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3,694,342

CATALYTIC LIQUEFACTION OF COAL USING SYNTHESIS GAS

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4 Claims

ABSTRACT OF THE DISCLOSURE

The liquefaction of coal in a hydrogen donor solvent is carried out in the presence of a carbon monoxide sensitive catalyst and a carbon monoxide-containing treat gas under reaction conditions including a temperature from about 750 to about 900° F., a pressure from about 500 to about 4500 p.s.i.g., a treat gas-to-solvent ratio from about 2,000 to about 15,000 s.c.f./b., a solvent-to-coal ratio from about 1.0 to about 2.5 lb./lb., and a slurry/catalyst ratio from 0.25 to 4 w./hr./w. Steam is introduced into the liquefaction zone at a rate from about 1 to about 4 mols of steam per mol of carbon monoxide, whereby said coal is liquified without undue deactivation of said catalyst by said carbon monoxide.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention is directed to the use of carbon monoxide-containing synthesis gas in a process for liquefying solid coal, wherein a hydrogenation catalyst is employed which is sensitive to carbon monoxide. By the present invention, the use of expensive high-purity hydrogen is avoided by employing the less expensive synthesis gas, which contains carbon monoxide. Further, the solvent employed need not be a hydrogen-donor, thus allowing the use of non-hydrogenated recycle stock as the solvent.

(2) Description of the prior art

The solvent liquefaction of coal is well known in the art, as exemplified in the Gorin patents, 3,018,241 and 3,018,242. The use of extrinsically added hydrogen, a hydrogen donor solvent and a hydrogenation catalyst is taught by the Gorin patents. However, although an increase in conversion is obtained by the use of hydrogen and a hydrogenation catalyst, the cost of hydrogen is extremely high and renders the process economically unattractive. Synthesis gas has been disclosed as useful in the noncatalytic liquefaction of coal (Eastman et al. Patent 3,075,912). However, because carbon monoxide inhibits the activity of most hydrogenation catalysts, it has been thought to be necessary to remove the CO from synthesis gas (by conversion to CO and CH₄) before the synthesis gas can be used as a source of hydrogen for catalytic liquefaction. Alternatively, a circulating nickel catalyst may be employed which forms nickel carbonyl, but the nickel carbonyl is decomposed before the catalyst is readmitted into the liquefaction zone. See the Maryland patent U.S. 2,756,194. The present invention avoids the need for such decomposition, allows the use of less expensive recycle solvent, and allows the use of less expensive sources of hydrogen.

SUMMARY OF THE INVENTION

The present invention is directed to a catalytic process for liquefying coal, utilizing a carbon monoxide-containing synthesis gas as a source of hydrogen for the conversion of coal to a liquified product. A carbon monoxide-sensitive hydrogenation catalyst is used in the lique-

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faction zone. Deactivation of the hydrogenation catalyst is avoided by introducing steam into the reaction zone at a rate sufficient to offset the deactivation tendencies of carbon monoxide. The steam may be admitted as such or may be obtained, wholly or in part, by the evaporation of water which is present in the coal feedstock. As referred to hereinafter, the addition of steam is inclusive of both sources.

The liquefaction of coal is carried out by first forming a slurry of coal in a suitable liquid. The coal is mixed with a solvent to form a slurry which is then passed into the liquefaction zone wherein the coal is depolymerized, cracked and partially hydrogenated. The catalyst is maintained in the reaction zone, for example, as a fluidized bed. The hydrogen/carbon monoxide treat gas is passed continually through the liquefaction zone during the liquefaction step, providing molecular hydrogen for the reaction. Products are recovered from the effluent stream removed from the liquefaction reactor. All of these matters are more fully discussed hereinafter.

Solid feed.—The basic feedstock to the process of the present invention is a solid, particulate carbonaceous material, such as bituminous coal, subbituminous coal, lignite, brown coal, etc. Although it is desirable to grind the coal to a particle size distribution from about 8 mesh and finer, it has been found that the solvation reaction will result in a size reduction even if particles as large as ¼ inch on the major dimension have been introduced into the liquefaction zone. Thus, it is possible to charge large chunks of coal rather than the preferred finely divided coal. A typical inspection of the feed coal thus far experimented with is given in Table I, below.

TABLE I.—TYPICAL FEED COAL INSPECTIONS

Moisture, saturated	13.0
Ash, dry	10.6
Mineral matter, dry	12.8
Vol. matter, DMF ¹	45.1
Fixed carbon, DMF ¹	54.9
Carbon, DMF ¹	79.1
Hydrogen, DMF ¹	5.59
Oxygen, DMF ¹	10.6
Nitrogen, DMF ¹	1.24
Sulfur, total, dry	4.70
Sulfur, pyritic, dry	1.71
Sulfur, organic, DMF ¹	3.42
B.t.u./lb., dry	12610
B.t.u./lb., DMF ¹	14360

¹ Dry, mineral-free.

