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(21) International Application Number: PCT/US91/00562 (22) International Filing Date: 28 January 1991 (28.01.91) (30) Priority data: 481,345 15 February 1990 (15.02.90) US (71) Applicant: AMOCO CORPORATION [US/US]; Mail Code 1907, Patents and Licensing Department, P.O. Box 87703, Chicago, IL 60680-0703 (US). (72) Inventor: JOSEPH, Joseph, Thenganpallil ; 5 South 276 Tartan Lane, Naperville, IL 60563-1960 (US). (74) Agents: MICKELSON, Carole, A. et al.; Amoco Corpora- tion, Patents and Licensing Department, Mail Code 1907, P.O. Box 87703, Chicago, IL 60680-0703 (US).		(81) Designated States: AT (European patent), AU, BE (Euro- pean patent), CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), JP, LU (European patent), NL (European patent), PL, SE (European pa- tent). Published <i>With international search report.</i>
(54) Title: COAL LIQUEFACTION PRE-TREATMENT (57) Abstract <p>Disclosed is a pre-treatment method for swellable solid carbonaceous materials, and especially coal, which enhances hydroliquefaction yields and product quality in which a swelling agent and a catalyst are mixed with the solid carbonaceous materials to be hydroliquified for a time and at conditions sufficient to cause swelling of the solid carbonaceous materials and to deposit catalyst thereon. Thereafter, the swelling agent may be removed prior to the hydroliquefaction of the swollen solid carbonaceous materials. Enhanced liquefaction yields may also be obtained by prehydrogenation accomplished in the pre-treatment method by subjecting the solid carbonaceous material/catalyst/swelling agent mixture to hydrogen under a relatively mild pressure as compared to pressures used in liquefaction processes.</p>		

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COAL LIQUEFACTION PRE-TREATMENT

Field of the Invention

5 This invention relates to a hydrocarbon conversion method and more particularly to a method for pre-treating solid carbonaceous materials for recovering upgraded products from subsequent hydroconversion.

Background of the Invention

10 The uses of coal, which were extensive in the past in many countries including the United States, have declined substantially, being replaced by oil and gas. Up until the 1970's, the convenience in handling oil and gas and the price differential between coal and oil or gas resulted in the decline of coal as a power source.

15 However, the volatility of the oil markets, especially in 1973 and 1979, and rapidly dwindling petroleum reserves have prompted renewed interest in coal-based fuel technologies. Many processes, including hydroliquefaction, have been developed to utilize coal and other solid carbonaceous materials such as coke, lignite, tar sands and oil shale for
20 conversion to organic liquids and gases useful as fuel.

In coal hydroliquefaction, the coal is ground up, often into a slurry, and then subjected to high pressures and temperatures in the presence of hydrogen in order to convert coal to relatively short chain carbon molecules, such as alkanes. The hydrogen can be furnished in
25 molecular form or by way of an organic donor. Catalytic hydroliquefaction further includes a catalyst to enhance the process. The product is depressurized and fractionated and produces gaseous liquid and solid products.

The advantage of coal liquefaction is that a wide range of
30 useful products are produced, including heavy fuels which may be used for electric utilities, distillate fuel oil, gasoline and light hydrocarbons or gases which can be further processed to give naphtha, substitute natural gas (SNG), and liquified petroleum gas (LPG).

There are production constraints in liquefaction processes
35 which result in low conversion rates of coal and other solid carbonaceous materials to useful products. More particularly, coal conversion problems result from the fact that 90% of the surface area of coal is in micropores

having a diameter of less than 10 Angstroms, which limits the accessibility of the reactive sites in coal by reagents such as solvents.

In catalytic hydroliquefaction of coal, it is necessary that the coal surface be intimately contacted with both the catalyst and hydrogen source for effective hydrogenation to produce desired products and also to reduce undesirable reactions. The microporous structure of coal hinders this intimate contact. Therefore, rather harsh conditions must be used to produce satisfactory yields. These include high temperatures and pressures and grinding to a fine particle size.

The present invention is directed to overcoming one or more of the above problems.

Summary of the Invention

It is a general object of the present invention to provide a method for converting solid carbonaceous materials to useful liquid and gaseous products.

It is another object of the invention to provide a method of pre-treating solid carbonaceous materials, and particularly coal, prior to hydroliquefaction in order to enhance and improve liquefaction yields.

It is another object of the invention to provide a pre-treatment method for solid carbonaceous materials which avoids the requirement of fine grinding prior to and the use of harsh conditions during hydroliquefaction of the solid carbonaceous materials.

The objects of the invention are achieved in a method which includes the step of contacting the solid carbonaceous materials with a swelling agent or solvent and a catalyst for a time and at conditions sufficient to swell the materials and deposit the catalyst thereon. The swelling agent swells the solid carbonaceous materials to enlarge the micropores thereof. The enlargement facilitates intimate contact between required reagents, such as catalysts, and the solid carbonaceous materials.

The pre-treatment method may take place at relatively mild conditions, i.e. substantially ambient temperatures and pressure. Removal of the swelling agent prior to catalytic hydroliquefaction is contemplated. Removal results in products characterized by an absence of the swelling agent as it is often the case that the swelling agent can be incorporated into the coal and its liquefaction products causing problems

in later use of the products, particularly where the swelling agent contains nitrogen compounds.

5 This embodiment allows the catalyst to be deposited on the solid carbonaceous materials surface prior to and, optionally, avoiding its addition in the subsequent liquefaction process, and also results in enhanced liquefaction yields.

10 Another embodiment of the invention includes subjecting the solid carbonaceous materials, catalyst, and swelling agent mixture to hydrogen at a relatively mild, slightly elevated pressure and at substantially ambient temperature. When used on coal, this embodiment results in increased liquefaction yields at least partially due to pre-hydrogenation of the aromatics in the coal prior to liquefaction.

