular weight material.

Table 2 shows the results of preheater tests which were all conducted at 450°C. Certain of the tests were conducted at a very low preheater residence time of 0.035 hours and other tests were performed at somewhat longer preheater residence times.

TABLE 2

TEST NUMBER	1	2	3	4	5
H_2 Pressure, kg/cm²	70	70	70	70	70
Max. Preheater Temp., °C.	450	450	450	450	450
LHSV	28.36	28.35	28.35	15.23	7.74
GHSV	3035	2964	2953	3012	3083
1/LHSV: Hr.	0.035	0.035	0.035	0.066	0.129
YIELDS ON MAF COAL BASIS — %					
CO	0.03	0.03	0.07	0.06	0.25
CO_2	0.35	0.35	0.35	0.45	0.51

TABLE 2 – Continued

TEST NUMBER	1	2	3	4	5
H_2S	0.94	0.97	1.73	1.49	2.66
Hydrocarbon Gas	0.31	0.31	0.21	0.65	0.76
H_2O	0.66	–1.42	1.11	0.91	–0.12
Excess Solvent	–38.47	–59.30	–39.61	7.84	11.80
Vacuum Bottoms	65.57	136.21	105.31	75.78	69.93
Insoluble Organic Matter	71.06	23.20	31.34	13.21	15.23
TOTAL	100.45	100.35	100.55	100.39	101.02
DATA					
Recovery, weight %	94.14	95.46	96.80	90.68	95.94
MAF Conversion, weight %	28.94	76.80	68.66	86.79	84.77
VACUUM BOTTOMS FUEL PRODUCT PROPERTIES					
Carbon, weight %	—	—	—	—	84.00
Hydrogen, weight %	—	—	—	—	5.71
Nitrogen, weight %	—	—	—	—	1.93
Sulfur, weight %	—	—	—	—	1.38
Oxygen, weight %	—	—	—	—	6.59
Ash, weight %	—	—	—	—	0.39

As shown in Table 2, at the lowest residence time tests there is a net loss of liquid solvent (due to binding of the solvent in a gel). Also the percent conversion of MAF coal is low in the low residence time tests. However, at the higher residence times indicated in Table 2 there is a net production of solvent and the percent conversion of MAF coal is considerably higher. Therefore, it is apparent that while excessive preheater residence time is detrimental in that repolymerization will occur (as evidenced by a second increase in Relative Viscosity to a level above 10), a deficiency in residence time in the preheater at a desired preheater temperature is also undesirable in that the process cannot sustain its solvent needs and in that there is inadequate conversion of coal. It is necessary to an economic process that solvent be supplied from an external source only at process start-up, and that once the process achieves equilibrium it must satisfy its own solvent requirements and not depend upon an external solvent supply.

The data in Table 3 illustrate the interchangeability of time and temperature in preheater operation.

TABLE 3

TEST NUMBER	1	2	3	4	5	6
H_2 Pressure, kg/cm²	70	70	70	70	70	70
Max. Preheater Temp., °C.	475	475	475	500	500	450
LHSV	27.57	13.65	7.81	28.36	7.68	7.74
GHSV	3102	3126	3095	2988	3066	3083
1/LHSV: Hr.	0.036	0.073	0.128	0.035	0.130	0.129
YIELDS ON MAF COAL BASIS — %						
CO	0.14	0.36	0.25	0.17	0.13	0.25
CO_2	0.46	0.58	0.63	0.66	0.77	0.51
H_2S	1.57	2.59	2.01	1.77	2.94	2.66
Hydrocarbon Gas Product	0.62	1.29	3.27	1.85	5.11	0.76
H_2O	–2.43	0.29	0.63	–1.50	0.64	–0.12
Excess Solvent (Liquid Fuel Product)	–11.13	13.09	17.11	13.43	25.45	11.80
Vacuum Bottoms (Solid Fuel Product)	101.97	69.57	63.15	71.17	52.56	69.93
Insoluble Organic Matter	9.09	13.38	14.21	12.83	13.17	15.23
TOTAL	100.29	101.15	101.26	100.38	100.77	101.02
DATA						
Recovery, weight %	99.85	98.30	96.75	98.38	96.79	95.94
MAF Conversion, weight %	90.91	86.62	85.79	87.17	86.83	84.77
VACUUM BOTTOMS (SOLID FUEL) PROPERTIES						
Carbon, weight %	—	84.62	84.87	86.67	88.30	84.00
Hydrogen, weight %	—	5.56	5.42	5.33	4.96	5.71
Nitrogen, weight %	—	1.90	2.04	1.78	2.10	1.93
Sulfur, weight %	—	1.34	1.29	1.21	0.80	1.38
Oxygen, weight %	—	6.23	5.42	4.90	4.19	6.59
Ash, weight %	—	0.35	0.96	0.11	0.15	0.39