The carbonaceous material may be dried to remove excess water, although it is preferred to charge the "wet" coal if the amount of water in the coal is not too variable, so that the addition of steam can be accurately controlled. If necessary, however, the coal can be dried to a constant moisture content by conventional techniques prior to introduction into the mixer used to establish the slurry feed for liquefaction.

Solvent.—In the mixer, the coal feedstock at ambient temperature is admixed with a liquid solvent, which is at a temperature from 500° F. to 700° F. The solvent/coals weight ratio is within the range from 1/1 to 2.5/1, resulting in a slurry temperature within the range from 300° F. to 350° F. A mechanical propeller or other agitating device may suitably be provided in the mixing zone so as to obtain a uniform slurry concentration.

The solvent stream will boil within the range from 350° F. to 900° F. (preferably from about 375° F. to about 800° F.) so as to remain in the liquid phase after the slurry has been formed.

Where the solvent stream is a recycle solvent fraction (as is preferred), the composition of the equilibrium sol-

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vent will vary somewhat, depending upon the source of the coal used as a feedstock to the system and the operating conditions in the liquefaction and downstream processing sections. However, a typical description of the recycle solvent fraction will be similar to that shown in Table II.

TABLE II.—TYPICAL RECYCLE SOLVENT

Temperature, ° F.:	Volume percent	Weight percent	Specific gravity
400-----	IBP		
422-----	10.0	8.96	1.0008
432-----	20.0	17.92	1.0028
446-----	30.0	26.89	1.0088
466-----	40.0	35.85	1.0058
492-----	50.0	45.28	1.0189
557-----	60.0	54.72	1.0419
602-----	70.0	64.15	1.0640
650-----	80.0	74.06	1.1002
711-----	90.0	83.96	1.1172
783-----	98.2	92.45	
862-----		98.0	
1,000-----			

See the following table:

Elemental analysis:	Weight percent
C-----	89.23
H-----	7.25
S-----	0.06
O-----	3.46
	100.00
Distribution of aromatic rings:	
Non-aromatics-----	0.0
1 ring aromatics-----	31.24
2 ring aromatics-----	53.60
3 ring aromatics-----	10.47
4 ring aromatics-----	4.67
5 ring aromatics-----	0.02
	100.00

¹ Average molecular weight 154.0.

Catalyst.—The catalyst employed in the present invention has a hydrogenation activity and may also possess an activity for cracking hydrocarbons. A suitable catalyst for hydrogenation and cracking of the coal during the liquefaction reaction is a silica-alumina support (either amorphous or crystalline) carrying one or more iron group metals and one or more metals of Group VI-B of the Periodic Table in the form of oxides or sulfides. The silica constituent provides cracking activity, and the amount of silica can be varied as desired. Where no cracking activity is needed, alumina will be employed as the support without the incorporation of silica.

It is preferred to employ a combination of one or more Group VI-B metal oxides or sulfides with one or more Group VIII metal oxide or sulfides. For example, suitable catalyst metal combinations are the oxides and/or sulfides of cobalt-molybdenum, nickel-tungsten, nickel-molybdenum-tungsten, cobalt-nickel-molybdenum and nickel-molybdenum. A preferred catalyst is one containing from 1 to 10 weight percent cobalt oxide, from 5 to 40 weight percent molybdenum oxide and the balance silica-alumina support. The silica content of the support moiety is from about 0 to about 30 weight percent. A specific catalyst would contain from 2 to 5 weight percent cobalt oxide and 10 to 30 weight percent molybdenum oxide, on a silica-alumina support containing 1.5 weight percent silica. The oxides and sulfides of iron, chromium, nickel, tungsten, etc., may also be employed alone or in combination, and the support material may be activated alumina, activated alumina-silica, crystalline silica-alumina zeolites, zirconia, titania, etc., and mixtures thereof. Activated clays, such as bauxite, bentonite and montmorillonite, may also be employed. These catalysts are sensitive to carbon monoxide, i.e., the CO is chemisorbed at the active sites, thereby blocking the hydrogen and hydrocarbons from reaching those sites. Thus, catalyst activity is reduced by the presence of CO in the reaction zone.

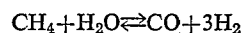
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The catalyst may be manufactured as an extrudate, e.g., in the form of $\frac{1}{32}$ " to $\frac{1}{8}$ " diameter prills about $\frac{1}{4}$ " in length. The catalyst may be used as a part of the slurry, passing through the liquefaction zone, or (preferably) in a fluidized bed in the reaction zone (e.g., as shown in Re. 25,770). In the case of a slurry-type operation, the reactor may be stirred in order to maintain the catalyst well dispersed in the reaction zone.