15 The result of the process in all its embodiments provides the advantages that the need for fine grinding or pulverization of the solid carbonaceous materials is avoided thus resulting in reduction of grinding costs, and that less severe conditions are required during the hydroliquefaction process.

Other objects and advantages will become apparent from the following description.

20

Description of the Preferred Embodiment

I. INTRODUCTION

25 Pre-swelling of solid carbonaceous materials such as coal, coke, lignite, tar sands and oil shale according to the invention increases subsequent hydroliquefaction yields and improves product quality. The invention contemplates pre-swelling of solid carbonaceous materials with a suitable swelling agent followed by removal of the swelling agent prior to hydroliquefaction of the coal to enhance coal conversion, (conversion being the combination of oil, asphaltenes and pre-asphaltenes products),
30 by 20%, and oil yield by 55-68% in subsequent liquefaction. Typical swelling agents are tetrabutylammonium hydroxide, tetrahydrofuran, methanol, hexane, toluene, diethyl ether, dimethoxyethane, triglyme, pyridine, 1-methyl naphthalene, panasol, O-cresol, quinoline, sodium hydroxide, process-derived solvents in which coal or any other process
35 material is used, and combinations thereof. The pre-treatment process is carried out at relatively mild temperatures and pressures as compared with the high temperatures and pressures conventionally used in hydroliquefaction processes, and, further, the pretreatment is

characterized by an absence of liquefaction of the solid carbonaceous materials.

5 The pre-treatment process optionally includes the deposition of a hydroliquefaction catalyst onto the swelled coal in the presence of the swelling agent. Suitable hydroliquefaction catalysts include iron pentacarbonyl, molybdenum hexacarbonyl, molybdenum trisulfide, rhodium trichloride, cupric chloride, iron^{II} oxide, iron^{III} oxide, iron^{II}, ^{III} oxide, cupric hydroxide, and combinations thereof. This deposition of catalyst in the presence of a swelling agent prior to hydroliquefaction results in an enhancement of the total liquefaction yield by 20% and, more significantly, an increase in oil yield by 68%. Preferably, it is accomplished at the same relatively mild temperatures and pressures as the swelling pre-treatment alone.

15 Another embodiment of the process includes subjecting the swelling agent/solid carbonaceous materials/catalyst mixture with hydrogen under a relatively mild pressure, (approximately 100 psig). After a sufficient time for pre-hydrogenation, the catalyst and swelling agent are removed. Both may be recycled or re-used, and the hydrogenated coal is hydroliquefied. Again, significant improvements and total yield result. 20 The increase in total yield is 40% and, in addition, the oil yield is increased by 50%.

II. SWELLING OF COAL

25 The following description of the preferred embodiment illustrates the use of coal in the process. However, it should be understood that other swellable solid carbonaceous materials may be used.

Some of the significant drawbacks of the current coal hydroliquefaction processes include 1) high hydrogen consumption, 2) occurrence of retrograde reactions producing high molecular weight materials and 3) formation of significant quantities of gases/low molecular weight hydrocarbons. Consequently, higher quality product yield is lowered and liquefaction cost is increased. These drawbacks can potentially be minimized by lowering the severity of the reaction conditions, modifying the coal structure through treatment prior to catalytic hydroliquefaction, and developing more efficient catalytic systems. 35

Another problem is that many swelling agents or solvents suffer from a serious drawback in that they can react irreversibly with the

liquefaction products thus incorporating into the products unacceptable amounts of certain contaminants, such as nitrogen or oxygen. As an example, the swelling agent tetrahydrofuran decomposes or polymerizes at temperatures at or above its boiling point and the resulting compounds tend to be become incorporated in the coal and its liquefaction products.

Significant improvements in liquefaction yield and product quality are achieved by pre-swelling coal with a swelling agent and removing the swelling agent prior to hydroliquefaction. When the coal matrix expands because of swelling, the internal surface of the coal becomes more readily accessible to reagents and therefore subsequent reactions are facilitated.

Further, the use of a hydroliquefaction catalyst in the presence of a swelling agent prior to hydroliquefaction also results in enhanced liquefaction yields. Specifically, swelling of the carbonaceous material apparently makes the surface of the carbonaceous material more accessible to the catalyst, which in turn enhances the reaction rate during hydroliquefaction.

Finally, a pre-treatment process involving pre-hydrogenation which subjects the coal mixture, which includes the swelling agent and the catalyst, to hydrogen at relatively mild conditions, namely at substantially ambient temperatures and mild, elevated pressures, also produces favorable liquefaction results.

In order to better understand the advantages of the process the physical structure of typical solid carbonaceous materials such as coal is hereinafter described. Coal is a microporous structure often having greater than 90% of its surface area enclosed in micropores less than 10 Angstroms in diameter. The reagent accessibility, or mass-transfer potential, to the reactive sites in coal micropores is therefore diffusion-limited.

In order to increase coal reactivity, the contact between the reagent and the coal surface should be maximized. Swelling provides a means to increase this contact. Most coals swell in suitable solvents. Under ambient conditions, swelling can be achieved by mixing coal with appropriate solvents or by exposing coal to solvent vapors.

At a constant temperature the extent of swelling depends on the nature of both the solvent and the rank of the coal. Different ranks of coal have different swell effects when subjected to certain solvents. For

example, tetralin under ambient conditions does not significantly swell Illinois No. 6 coal but it does swell certain cannel coals considerably.

5 In general the best swelling solvents are those containing nitrogen or oxygen atoms with a lone pair or pairs of electrons available for coordination with the electron bonds of the coal. The solvents are generally organic bases with common examples being pyridine, ethylenediamine, ethanolamine and tetrahydrofuran.

10 The extent of coal swelling caused by a solvent can be measured by the swelling ratio which is the ratio of the coal volume after swelling to its initial volume. The swelling efficacies of various solvents can be compared by measuring respective swelling ratios.