Table 3 shows a test at 475°C. employing the very low preheater residence time of 0.036 hour in which there is a net loss of solvent in the process. The loss is probably caused by the solvent being bonded in a gel with the coal from which the solvent has insufficient time to become disengaged, and from which the solvent cannot be separated by distillation. However, Table 3 shows that at 475°C. there is a net production of solvent in the process when the preheater residence time is increased. Table 3 further shows that if the temperature is increased to 500°C. the residence time can be reduced again while obtaining a high production of solvent in the process.

Table 4 shows tests performed at a relatively mild preheater temperature of 450°C. As shown in Table 4, even at the moderate preheater temperature of 450°C., lengthy preheater residence times result in hydrocar-

bon gas yields above 6 weight percent. Table 4 shows that as preheater residence times increase from about 0.5 to about 1.3 hours, at a constant preheater temperature of 450°C. the yield of vacuum bottoms (solid fuel) product gradually decreases while the yield of solvent (liquid fuel) product gradually increases, together with a disadvantageous increase in hydrocarbon gas yield. Although not shown by the data, the hydrogen content of the solvent produced at a low residence time is low as compared to solvent produced at a higher residence time at a given temperature, so that solvent produced at a low residence time tends to be of low quality for hydrogen donation in the preheater stage. These data illustrating the effect of preheater residence time indicate that with increasing preheater residence time at a preheater temperature of 450°C., there is a continous conversion of vacuum bottoms (solid fuel) product to solvent (liquid fuel) product, accompanied by a continuous conversion of product to hydrocarbon gases.

The data in Table 3 show that a high maximum preheater temperatures of 475° and 500°C. the effect of residence time tends to be greater than at lower preheater temperatures. Table 3 shows that at 475°C. a very low residence time of 0.036 hours resulted in highly incomplete conversion and a loss of solvent in the process. As the residence time increased at 475°C., conversion increased as indicated by a net production of solvent in the process together with a decrease in vacuum bottoms (solid fuel) yield. Table 3 shows that at 500 °C. with a 0.035 hour residence time, the increase in temperature tends to compensate for the low residence time so that there is a net production of solvent in the process, and the yield of solvent is increased at 500°C. (accompanied by a decrease in vacuum bottoms yield) by increasing the residence time to 0.130 hour. At a residence time of 0.130 hour a greater solvent yield and a lower vacuum bottoms yield is achieved at 500° than at 475°C., except that hydrocarbon gas yield is higher in the 500°C. test. For comparative purposes, Table 3 shows a test conducted at 450°c. and about the same residence time wherein the solvent yield is lower and the vacuum bottoms yield is higher than in the 500°C. test. Furthermore, the 500°C. test performed at 0.130 hour produced a vacuum bottoms product having only 0.8 percent sulfur which is the lowest sulfur level vacuum bottoms product of all the tests of Table 3. However, the 500°C. test at the 0.130 hour residence time shows the amount of vacuum bottoms produced is diminished in favor of not only liquid product but also gaseous product. As the vacuum bottoms level diminishes, it is seen that conversion to gases becomes increasingly favored, and this therefore tends to ultimately limit the extent of conversion of vacuum bottoms to liquid product. However, if facilities are available to collect and purify gaseous product, a high level of hydrocarbon gas production can be advantageously utilized as a commercial fuel.