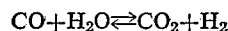
From 25 to 200 weight percent (preferably 100 weight percent) of catalyst is employed based upon the weight of MAF coal charged into the system per hour.

The treat gas.—The treat gas is a carbon monoxide-containing stream which can be derived by the steam reforming of carbonaceous solids or of hydrocarbon liquids and gases. In the liquefaction of coal, an unconverted char product is obtained which is a logical feedstock for steam reforming. Gases, such as methane and ethane, are also produced which are suitable feedstocks for steam reforming.

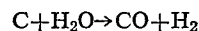
Using methane as an example, the steam reforming reaction is as follows:



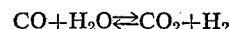
Some of the carbon monoxide product will react with steam to produce more hydrogen:



Thus the final synthesis gas will contain some CO_2 as well as CO and H_2 . The synthesis gas produced from char will be richer in CO, since the carbon/hydrogen mol ratio will be higher than in methane. For pure carbon, the reaction would produce 50% CO and 50% H_2 :



Thus, the synthesis gas may contain up to 50% CO. Where the shift reaction is to be carried out, the resultant gas will contain as little as 2% CO. Even this small amount of CO, however, is sufficient to inhibit the activity of the catalyst in the liquefaction zone. The shift reaction,



is commonly carried out over an iron oxide catalyst at high temperatures, all as is well known in the art.

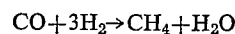
Exemplary treat gases are shown below in Table III.

TABLE III.—SYNTHESIS GAS ANALYSES

	Raw syn gas from methane	Raw syn gas from char	Shifted syn gas from char ¹
H_2 , volume percent-----	75	50	97
CO , volume percent-----	18	35	3
CO_2 , volume percent-----	7	15	0
Total-----	100	100	100

¹ Not subjected to methanation, but after CO_2 removal.

Note that the synthesis gas, even after being passed through the water-shift reaction, contains some unreacted CO. The current practice is to pass this stream through a methanation zone to convert the CO into methane. However, as is seen from the reaction:



this approach consumes three mols of hydrogen for each mol of carbon monoxide. In the example shown above, this would result in a loss of 10% of the hydrocarbon which had been produced. Thus, the importance of the present invention becomes apparent—not only is it unnecessary to remove the CO, but the incremental hydrogen is used for hydrogenation of the coal rather than for CO removal.

The inhibitory action of CO is offset in the liquefaction zone by charging steam into the reactor along with the

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treat gas. Suitably, the steam-to-carbon monoxide ratio will range from about 1 to about 4, preferably about 1.5 mols of steam per mol of carbon monoxide.

Liquefaction zone.—The treat gas and slurry of coal in solvent is passed into a catalytic liquefaction zone, where the convertible portion of the coal is allowed to dissolve and depolymerize to form free radicals. At the temperature maintained within the liquefaction zone (e.g., about 850° F.), the coal softens almost instantaneously and the expanding gases trapped within the coal particles cause vesiculation and swelling of the particles. Where, as is preferred, the slurry is preheated in a furnace-type heater before introduction into the liquefaction zone, the softening begins while the coal particles are in the furnace-type heater. Within approximately five minutes, the coal particles disintegrate to produce some low molecular weight, benzene-soluble materials which are stabilized and hydrogenated by the catalyst and treat gas in the system. The dispersed fragments (not necessarily liquefied) are thermally and catalytically cracked to produce free radicals which can recombine to form material which is not soluble even in pyridine. If a catalyst is used which has a significant cracking activity, this cracking reaction is enhanced. Since the catalyst and treat gas are present, however, the tendency to recombine is substantially inhibited. Since the depolymerized (cracked) coal molecules can either recombine with each other or be stabilized by accepting hydrogen, the degree of inhibition will depend on the amount of hydrogen which is present.

Liquefaction conditions which are suitable may include a temperature from 750° F. to 900° F., a pressure from 500 p.s.i.g. to 4500 p.s.i.g., a solvent/coal weight ratio from 1/1 to 2.5/1, a treat gas rate from about 2,000 to about 15,000 s.c.f./b. (based on the coal slurry charged into the liquefaction zone in the slurry), a steam/CO mol ratio from about 1 to about 4, and an oil residence time of 5 to 60 minutes. The conversion is expressed as the percent of moisture and ash-free (MAF) coal that is converted to materials which are soluble in cyclohexane. It is calculated by the equation:

$$\text{Percent conversion} = \frac{S_t - S_p}{S_t(1 - 0.01a)} (100)$$

wherein:

a = percent ash in the moisture-free coal feedstock,
 S_t = percent solids in the feed slurry,
 S_p = percent solids in the product slurry.