15 The technique used for determining the swelling ratio was essentially a volumetric bulk swelling technique. The following is a brief description of the procedure. A sample of powdered coal was treated with tetrahydrofuran (THF) to remove the extractable portion of coal. After drying overnight in a vacuum oven at approximately 110°C, 2 grams of the coal residue remaining after extraction was placed in a graduated glass tube and centrifuged at 3000 RPM for 0.5 hrs. in a constant temperature centrifuge. The temperature used in the centrifuge was 20°C. After
20 recording the height (H_o) of the packed column, approximately 6 milliliters of the swelling agent was placed in the graduated glass tube. The tube was then capped and shaken to ensure complete wetting of the coal powder in the solvent. The mixture was then allowed to stand overnight at room temperature. The tube and its contents were again centrifuged at
25 the same conditions. The constant height of the coal column (H_s) was then measured. The swelling ratio, I , was then calculated by the equation $I = H_s/H_o$.

30 In illustrating the advantages of this invention a bituminous coal, a sub-bituminous coal, and a lignite were investigated. More specifically, Illinois No. 6, Wyodak, and Kinneman Creek (North Dakota) coals, respectively, were used. Illinois No. 6 coal has the highest rank followed by Wyodak, then Kinneman Creek.

35 The proximate analysis of the three coals used in the investigation are in Table I, while the ultimate analysis of these coals are presented in Table II.

TABLE IPROXIMATE ANALYSIS (Dry Basis)

5				
	Properties	<u>Illinois No. 6</u>	<u>Wyodak</u>	<u>Kinneman Creek</u>
	Ash (%)	11.8	8.9	11.7
10	Volatile (%)	39.7	44.7	44.5
	Fixed Carbon (%)	48.5	46.4	43.8

TABLE II

ULTIMATE ANALYSIS
(Dry, Mineral Matter-free Basis)

15				
20	<u>Element, Wt%</u>	<u>Illinois No. 6</u>	<u>Wyodak</u>	<u>Kinneman Creek</u>
	Carbon	78.9	76.0	67.7
	Hydrogen	5.4	5.3	5.0
	Nitrogen	1.2	1.4	1.4
25	Sulfur	4.4	0.6	1.3
	Chlorine	0.1	0.0	—
	Oxygen (diff)	10.0	16.7	24.6
	<u>Sulfur Forms</u>			
30	% Pyritic	2.1	0.11	0.25
	% Sulfate	0.02	0.01	0.09
	% Organic	2.4	0.48	0.99

35 While tetrabutylammonium hydroxide (TBAH), tetrahydrofuran (THF) and methanol were the swelling agents used to illustrate the invention, the invention is not so limited, as other suitable solvents may be used. Other solvents, for example, include hexane, toluene, diethyl ether, dimethoxyethane, triglyme, pyridine, 1-methyl naphthalene (MN), panasol,

sodium hydroxide, and tetralin in combinations with 1-methyl/naphthalene, O-cresol and 1-methyl naphthalene, quinoline and 1-methyl naphthalene, and process-derived solvents. Table III indicates the swelling ratios for Illinois No. 6 coal using different solvents.

5

TABLE III

**SWELLING RATIOS FOR ILLINOIS
NO. 6 COAL IN VARIOUS SOLVENTS**

10

<u>Solvent</u>	<u>Swelling Ratio</u>
Hexane	1.1
Toluene	1.4
Diethyl ether	1.4
15 Dimethoxyethane	1.6
Methanol	1.5
Triglyme	2.0
Tetrahydrofuran	2.0
Pyridine	2.3
20 1-Methyl Naphthalene (MN)	1.2
30% Tetralin in MN	1.3
30% Tetralin, 10% o-Cresol in MN	1.6
30% Tetralin, 20% o-Cresol in MN	1.6
30% Tetralin, 10% quinoline in MN	1.4
25 30% Tetralin, 20% quinoline in MN	1.5
Panasol	1.3
Tetrabutylammonium Hydroxide (28% in water)	2.9

30

As previously stated, nitrogen or oxygen containing solvents normally give higher swelling ratios than hydrocarbon solvents due to the availability of lone pairs of electrons for coordination with suitable electron deficient sites in the coal. These solvents are generally organic bases. Thus, pyridine and tetrahydrofuran, both organic bases, swell coal considerably more than hydrocarbon solvents or even alcohols. A 287% aqueous or methanolic solution of tetrabutylammonium hydroxide (TBAH),

35

by virtue of its higher basicity than pyridine, swells coal more than pyridine. The solvent mixtures tested in Table III, in spite of the presence

of cresol or quinoline in some, are not highly effective in swelling Illinois No. 6 coal.

Inorganic bases are less efficient swelling agents than organic bases. A comparison of the swelling ratios of Illinois No. 6 coal in organic and inorganic bases is given in Table IV.

TABLE IV

**SWELLING RATIOS OF ILLINOIS
NO. 6 COAL IN ORGANIC AND INORGANIC BASES**

<u>Solvent</u>	<u>Swelling Ratio</u>
A. ORGANIC BASES	
0.3M (7.6%) TBAH in methanol or water	2.3
1.1M (28%) TBAH in water	2.9
Pyridine	2.3
B. INORGANIC BASES	
0.5M NaOH in water	1.2
1.0M NaOH in water	1.4
4.0M NaOH in water	1.5
0.5M NaOH in methanol	1.8
1.0M NaOH in methanol	1.8
4.0M NaOH in water + methanol	1.8

The swelling ratio in 1.1M TBAH was 2.9, while that in 4.0M sodium hydroxide solution in aqueous methanol was only 1.8. These results indicate that basicity is not the only factor influencing coal-solvent interactions. The reasons for the lower swelling ratios in inorganic bases compared to organic bases is not completely understood, however, a possible explanation is that inorganic bases are generally highly polarized "small" ions with negative charge. They can interact only with acidic sites in coal. Because of the small size, the basic ions may not be

able to push the macro-molecular segments of coal apart considerably. Consequently, the coal does not swell to a large extent.