Table 3 indicates that at temperatures as high as 475° or 500°C., gas production exerts a limitation on total fueld product (liquid fuel plus solid fuel). Test 3 of Table 4 realized the highest liquid plus solid fuel yield of all the tests of Table 3 (84.6 percent), and this yield is greater than that shown in Tests 3 and 5 because of the relatively low yield of hydrocarbon gases in Test 4.

Comparing Tables 3 and 4, it is seen that a maximum preheater temperature of 450°C. is sufficiently low that lengthy preheater residence times of more than 0.5 hour are required to achieve significantly high yields of excess solvent (liquid fuel product). At higher preheater temperatures of 475° and 500°C., higher excess solvent yields are achieved at lower residence times. Most importantly, at the elevated preheater temperatures of Table 3, excess solvent yield is much more sensititve to slight changes in residence time than at 450°C. At 450°C., large increases in residence time are required to achieve significant increases in solvent yield. Of all the tests in Tables 3 and 4, the combination in Table 3 of a preheater temperature of 500°C. and a preheater time of 0.130 hour achieved the highest solvent yield and the lowest vacuum bottoms yield. The data show that the solvent yield was reduced by one-half at a lower residence time at a preheater temperature of 500°C. and was also reduced by about one-third at about the same residence time but at a lower preheater temperature of 475°C., while it was reduced by more than one-half at the same residence time and a still lower preheater temperature of 450°C. It is seen that there is a considerable interdependence between preheater temperature and preheater residence time.

A fundamental distinction between 500°C. preheater operation at which the highest solvent yields are achieved as compared with 450°C. temperature preheater operation, is that the low temperature operation is not subject to as rapid polymerization of free radicals produced in the solvation operation. Tables 3 and 4 show that solvent-insoluble organic matter, which tends to be produced by free radical polymerization in the process and which decreases desired fuel product, tends to be higher in the 500°C. tests than in the 450°C. tests, even though the preheater residence times are very long in the 450°C. tests. Furthermore, very careful control of residence time in the preheater at 500°C. operation is required if plugging of the tubular preheater due to coke formation is to be avoided, which is a less severe problem in 450°C. operation.

Table 4 shows data to illustrate the effect upon product sulfur level when increasing residence time in the preheater at a constant preheater temperature of 450°C.

TABLE 4

TEST NUMBER	1	2	3	4	5
H_2 Pressure, kg/cm²	70	70	70	70	70
Max. Preheater Temp., °C.	450	450	450	450	450
LHSV	1.96	1.91	1.34	1.09	0.74
GHSV	208	225	231	228	235
1/LHSV: Hr.	0.510	0.524	0.746	0.917	1.351
YIELDS ON MAF COAL BASIS — %					
CO	0.21	0.18	0.47	0.25	0.37
CO_2	1.26	1.11	1.45	1.02	1.37
H_2S	1.74	2.58	1.50	2.42	2.86

TABLE 4 — Continued

TEST NUMBER	1	2	3	4	5
Hydrocarbon Gas Product	4.89	3.86	6.31	5.34	8.83
H_2O	6.00	7.08	1.81	3.75	2.30
Excess Solvent (Distillate Fuel Product)	6.00	11.73	14.74	16.98	18.97
Vacuum Bottoms (Solid Fuel Product)	69.78	65.02	64.36	61.32	58.83
Insoluble Organic Matter	11.10	10.62	10.60	10.12	9.64
TOTAL	100.98	102.18	101.24	101.20	103.17
DATA					
MAF Conversion, weight %	88.90	89.38	89.40	89.88	90.36
VACUUM BOTTOMS PROPERTIES					
Carbon, weight %	87.94	86.85	87.57	87.57	88.57
Hydrogen, weight %	5.07	5.47	5.44	5.37	5.24
Nitrogen, weight %	2.02	2.07	1.96	2.01	2.01
Sulfur, weight %	1.04	1.01	0.85	0.80	0.70
Oxygen, weight %	3.82	4.46	4.05	4.00	3.36
Ash, weight %	0.11	0.14	0.13	0.25	0.12
H/C Atomic Ratio	0.686	0.750	0.740	0.731	0.705

As shown in Table 4, the percent MAF conversion is substantially maximized at all the residence times tested. However, product sulfur yields advantageously decrease with increasing residence times.