Before measuring S_p , cyclohexane is added to the product slurry as a solvent, in the ratio of 5 volumes of cyclohexane for each volume of party slurry. The results so obtained are referred to as "cyclohexane conversion." This conversion may suitably range from about 60 to about 90%.

When a fluidized catalyst bed is employed, the weight hourly space velocity (slurry/catalyst) may range from 0.25 to 4 w./hr./w., preferably about 1 w./hr./w. In a preferred mode, the temperature will be about 850° F., the pressure about 3,000 p.s.i.g., a solvent/coal weight ratio of about 1.2, and an oil residence time of about 30 minutes. A fluidized bed of catalyst will be used, at a slurry/catalyst weight hourly space velocity of about 1.0 w./hr./w. and a treat gas rate of about 12,000 s.c.f./b. The steam/CO mol ratio is about 1.5.

A liquid product is removed from the liquefaction zone and separated from the unreacted constituents of the coal feedstock (e.g., by distillation, centrifugation and/or filtration). This liquid product may be further upgraded (e.g., by hydrocracking) if desired.

A gaseous phase product is removed from the liquefaction zone as well as the liquid slurry. An exemplary composition of the gas product is given below in Table IV.

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TABLE IV.—EXEMPLARY GAS PRODUCT

Composition:	Wt. percent
CO	26.9
CO ₂	45.2
H ₂ S	0.9
CH ₃ SH	—
H ₂	4.8
C ₁	14.0
C ₂	5.2
C ₃	
C ₃ =	2.3
C ₄	
C ₄ =	0.6
C ₅	
	0.1
	100.0

EXAMPLES

In order to illustrate the utility of the present invention, a subbituminous coal from Illinois No. 6 Mine was liquefied in a small batch reactor as follows.

1.0 gram of finely divided coal, having a particle size range from 100 to 300 mesh Tyler, were introduced into a small (12 cc.) batch reactor and raised to a temperature of 850° F. 2.3 g. of unhydrogenated coal-derived solvent (creosote oil) were introduced into the reactor, along with 1.0 g. of a powdered cobalt-molybdate catalyst.

A treat gas containing 60 mol percent CO, 10 mol percent CO₂ and 30 mol percent H₂ was charged to the reaction zone in the ratio of 50 weight percent on coal.

The weight ratio of catalyst to coal was about 0.5, the weight ratio of solvent to coal was about 2.3, and the weight ratio of steam to coal was about 1.0. The reaction was carried out batchwise in a sealed tubing bomb.

At the conclusion of the run, it was found that the yield of cyclohexane soluble material was about 65%. This is equivalent to about a 65% conversion of coal into 1000° F.—material (gas+liquid). By comparison, under similar conditions, but utilizing hydrogen instead of synthesis gas and steam, 70% conversion to cyclohexane soluble materials was obtained. Under the same conditions, but without the presence of the catalyst, the conversion was only about 50%.

Had the catalyst been subject to carbon monoxide poisoning, the conversion would have been much less.

Thus, it is seen that a carbon monoxide-containing gas can be used in the catalytic liquefaction of coal without the use of hydrogen-donor solvents.

We claim:

1. A process for liquefying coal which comprises introducing into a liquefaction zone a slurry of said coal in a solvent oil containing less than 10 mol percent hydrogen donor compounds, a carbon monoxide-containing synthesis gas, and from 1 to 4 mols of steam per mol of carbon monoxide in said synthesis gas,

reacting said coal in said liquefaction zone in contact with a fluidized bed of a carbon monoxide sensitive hydrogenation and hydrocracking catalyst,

under reaction conditions including
 a temperature from 750 to 900° F.,
 a pressure from about 500 to 4,500 p.s.i.g.,
 a slurry/catalyst ratio from about 0.25 to about 4 w./hr./w.,
 a synthesis gas-to-slurry ratio from about 2,000 to 15,000 s.c.f./b., and
 a solvent-to-coal ratio from about 1.0 to about 2.5 pounds per pound,

whereby said coal is liquefied without undue deactivation of said catalyst by the carbon monoxide in the treat gas.

2. A process in accordance with claim 1 wherein the hydrogenation and hydrocracking catalyst is chosen from the oxides and sulfides of Group VI-B metals and Group

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VIII metals, and mixtures thereof, on a silica-aluminum support.

3. A process in accordance with claim 2 wherein the catalyst is a mixture of cobalt oxide and molybdenum oxide on silica-alumina, such catalyst containing from 1 to 10 weight percent cobalt oxide and from 5 to 40 weight percent molybdenum oxide, and a silica alumina support containing from about 0 to about 30 weight percent silica.

4. A process in accordance with claim 1 wherein the treat gas is a synthesis gas containing 30% hydrogen, 60% carbon monoxide and 10% carbon dioxide.

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