In contrast, the organic bases are generally large molecules with a basic group (not necessarily totally polarized) and a lipophilic hydrocarbon chain. Therefore, they are capable of dual interaction with the coal macromolecule. The size of the organic bases will help the coal macromolecular segments to separate, thus resulting in considerable swelling. The large organic base molecules may swell coal enough to cause changes in the orientation within the coal macromolecule, and it is likely that upon removal of the swelling agent the coal will not return to its initial configuration; and there need be no time limitation respecting the performance of subsequent processing. However, where the swelling is partially or completely reversible, the subsequent hydroliquefaction should take place before an appreciable amount of the swelling subsides.

The swelling ratios of the coals using the TBAH, tetrahydrofuran and methanol as the swelling agents are shown in Table V.

TABLE V

20

SWELLING RATIOS OF COALS

<u>Coal</u>	<u>TBAH</u>	<u>THF</u>	<u>METHANOL</u>
Illinois No. 6	2.9	2.0	1.5
Wyodak	3.3	1.5	1.4
Kinneman Creek	3.7	1.3	1.5

25

As illustrated by the results in Table V, of the three solvents used, TBAH was the best swelling solvent for all three coals. Moreover the swelling ratio in TBAH increased with decreasing coal rank, while this trend was reversed when using THF. Methanol was the least effective swelling agent of the three solvents and its swelling effect was coal rank independent.

35

The differences in swelling efficacies of these various solvents may be explained on the basis of their interactions with the various types of effective crosslinks in coal. There are mainly four types of "effective crosslinks" in coal. They are formed through 1) covalent bonding, 2) ionic

bonding, 3) hydrogen bonding and 4) charge transfer complexing. Swelling of coal is caused by the breaking of these crosslinks. The extent of swelling depends on the type of crosslinks predominant in a certain type of coal and the solvent which is capable of breaking the crosslinks. Ordinarily the covalent bonds are not broken by common solvents. Therefore only ionic and hydrogen bonding and charge transfer complexing are important in the swelling phenomenon. Ionic and hydrogen bonds are predominant in low rank coals because of the presence of relatively large number of polar functional groups such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-CO-) groups. Charge transfer complexing is expected to be predominant only in higher rank coals because of a higher aromatic content than found in the lower rank coals.

Given the difference in their electronic properties, the various solvents react differently with the crosslinks mentioned above. As to the swelling agents used in the investigation, TBAH, being a strong base, disrupts both ionic and hydrogen bonds easily and therefore swells the low rank coals more than the bituminous coals. In contrast, tetrahydrofuran and methanol are not strong enough bases to break the ionic bonds and so they will not swell low rank coals to the same degree as TBAH.

Since charge transfer complexing is expected to be more pronounced in the bituminous coals than in the lower ranking coals, tetrahydrofuran, which can disrupt such bonding, will swell bituminous coals more than sub-bituminous coals or lignites. Methanol, being the least effective of the three solvents in disrupting any of the bonding types mentioned above is obviously the least efficient swelling agent. It has also been determined that the effective concentration of the swelling agent on a swelling ratio is important. Generally, as the concentration of the swelling agent increases, the swelling ratio also increases as indicated in Table VI using Kinneman Creek coal as an example.

TABLE VI

**EFFECT OF CONCENTRATION OF
SWELLING AGENT ON SWELLING OF KINNEMAN CREEK COAL**

5	<u>TBAH Concentration (wt%)</u>	<u>Swelling Ratio</u>
	1.5	1.65
	2.5	1.83
	5.0	2.28
10	10.0	2.84
	15.0	3.52
	20.0	3.67

As can be seen, a ten-fold increase in concentration from 1.5 to 15 wt% more than doubled the swelling ratio.

**III. PRE-SWELLING EFFECTS ON SUBSEQUENT
HYDROLIQUEFACTION**

In investigation to determine pre-swelling effects on liquefaction, the coal samples were ground to -325 mesh and then dried at 110°C. to a constant weight in a vacuum oven with a slow purge of nitrogen. For Illinois No. 6 coal approximately 16 hours of drying is sufficient, but for sub-bituminous coals and lignites, longer drying times, and generally around 48 hours, are required.

The dry coal samples were then mixed with the swelling agents and stirred overnight at approximately room or ambient temperature and under nitrogen. In the case of methanol and tetrahydrofuran, the swelling agent was removed by evaporation under reduced pressure at room temperature. In the case of TBAH a large excess of water was added to the mixture to dilute the TBAH to minimize incorporation of the swelling agent into the coal. The coal was then removed by vacuum filtration and washed with copious amounts of water (Note: TBAH is freely miscible with water). Using soxhlet apparatus, the coal was then extracted overnight with methanol to remove as much of the swelling agent and water as possible. The residual coal was then dried as before.

The above procedures remove swelling agents such as methanol and tetrahydrofuran completely. However, while removing a substantial portion of the TBAH, traces are retained in the coal. The

amount of TBAH retained by coal increases with decrease in coal rank. For example, Illinois No. 6 coal retained about one weight percent of TBAH, while the Kinneman Creek lignite retained about 3.5 weight percent of TBAH under investigation conditions when a 15% solution of TBAH was used as the swelling agent. The swelling agents, upon removal, can be re-used or recycled.

The hydroliquefaction procedure used was performed in a 300-cc Hasteloy-C stirred autoclave equipped with a glass liner, using tetralin as a hydrogen donor in a ratio of 5:1 (tetralin:coal) at 400°C for 0.5 hours under 500 psig hydrogen initial pressure. The reaction products were then extracted with hexane, toluene and tetrahydrofuran, (listed in increasing order of dissolving ability), for determining the yield, respectively, of oils and gases, asphaltenes, and pre-asphaltenes. The sum of the three fractions is considered total coal conversion. [It should be noted that a few of the sums of the three fractions do not coincide exactly with the total yield in the following tables due to rounding of the numbers.]