Table 5 shows the results obtained when varying the outlet or maximum preheater temperature without varying total preheater residence time.

TABLE 5

TEST NUMBER	1	2	3	4	5
H_2 Pressure, kg/cm²	70	70	70	70	70
Max. Preheater Temp., °C.	200	300	350	400	450
LHSV	28.09	28.09	27.96	28.36	28.36
GHSV	2978	2978	2978	2987	3035
1/LHSV: Hr.	0.035	0.035	0.036	0.035	0.035
YIELDS ON MAF COAL BASIS — %					
CO	0.00	0.00	0.00	0.24	0.03
CO_2	0.07	0.14	0.11	0.28	0.35
H_2S	0.04	0.07	0.07	0.66	0.94
Hydrocarbon Gas Product	0.00	0.00	0.00	0.03	0.31
H_2O	−0.95	0.25	0.35	0.87	0.66
Excess Solvent (Liquid Fuel Product)	−153.91	−172.38	−134.95	−129.56	−38.47
Vacuum Bottoms (Solid Fuel Product)	147.91	193.61	167.60	187.58	65.57
Insoluble Organic Matter	106.84	78.52	67.03	40.21	71.06
TOTAL	100.00	100.21	100.21	100.31	100.45
DATA					
Recovery, weight %	95.21	118.58	27.02	92.19	94.14
MAF Conversion, weight %	−6.84	21.48	32.97	59.79	28.94

As shown in Table 5, at a constant residence time of 0.035 hour, solvent is consumed due to gel formation at low preheater temperatures. The solvent loss tends to diminish with elevation of preheater temperatures, but even at high preheater temperatures the employment of extremely low residence times does not permit complete breaking of the gel and release of the solvent. The data of Table 5 show that adequate residence time must lapse to provide a net production of solvent, whereby the process can be self sustaining in solvent. Minimum preheater residence times must be adequate to at least achieve a net production of solvent.

The data in Table 5 illustrate the earlier explanation of rise in Relative Viscosity as the feed slurry begins its transit through the preheater in plug flow. The increase in Relative Viscosity in a stream increment to a value above 20 is due to formation of a gel between the pulverized or ground coal feed and the solvent as the temperature of the coal-solvent slurry starts to rise in the preheater. This gel is caused by the onset of hydrogen donation from the hydroaromatic solvent to the coal and the gel forms by binding of the solvent and coal during onset of hydrogen transfer. This binding is so tight that the solvent involved in the gel cannot be distilled from the gel at this stage of the reaction. As the temperature of the increment continues to increase along the length of the preheater to a level of about 300°C., hydrogen transfer from the solvent to the coal proceeds further to an extent that the gel is broken and high viscosity hydrocarbon polymer is dissolved out of the coal and enters into solution with the solvent, causing the Relative Viscosity of the solvent solution containing this polymer to decline to a value below 20. With continued flow to a higher preheater temperature region, heteroatom sulfur and oxygen are removed from the dissolved polymer causing the polymer to depolymerize and form free radicals, resulting in a further drop in the viscosity of the solution. Ultimately, the Relative Viscosity drops to a value below 10 generally, or to a value below 5, or even below 2. The free radicals of depolymerized coal will tend to repolymerize under the elevated temperature conditions near the

preheater exit unless the holding time in the preheater is terminated and the solution temperature is forced to drop. At this time, the preheater stream is withdrawn from the preheater, quenched or otherwise cooled and passed to a lower temperature dissolver stage before the free radicals can repolymerize to an extent that the Relative Viscosity increases again to a value above 10.

Table 6 shows the results of tests conducted with maximum preheater temperatures of 450°C, and 500°C. and with variable preheater residence times.