In the investigation, the gas-make in the liquefaction under the present conditions was less than 2% of the starting coal. Therefore, for the sake of simplicity, gas-make and hexane solubles are counted together as oils.

Table VII indicates the effect of pre-swelling on coal liquefaction in which the swelling agent used is 1.5% TBAH in a 50/50 mixture of methanol and water. This dilute solution of TBAH used to reduce the retention of TBAH in the coal.

TABLE VIIEFFECT OF PRE-SWELLING ON COAL HYDROLIQUEFACTION

5	<u>Coal Sample</u>	<u>Liquefaction Yield (%)</u>			
		<u>Total</u>	<u>Oils</u>	<u>Asph⁽¹⁾</u>	<u>Preasph⁽²⁾</u>
	Illinois No. 6, Raw	69	22	31	16
10	Illinois No. 6, pre-swollen	83	37	33	13
	Wyodak, raw	67	32	22	13
15	Wyodak, pre-swollen	79	50	19	10
	Kinneman Creek, raw	56	33	15	8
20	Kinneman Creek, pre-swollen	68	51	12	5

(1) Asphaltenes

(2) Pre-asphaltenes

25

For Illinois No. 6 coal, pre-swelling enhanced the total liquefaction yield by 20% over the untreated coal. More significantly, the oil yield (hexane solubles) increased by 68%, from 22% to 37%.

30

For the sub-bituminous coal, Wyodak, the total yield increased from 67% for the untreated coal to 79% for the pre-swollen coal. The increase in oil yield in this case, 56%, although significant, was not as dramatic as in the case of the bituminous coal.

35

For the lignite, Kinneman Creek, a 21% increase in total conversion and a 55% increase in oil yield were similar to those for Wyodak coal.

It appears that effective pre-swelling and product quality is influenced by coal rank. The effect of pre-swelling on hydroliquefaction yields is quite remarkable for the higher rank coals and gradually declines in the lower rank coals.

5 Table VIII indicates the effect of the use of particular pre-swelling agents used in coal liquefaction.

TABLE VIII

10 EFFECT OF TYPE OF PRE-SWELLING
AGENT ON COAL HYDROLIQUEFACTION

	Swelling	Swelling	Liquefaction Yield (%)			
	Agent	Ratio	Total	Oil	Asph	Preasph
15	ILLINOIS NO. 6					
	None	—	69	22	31	16
	TBAH	2.9	83	37	33	13
20	THF	2.0	89	28	37	24
	Methanol	1.5	88	28	31	29
	WYODAK					
25	None	—	66	44	10	12
	TBAH	3.3	78	50	22	6
	THF	1.5	74	52	13	9
	Methanol	1.4	67	44	13	10
30	KINNEMAN CREEK					
	None	—	56	33	15	8
	TBAH	3.7	63	41	16	6
	THF	1.3	56	33	16	7
35	Methanol	1.5	56	34	15	7

The liquefaction behavior of the coals changed considerably with the particular swelling agent used. Among the coals, the Illinois No. 6 coal shows, for each solvent, the most significant increase in liquefaction yield as well as in the yield of each solubility fraction. In this case, TBAH was the most effective in increasing the oil yield even when a dilute solution was used in the pre-swelling. The dilute solution of TBAH was used to minimize the incorporation of TBAH into the coal. Pre-swelling of Illinois No. 6 coal with tetrahydrofuran and methanol also resulted in higher oil yields, but in contrast to TBAH, asphaltene and preasphaltene yields were more significant.

The results for methanol pre-swelling of the bituminous coal are noteworthy because they illustrate that significantly enhanced liquefaction yields can be achieved even when the solvent produces limited swelling.

The liquefaction oil yields from Wyodak coal were enhanced as a result of pre-swelling with TBAH and tetrahydrofuran but not with the methanol. It should be noted that the swelling ratio of Wyodak coal in methanol was only slightly lower than that in tetrahydrofuran.

In the case of Kinneman Creek lignite, only pre-swelling with TBAH caused any improvement in subsequent liquefaction yields and product quality whereas both tetrahydrofuran and methanol were ineffective.

IV. EFFECT OF PRE-SWELLING AND PRE-CATALYZING ON HYDROLIQUEFACTION

Various metals and metal compounds or complexes may be used as catalysts in hydroliquefaction processes. The catalyst is usually mixed with coal in a number of ways. These include dry mixing, slurry mixing, impregnation, etc. Dry mixing is the simplest but the most inefficient procedure because the chances of obtaining intimate contact between coal and catalyst are minimal. Slurry mixing involves mixing the solid catalyst with coal slurry and the liquefaction solvent. The impregnation technique involves mixing powdered coal with the solution of the catalyst and a suitable solvent and evaporating the solvent under reduced pressure.

Of the three catalyst deposition techniques referred to above, impregnation is preferred because the possibility of the catalyst penetrating the coal matrix is the greatest. However, impregnation can be used with soluble catalysts only. Catalyst dispersion and catalytic activity depend on the extent of accessibility of the catalyst to the coal micropores where most

of the coal surface is enclosed. As mentioned earlier, because of the highly microporous nature of coal most coal reactions are inhibited by mass transport limitations.

5 In determining the effect on hydroliquefaction of depositing catalyst during the swelling pre-treatment, powdered coal was stirred overnight at substantially ambient conditions, i.e. room temperature and pressure, with a swelling agent and the catalyst. A large excess of water was added to the mixture to precipitate any dissolved coal. The coal was separated by suction filtration and using soxhlet apparatus, thereafter
10 extracted with water and methanol to remove the swelling agent, which may be recycled, and then dried in a vacuum oven at 110°C. under a slow purge of nitrogen. The quantity of catalyst retained on coal can be determined by inductively coupled plasma analysis.

A mixture of TBAH and tetrahydrofuran was used as the swelling
15 agent, tetrahydrofuran being used to enhance the solubility of the catalyst in the solvent mixture.

Catalysts used in the investigation included iron pentacarbonyl ($\text{Fe}(\text{Co}_5)$), molybdenum hexacarbonyl, ($\text{Mo}(\text{Co}_6)$), molybdenum trisulfide (MoS_3), rhodium trichloride (RhCl_3) and cupric chloride, (CuCl_2), although
20 the invention is not so limited. Both iron and molybdenum carbonyls are soluble in tetralin and TBAH/tetrahydrofuran. Molybdenum trisulfide is not soluble in either solvent system.

The hydroliquefaction portion of the investigation was carried out by mixing the coal with the liquefaction solvent used, namely tetralin, which
25 is a hydrogen donor solvent. The hydroliquefaction conditions were the same as those previously disclosed for determination of the pre-swelling effect on hydroliquefaction.

The effect of catalyst pre-deposition using TBAH/THF as a swelling agent on the liquefaction behavior of Illinois No. 6 coal is
30 illustrated by the results shown in Table IX.

TABLE IX

**EFFECT OF SWELLING AGENT AND CATALYTIC
PRE-DEPOSITION ON HYDROLIQUEFACTION OF ILLINOIS NO. COAL**

5

	<u>Catalyst</u>	<u>Pre-treatment Catalyst Loading (%)</u>	<u>Swelling Agent</u>	<u>Liquefaction Yield (%)</u>			
				<u>Total</u>	<u>Oils</u>	<u>Asph</u>	<u>Preasph</u>
10	None	None	None	69	22	31	16
	Fe(CO) ₅	Fe(2.13)	None	60	17	28	15
15	Fe(CO) ₅	Fe(0.47)	None	72	9	42	21
	Fe(CO) ₅	Fe(0.34)	TBAH	91	41	36	14
20	Mo(CO) ₆	Mo(2.0)	None	67	12	35	20
	Mo(CO) ₆	Mo(0.45)	TBAH	87	37	38	12
25	MoS ₃	Mo(0.5)	None	80	10	46	24
	MoS ₃	Mo(0.5)	TBAH	88	36	49	3

30

Even though the metal carbonyls used are soluble in tetralin, mixing these catalysts with coal and tetralin prior to liquefaction did not enhance liquefaction yields. Rather with both iron and molybdenum, the oil yields were significantly reduced when the catalysts were simply mixed with tetralin and coal. Increasing the amount of iron on the coal surface by this technique had no beneficial effect on liquefaction yields.

35

In sharp contrast, significant improvements in total conversion and oil yields were observed when the catalysts were deposited in the presence of a swelling agent. For example when 0.34% of iron was

deposited in the presence of a swelling agent, the total yield increased from 69% to 91%, and the oil yield increased from 22% to 41%. Similar increases were observed in the cases of the other catalysts as well.

5 It is noteworthy that molybdenum sulfide, which is insoluble in the solvent system used, also enhanced the total yield and especially product quality, that is, the oil yield, as a result of deposition in the presence of the swelling agent. This leads to the conclusion that swelling introduced microscopic cracks and fissures in the coal structure sufficient in size to permit effective deposition of even insoluble catalysts which resulted in
10 enhanced catalytic activity for liquefaction. Accordingly, the examination of the raw and TBAH-swollen Illinois No. 6 coal (after removal of the swelling agent) by transmission electronmicroscopy showed that the swollen coal had undergone significant changes in its physical structure. The raw coal showed distinct needle-like structures while the swollen coal had a fluffier,
15 more cloud-like structure indicating the expansion of the needle-like structures.

The beneficial effect of catalyst deposition in the presence of a swelling agent on liquefaction is also observed for Wyodak sub-bituminous coal. In this case, iron, molybdenum and copper were used as catalysts
20 and a mixture of TBAH and tetrahydrofuran was used as the swelling agent. The results for the Wyodak sub-bituminous coal are summarized in Table X.

TABLE X

**EFFECT OF SWELLING AGENT AND CATALYST
PRE-DEPOSITION ON HYDROLIQUEFACTION OF WYODAK COAL**

5	<u>Catalyst</u> <u>Preasph</u>	Pre-treatment Catalyst <u>Loading (%)</u>	Swelling <u>Agent</u>	<u>Liquefaction Yield(%)</u>		
				<u>Total</u>	<u>Oils</u>	<u>A s p h</u>
10	None	None	No	67	32	22
	None	None	TBAH	79	50	19
15	Fe(CO) ₅	0.5	No	64	29	25
	Fe(CO) ₅	0.64	TBAH	86	57	23
20	MoS ₃	0.5	No	68	23	32
	MoS ₃	0.48	TBAH	80	51	22
25	CuCl ₂	0.75	No	67	37	19
	CuCl ₂	1.14	TBAH	83	51	20

30

35

As in the case of the Illinois No. 6 coal, catalyst deposition in the presence of the swelling agent in the pre-treatment process enhanced liquefaction yield and improved product quality for the Wyodak coal. For example, deposition of iron on the coal surface by mixing coal and iron carbonyl dissolved in tetralin resulted in only 64% total yield and 29% oil yield. In sharp contrast, deposition of iron by the swelling technique increased the total yield to 86% and the oil yield to 57%. Similar increases were observed for other catalysts as well.

Investigation was also conducted to demonstrate and determine the effect of the nature of the swelling agent on the performance of the catalyst deposited. As indicated earlier, different solvents swell coal to different degrees and, therefore, it is likely that the catalytic activity may be affected. The investigation in this regard on the three test coals used molybdenum hexacarbonyl as the catalyst and TBAH, tetrahydrofuran and methanol as the swelling agents. The results are summarized in Table XI.