TABLE 6

TEST NUMBER	1	2	3	4
H_2 Pressure, kg/cm²	70	70	70	70
Max. Preheater Temp., °C.	450	450	450	500
LHSV	28.36	28.35	15.23	28.36
GHSV	2967	2953	3012	2988
1/LHSV: Hr.	0.035	0.035	0.066	0.035
YIELDS ON MAF COAL BASIS — %				
CO	0.03	0.07	0.06	0.17
CO_2	0.35	0.35	0.45	0.66
H_2S	0.97	1.73	1.49	1.77
Hydrocarbon Gas Product	0.31	0.21	0.65	1.85
H_2O	−1.42	1.11	0.91	−1.50
Excess Solvent (Liquid Fuel Product)	−59.30	−39.61	7.84	13.43
Vacuum Bottoms (Solid Fuel Product)	136.21	105.31	75.78	71.17
Insoluble Organic Matter	23.20	31.34	13.21	12.83
TOTAL	100.35	100.55	100.39	100.38
DATA				
Recovery, weight %	95.46	96.80	90.68	98.38
MAF Conversion, weight %	76.80	68.66	86.79	87.17
VACUUM BOTTOMS (SOLID FUEL) PROPERTIES				
Carbon, weight %	—	—	—	86.67
Hydrogen, weight %	—	—	—	5.33
Nitrogen, weight %	—	—	—	1.78
Sulfur, weight %	—	—	—	1.21
Oxygen, weight %	—	—	—	4.90
Ash, weight %	—	—	—	0.11
H/C Atomic Ratio	—	—	—	0.733

As shown in Table 6, at the preheater temperature of 450°C. and the low residence time of 0.035 hour, there is a net loss of solvent. Table 6 shows that the preheater is capable of a net production of solvent either by lengthening the residence time at a preheater temperature of 450°C. or by increasing the final preheater temperature to 500°C., without increasing the residence time. Table 6 further illustrates the interchangeability of preheater temperature and preheater residence time.

FIG. 1 shows the relationship between percent conversion of MAF coal and maximum preheater temperature at a space time of 0.035 hour. FIG. 1 shows that very high yields are obtained at temperatures of at least 450°C. at a constant low residence time.

FIG. 2 shows percent conversion of MAF coal as a function of residence time in the preheater. FIG. 2 is based on data taken at 450°C. and shows that substantially maximum conversion (80 or 85 percent) is achieved very quickly in the preheater and that continuance of preheater holding time for a considerably greater duration has a very small effect on total conversion. Therefore, at a 450°C. preheater temperature, after about 0.05, 0.1 or 0.25 hours the preheater time is substantially removed as a process factor in regard to conversion.

FIG. 3 shows the sulfur content in the deashed coal product as a function of total preheater and dissolver residence time at various maximum preheater temperatures. FIG. 3 shows that residence time exerts a greater effect on sulfur level in the vacuum bottoms product at high temperatures than at low reaction temperatures. FIG. 3 shows that if significant sulfur is to be removed without utilizing relatively high temperatures, a prolonged residence time must accompany low temperature operation. Therefore, the present process employs a dissolver at a relatively low temperature and a relatively long residence time at a relatively high hydrogen pressure to accomplish a degree of sulfur removal beyond that which is possible in the preheater alone, which operates at a higher temperature at which long residence times and very high hydrogen pressures are prohibitive due to the onset of hydrocracking. In this manner, a dual temperature and hydrogen pressure process produces a product having a lower sulfur level than the sulfur level that is obtained by operating both the preheater and the dissolver at a uniform temperature level, even if the uniform temperature is higher than either temperature of the dual temperature operation. It is important that there is no advantage in regard to sulfur removal in utilizing a higher average but uniform temperature in both the preheater and the dissolver, but better results are obtained with a split temperature wherein the relatively lower temperature in the dissolver stage is compensated by a relatively longer residence time.

FIG. 4 shows the fraction of organic sulfur removed from the vacuum bottoms (deashed solid fuel) product versus residence time at various temperatures. As shown in FIG. 4, a high level of sulfur removal is least dependent upon residence time at elevated temperatures while residence time becomes increasingly impor-

tant to a high level of sulfur removal at lower temperatures. FIG. 4 again illustrates the basis for employing a relatively low temperature dissolver coupled with an extended residence time in cooperation with a relatively high temperature preheater coupled with a relatively short holding time.