TABLE XIEFFECT OF SWELLING AGENT ON PRE-DEPOSITED CATALYST PERFORMANCE

5	<u>Coal</u>	<u>Pre-swelling Solvent/Catalyst</u>	<u>Liquefaction Yield(%)</u>			
			<u>Total</u>	<u>Oils</u>	<u>Asph</u>	<u>Preasph</u>
10	<u>Illinois No. 6</u>	None (No catalyst)	69	22	31	16
		TBAH (with catalyst)	87	37	38	12
		THF (with catalyst)	91	27	33	32
		Methanol (with catalyst)	90	25	37	28
20	<u>Wyodak</u>	None (no catalyst)	66	32	22	12
		TBAH (with catalyst)	90	55	30	5
		THF (with catalyst)	88	48	20	21
		Methanol (with catalyst)	76	42	21	14
30	<u>Kinneman Creek</u>	None (no catalyst)	56	33	15	8
		TBAH (with catalyst)	88	44	32	12
		THF (with catalyst)	57	36	15	7
		Methanol (with catalyst)	55	33	15	7

50 The results in Table XI indicate that, in general, TBAH was the most effective swelling agent for enhancing the activity of the pre-deposited catalyst in all three coals. Tetrahydrofuran and methanol were effective in

increasing the total yield during molybdenum-catalyzed liquefaction of both Illinois No. 6 and Wyodak coals but the product quality was not as high as when TBAH was used.

5 In the case of the lignite, only TBAH was effective while terahydrofuran and methanol were totally ineffective.

10 The next aspect inspected was the effect of particle size of the coal used in pre-swelling on liquefaction. Since coal swelling enhances reagent accessibility to the coal pore structures, it was of interest to determine the effect of particle size on pre-swelling and subsequent liquefaction.

15 Conventionally, coals are ground to a fine particle size for pilot plant liquefaction studies. As an example, coal can be crushed to -200 mesh. The investigation used -325 mesh coals. It was theorized that if the beneficial effects due to swelling also occurred in larger particles, pre-swelling would lead to a reduction in grinding and its associated cost.

To determine the effect of the particle size, the liquefaction behavior of Wyodak coal ground to two different particle sizes, (8x70 and - 325 mesh) was investigated. Results are summarized in Table XII.

TABLE XIIEFFECT OF PARTICLE SIZE ON SWELLING AND HYDROLIQUEFACTION

5	Run No.	Feed Coal Particle Size (Mesh)	Pre- Swelling	Particle Size After Swelling (mesh)	Total	Liquefaction Yield (%)		
						Oils	Asph ¹	PA ²
10	1	-325	No	-325	69	40	23	6
	2	8x70	No	8x70	57	39	13	5
	3	-325	Yes	-325	79	50	19	10
15	4	8x70	Yes	8x70 ⁽³⁾	77	56	14	7
	5	8x70	Yes	-325 ⁽⁴⁾	77	55	16	6

- 20 (1) Asphaltenes
 (2) Preasphaltenes
 (3) Analysis by sonic sifter showed that 97% of the coal sample was +70 mesh, although the particles crumbled easily when a slight pressure was applied.
- 25 (4) For this investigation, the pre-swollen coal(8x70) was ground to -325 mesh.

30 Comparison of the results of Runs 1 and 2 in Table XII indicate that liquefaction of the raw 8x70 mesh coal produced 12% less total yield and 10% less asphaltenes in the -325 mesh coal. This shows that liquefaction of coal is facilitated by fine grinding and this behavior is consistent with expected lower diffusional effects during liquefaction of a smaller particle sized coal.

35 Runs 3 and 4 indicate that after swelling the coal behaved in the same manner during liquefaction regardless of the initial particle size. Significantly, grinding of the pre-swollen 8x70 mesh sample to -325 mesh did not enhance the liquefaction yield as shown by Run 5.

These results indicate that pre-swelling of coal is not only beneficial for enhancing liquefaction yields and product quality, but also obviates the need for fine grinding of coals. This beneficial effect, obviously, can result in significant savings in grinding costs.

5

V. PRE-HYDROGENATION AND HYDROLIQUEFACTION

Catalytic hydrogenation of coal under mild conditions is considered virtually impossible due to the microporous structure of the coal. However, in another embodiment of the invention, an improved pre-treatment method for coal liquefaction, pre-hydrogenation, includes the
10 aforementioned process in which the hydroliquefaction catalyst/swelling agent/coal mixture is subjected to hydrogen under a relatively mild pressure, as compared to pressures used in hydroliquefaction, and at substantially ambient temperatures. Thereafter, the swelling agent and,
15 optionally the catalyst, are removed prior to hydroliquefaction. Once removed, both the swelling agent and the catalyst may be recycled or re-used.

The process for this pre-treatment included mixing powdered coal with the hydroliquefaction catalyst, rhodium trichloride, and a coal
20 swelling agent, TBAH, in the presence of hydrogen at substantially room temperature for 15 to 20 hours. The hydrogen was at a pressure of approximately 100 psig. Thereafter the catalyst and the swelling agent were removed by methanol extraction and the coal was dried. Subsequently, the coal was liquified at 400°C in the presence of tetralin as
25 a hydrogen donor solvent. A sample of untreated coal was also liquified for comparison, and the results are summarized in Table XIII.

TABLE XIIIEFFECT OF PRE-HYDROGENATION ON COAL LIQUEFACTION

5	<u>Prehydrogenation Conditions</u>			<u>Liquefaction Yield (wt%)</u>			
	<u>Swelling Agent</u>	<u>Catalyst</u>	<u>Hydrogen (psig)</u>	<u>Total*</u>	<u>Oils</u>	<u>Asph.</u>	<u>PreAsph.</u>
	None	None	None	62	15	25	22
10	None	6% RhCl ₃	100	63	16	26	21
	16% TBAH	None	100	63	16	22	25
15	16% TBAH	6% RhCl ₃	100	87	31	41	15

*Tetrahydrofuran Solubles

As a result of the pre-hydrogenation pre-treatment, a total coal liquefaction yield increased by 40%. In addition, the oil yield doubled and the pre-asphaltene yield decreased by 32%, showing significant improvement in product quality.