FIG. 5 illustrates the relationship of hydrocarbon gas yield to preheater outlet temperature and shows that hydrocracking to gases increases rapidly as the temperature is increased above 400, especially above 450°C. The present invention permits the achievement of high conversion without excessive hydrocracking by utilizing a high temperature only for a short duration (preheater stage) and only with a relatively low hydrogen pressure followed by a relatively low temperature for a longer residence time (dissolver stage). In this manner, a high conversion is achieved without an excessive yield of hydrocarbon gases. Production of hydrocarbon gases constitutes a waste of product and a needless consumption of hydrogen.

FIG. 6 illustrates the effect of temperature and residence time on hydrogen consumption and shows that at low residence time hydrogen consumption is not affected by temperature but that at higher residence times hydrogen consumption is affected by temperature. Either low residence times or low temperatures favor low hydrogen consumptions. Therefore, in the present process, a low residence time is employed in the relatively high temperature preheater while a relatively long residence time is employed in the relatively low temperature dissolver.

FIG. 7 shows schematically the process of the present invention. As shown in FIG. 7, pulverized coal is charged to the process through line **10**, contacted with recycle hydrogen-containing gases from line **40** and forms a slurry with recycle solvent which is charged through line **14.** The slurry passes through line **16** to preheater tube **18** having a length to diameter ratio greater than 100, generally, and, preferably, greater than 1,000 to permit plug flow. Preheater tube **18** is disposed in a furnace **20** so that in the preheater the temperature of a plug of feed slurry increases from a low inlet value to a maximum temperature at the preheater outlet.

The high temperature effluent slurry from the preheater is then passed through line **22** where it drops in temperature before reaching dissolver **24** due to flashing in flash chamber **23** and the addition of cold makeup hydrogen through line **12.** Other methods for cooling can include water injection, a heat exchanger or any other suitable means. Gases removed in flash chamber **23** are fed to gas scrubber **36** through line **35** while residue liquid slurry from flash chamber **23** is mixed with scrubbed hydrogen coming from scrubber **36** through line **34** and/or makeup hydrogen from line **12** and then fed to dissolver **24.** If desired, gas scrubber **36** can be dispensed so that only makeup hydrogen is charged to dissolver **24.** Charging makeup hydrogen directly to dissolver **24** results in a relatively high hydrogen pressure in dissolver **24.** The residence time in dissolver **24** is substantially longer than the residence time in preheater **18** by virtue of the fact that the length to diameter ratio is considerably lower in dissolver **24** than in preheater **18,** causing backmixing and loss of plug flow. The slurry in dissolver **24** is not in plug flow but is at substantially a uniform temperature whereas the slurry in preheater **18** is in plug flow and increases in temperature from the inlet to the exit end thereof.

The slurry leaving dissolver **24** passes through line **26** to flash chamber **46.** Overhead from flash chamber **46** is passed to distillation column **28** through line **48** while bottoms is passed to filter **50** through line **52.** Ash is removed from filter **50** through line **54** while filtrate is passed to distillation column **28** through line **58.** Gases, including hydrogen and impurities, are removed overhead from distillation column **28** and are either withdrawn from the process through line **30** or passed through line **40** without scrubbing of contaminants for recycle to preheater **18.** The gases are recycled to preheater **18** without scrubbing of impurities so that the hydrogen pressure in the preheater will be relatively low.

A distillate liquid product of the process is removed from a mid-region of distillation column **28** through line **42** and recovered as liquid fuel product. Since the process produces sufficient liquid to be withdrawn as liquid fuel product plus sufficient liquid to be recycled as solvent for the next pass, a portion of the liquid product is passed through line **44** for recycle to line **14** to be employed to dissolve pulverized coal in the next pass.

Deashed vacuum bottoms is removed from distillation column **28** through line **46** and passed to conveyor belt **60** on which the bottom product is cooled to room temperature, at which temperature it solidifies. Solid fuel containing as low an ash content as is practical is removed from conveyor belt **60** by a suitable belt scrapper means, as indicated at **62.** As shown in FIG. 7, the only material removed from the process between the preheater and the dissolver is gaseous impurities. otherwise, all material entering the preheater gases through both the preheater and dissolver before any product fuel separation occurs. Gaseous impurity separation is accomplished between the preheater and the dissolver by passing gases from flash chamber **23** through line **35** to scrubber **36,** from which hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, methane, ethane, and other gaseous hydrocarbons are removed through line **38.** Cool purified hydrogen is recycled through line **34,** if desired.