VI. CONCLUSION

From the above description, it is apparent that the objects of the present invention have been achieved. While only certain embodiments have been set forth, alternative embodiments and various modifications will be apparent from the above description and those skilled in the art. These are considered equivalents and within the scope and spirit of the present invention.

CLAIMS

1. A pre-treatment method for solid carbonaceous material prior to hydroliquefaction comprising:

5 contacting solid carbonaceous material with at least one swelling agent and at least one catalyst for a time and under conditions sufficient to swell said solid carbonaceous material and deposit catalyst thereon.

10 2. The method as recited in claim 1 further including the steps of:

 subjecting said solid carbonaceous material, swelling agent, and catalyst mixture to hydrogen at a relatively mild pressure and at a substantially ambient temperature for a time sufficient to effect hydrogenation on said solid carbonaceous material; and

15 removing a substantial portion of said swelling agent.

 3. The method as recited in claim 1 further including the step of hydroliquefying at least a portion of said swollen solid carbonaceous material.

20

 4. The method as recited in claim 1 wherein said swelling agent is selected from the group consisting of tetrabutylammonium hydroxide, tetrahydrofuran, methanol, hexane, toluene, diethyl ether, dimethoxyethane, triglyme, pyridine, 1-methyl naphthalene, panasol, sodium hydroxide, O-cresol, and quinoline, solid carbonaceous material derived solvents, and combinations thereof.

25

5. A method for pre-treating solid carbonaceous materials prior to liquefaction of said solid carbonaceous material comprising:

30 subjecting said solid carbonaceous material to a catalyst in the presence of a swelling agent for a time sufficient to swell said solid carbonaceous material and deposit catalyst thereon; and

 removing a substantial portion of said swelling agent from said mixture prior to liquefaction of said swollen solid carbonaceous material.

35

6. The method of claim 5 wherein the step of subjecting is followed by and the step of removing is preceded by the step of applying hydrogen to the swollen carbonaceous material with the catalyst thereon.

5 7. The method as recited in claim 6 further including the step of hydroliquefying at least a portion of said swollen solid carbonaceous material at an elevated temperature and pressure; and
 wherein said step of applying is performed at a pressure that
10 is substantially less than the elevated pressure used in said hydroliquefaction step.

 8. The method as recited in claim 5 further including the step of hydroliquefying at least a portion of said swollen solid carbonaceous material at an elevated temperature and pressure.

15 9. A method for pre-treating solid carbonaceous material prior to a hydroliquefaction process comprising:

 contacting solid carbonaceous materials selected from the group consisting of coal, coke, lignite, tar sands, oil shale and combinations thereof, with at least one swelling agent selected from the group consisting
20 of tetrabutylammonium hydroxide, tetrahydrofuran, methanol, hexane, toluene, diethyl ether, dimethoxyethane, triglyme, pyridine, 1-methyl naphthalene, panasol, O-cresol, quinoline, sodium hydroxide, solid carbonaceous material derived solvents, and combinations thereof, and at
25 least one catalyst selected from the group consisting of iron pentacarbonyl, molybdenum hexacarbonyl, molybdenum trisulfide, rhodium trichloride, cupric chloride, iron^{II} oxide, iron^{III} oxide, iron^{II,III} oxide, cupric hydroxide and combinations thereof, under a substantially ambient temperature and relatively mild pressure for a time sufficient to swell said solid
30 carbonaceous material and deposit catalyst thereon, said contacting step characterized by an absence of liquefaction of said solid carbonaceous material; and

 hydroliquefying at least a portion of said swelled solid carbonaceous material.

35 10. A pre-treatment method for solid carbonaceous material prior to hydroliquefaction comprising:

contacting solid carbonaceous material with at least one swelling agent and at least one catalyst for a time and under conditions sufficient to swell said solid carbonaceous material and deposit catalyst thereon;

5 subjecting said solid carbonaceous material, swelling agent, and catalyst mixture to hydrogen at a relatively mild pressure and at a substantially ambient temperature for a time sufficient to effect hydrogenation on said solid carbonaceous material;

 removing a substantial portion of said swelling agent; and
10 hydroliquefying at least a portion of said swollen solid carbonaceous material.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/00562

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ² According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5): C10G 01/06 U.S. Cl. 208/421		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S. Cl. 208/403, 421, 422, 423, 430, 435		
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ^{1, 6}		
Category ⁷	Citation of Document, ^{1, 6} with indication, where appropriate, of the relevant passages ^{1, 7}	Relevant to Claim No. ^{1, 8}
Y	US, A, 4,617,106 (Garg) 14 October 1986 (note col. 3, lines 49 - 54).	1-10
A	US, A, 2,118,940 (Pier et al.) 31 May 1938	1-10
A	US, A, 4,787,918 (HO) 29 November 1988	1-10
A	US, A, 4,299,684 (Liotta) 10 November 1981	1-10
A	Fuel, Vol. 67, August 1988, Rincon, J.M. and Cruz, S., "Influence of Preswelling On Liquefaction of Coal" pages 1162-1163.	1-10
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>⁹ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
07 March 1991	03 MAY 1991	
International Searching Authority ¹	Signature of Authorized Officer ¹⁰	
ISA/US	INTERNATIONAL DIVISION Curtis R. Davis/caw	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	Solid Fuel Chemistry, No. 5, 1987, Skripchenki et al "Certain Features Of Coal Swelling"	1-10
A	Fuel Society Journal, Vol. 66, 1987, Keizo et al. "Relationship Between Swelling Ratio And Liquefaction Yields Of Coals."	1-10

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out², specifically:

3. ☐ Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority does not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.