FIG. 7 shows that coal and solvent pass serially first through the preheater and then through the dissolver while hydrogen flows (in reverse) through the dissolver first and then the preheater. However, within the preheater and the dissolver units themselves, the hydrogen and coal slurry flow in the same direction.

We claim:

1. A process for preparing deashed solid and liquid hydrocarbonaceous fuel from hydrocarbonaceous feed coal containing ash comprising contacting the feed coal in a slurry with a solvent for the hydrocarbonaceous material in the coal with a contaminant containing hydrogen stream obtained from the dissolver step described below without scrubbing of contaminant gases, passing the slurry and said contaminant containing hydrogen through a preheater for a residence time between 0.01 and 0.25 hours, said preheater having a length to diameter ratio of at least 100 to inhibit backmixing so that an increment of said slurry gradually increases in temperature in passage through the preheater from a low inlet temperature to a maximum temperature at the preheater outlet, the maximum temperature at the preheater outlet being 400° to 525°C., the

viscosity of an increment of the slurry in passage through the preheater increasing initially to a value at least 20 times the viscosity of the solvent alone when each is measured at a temperature of 99°C., the viscosity of the slurry in continued passage through the preheater subsequently dropping to a value lower than 10 times the viscosity of the solvent alone when each is measured at 99°C., the viscosity of said slurry finally tending to increase to a value greater than 10 times that of the solvent alone when each is measured at 99°C. at the exit temperature of said preheater but the slurry and hydrogen containing contaminant gases being removed from said preheater after the relative viscosity drops to a value below 10 but before the relative viscosity finally increases to a value of 10, flashing hydrogen containing contaminant gases from the slurry, charging relatively purer hydrogen to said slurry, reducing the temperature of the slurry at least 10°C. after it leaves the preheater to a temperature at which the viscosity of the slurry does not increase to a value above 10 times that of the solvent alone when each is measured at 99°C., passing the cooled slurry to a dissolver maintained at a temperature between 350 and 475°C. which is below the temperature at the outlet of the preheater, the residence time of the slurry in the dissolver being greater than in the preheater, the hydrogen partial pressure in the dissolver being greater than in the preheater, removing the slurry from the dissolver and separating the slurry into hydrogen containing contaminant gases, a fraction which is liquid at room temperature and a deashed fraction which is solid at room temperature, passing hydrogencontaining contaminant gases to the preheater, and recycling at least a portion of said liquid fraction as solvent for said preheater step.

2. The process of claim **1** wherein makeup hydrogen is added between the preheater and dissolver steps.

3. The process of claim **1** wherein the maximum temperature in the preheater is below 470°C.

4. The process of claim **1** wherein the temperature in the dissolver is 400 to 450°C.

5. The process of claim **1** wherein the drop in temperature between the preheater and dissolver is at least 25°C.

6. The process of claim **1** wherein the preheater length to diameter ratio is at least 1,000.

7. The process of claim **1** wherein the residence time in the preheater is 0.01 to 0.15 hours.

8. The process of claim **1** wherein the dissolver residence time is 0.1 to 3 hours.

9. The process of claim **1** wherein less than 6 weight percent of hydrocarbon gases is produced based on moisture and ash free coal feed.

10. The process of claim **1** wherein the yield of deashed solid fuel is 20 to 80 weight percent based on moisture and ash free coal feed.

11. The process of claim **1** wherein the yield of deashed solid fuel is 40 to 80 weight percent based on moisture and ash free coal feed.

12. The process of claim **1** wherein the viscosity of the slurry in the preheater falls to a value at least as low as 5 times the viscosity of the solvent alone when each is measured at 99°C.

13. The process of claim **1** wherein the viscosity of the slurry in the preheater falls to a value at least as low as 2 times the viscosity of the solvent alone when each is measured at 99°C.

14. The process of claim **1** wherein said forced temperature reduction is accomplished by cooling the slurry stream in a heat exchanger.

15. The process of claim **1** including a scrubbing step for removing contaminants from the hydrogen stream flashed from the preheater effluent, followed by passage of the scrubbed hydrogen to the dissolver.

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