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3,748,254

**CONVERSION OF COAL BY SOLVENT
EXTRACTION**

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15 Claims

ABSTRACT OF THE DISCLOSURE

Coal is partially converted by solvent extraction to a mixture of extract, solvent and undissolved carbonaceous residue. The mixture is separated into a low solids-containing fraction and a high solids-containing fraction. The composition of the latter is adjusted so that its admixture of solids and liquid binder (i.e. extract and solvent) is such as to make it pelletizable. Pellets are formed from the pelletizable composition, preferably in a rotary drum and indurated either concurrently with formation or subsequently thereto. The indurated pellets serve either as solid fuel or as a source of carbon in carbon-steam reactions.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an improvement in coal conversion processes which involve solvent extraction of the coal.

Description of the prior art

Air pollution regulations severely restrict the use of high-sulfur coals in power stations. In order to comply with the regulations concerning permissible SO₂ concentrations in power station stacks, the fuel used should have a sulfur content less than 0.5 percent by weight. The coal reserves in the United States east of the Mississippi River now supply over 90 percent of the total U.S. production and constitute nearly 30 percent of the total U.S. coal reserves. A review by the Bureau of Mines has shown that there are virtually no Eastern reserves less than 0.7 percent sulfur; 80 percent of the reserves contain more than 1.1 percent sulfur and 43 percent contain more than 3.0 percent sulfur.

Coal has already been substantially displaced by low-sulfur fuel oil in many east coast areas, but supplies of this low-sulfur fuel oil are too limited for this to become a general practice. As stated by the 1970 National Academy of Engineering review of SO₂ removal technology, ". . . unless the necessary technology becomes available, the country may have to choose between clean air and electricity."

There are four distinct areas in which technology already exists, but is being further developed for solving coal's sulfur problems. They are (1) SO₂ removal from stack gas, (2) selective rejection of pyrites from the coal, (3) coal gasification, and (4) coal liquefaction.

The present invention lies in the field of coal liquefaction. The art of coal liquefaction is old. The ability to produce a substantially sulfur-free distillate from high-sulfur coals has been demonstrated in German practice. The patent literature is replete with processes for converting coal to liquids. Since hydrogenation is generally involved in such conversions, some desulfurization is always effected so that a liquid is produced which has a lower sulfur content than the coal. In recent years, the emphasis on the development of such liquefaction processes has been on partial conversion of the coal. The reason is, the correlation between hydrogen requirements and depth of conversion. More hydrogen is required per unit of coal

conversion as the depth of conversion is increased. There thus exists an economic optimum of depth of conversion which depends upon the coal used but is generally between 50 and 80 weight percent of the moisture- and ash-free coal.

Partial conversion of coal may be readily accomplished by solvent treatment, i.e. extraction, of the raw coal. The so-called solvent extraction processes for making distillate fuels include, but may not be limited to, three essential unit operations, namely, (1) extraction, (2) separation of extract from undissolved solid residue, and (3) hydrogenation of the extract. These three unit operations have been reasonably well demonstrated, if not in commercial practice, at least in pilot plants, the operation of which has been described in written publications. Many patents have been issued, especially in recent years, describing such processes. Illustrative of these are my own patents, U.S. Nos. 3,018,241; 3,018,242; 3,117,921; 3,143,489; 3,612,594; and 3,184,401.

The commercial feasibility of any solvent extraction process for converting coal to low-sulfur liquid fuel is critically dependent upon the amount and cost of the hydrogen requirements. The amount of the hydrogen requirements will be determined by the coal selected and the three unit operations just mentioned. However, the cost of the hydrogen is another matter. The hydrogen may be purchased or it may be manufactured from the by-products or rejects of the aforementioned unit operations.

In my above-cited Pat. No. 3,018,241, for instance, I described the production of hydrogen by the devolatilization of char obtained by carbonization of the solid residue separated from the extract. Additional hydrogen must be introduced from outside the system. U.S. Pat. No. 3,583,900, granted June 8, 1971, to J. G. Gatsis, reports the use of the char obtained by the carbonization of residue from extraction to make hydrogen by the water-gas reaction. Others have recognized that the residue from the extraction operation may well serve as a feedstock for making hydrogen.

However, the use of residue from solvent extraction is not without its attendant problems, mostly stemming from the manner and extent of separation used to separate extract from solid residue. Generally, such separation is effected by filtration, or centrifugation, or sedimentation (settling), or by use of hydrocyclones. The extent of separation depends on the quality of extract desired as well as on subsequent handling of the residue. Sometimes, even when the residue is separated to "dryness," that is, with essentially no adherent extract, it is not easy material to handle because of its caking tendency. This tendency is obviously promoted by incomplete separation, as with sedimentation or by use of hydrocyclones. The only commercially proven processes for making hydrogen from carbonaceous solids require a weakly caking or non-caking carbonaceous solid.

Thus, the primary object of the present invention is to provide an improved process for the conversion of coals to fuels wherein solvent extraction is employed for the partial conversion of the coals; and, in its preferred embodiment, to provide a solution to the problem of using the residue from solvent extraction as a feedstock to gasifiers requiring essentially non-caking feedstocks.

SUMMARY OF THE INVENTION

The present invention is an improvement in the process for partial conversion of coal by solvent extraction which comprises, in its broadest aspects, the following essential steps:

(1) Partial separation of the extraction product at an elevated temperature in a separation zone to yield

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- (a) a low solids-containing product which is useful per se as a fuel, or as an intermediate in the production of liquid fuels by hydrogenation, and
(b) a high solids-containing product;

(2) Adjustment of the relative proportions of solids, solvent, and extract in said high solids-containing product to yield a pelletizable product consisting essentially of solids and a liquid binder comprising said solvent and extract;

(3) Formation of pellets from said pelletizable product in a pelletizing zone; and

(4) Induration of the pellets, concurrent with or immediately subsequent to their formation. The indurated pellets may be used per se as solid fuel or as an intermediate in the production of gaseous and liquid fuels.

GENERAL DESCRIPTION

Before describing the preferred embodiment of the present invention, a general description of the process in its broadest aspects is given below.

Partial extraction of the coal

Any coal may be used in the process of this invention, non-limiting examples of which are lignite, bituminous coal and sub-bituminous coal. The feed coal, in a finely divided state and free of substantially all extraneous water, is subjected to solvent extraction in a suitable solvent extraction zone at an elevated temperature. The solvent extraction process may be any of the processes commonly used by those skilled in the art, for example, continuous, batch, countercurrent or staged extraction; and conducted at a temperature in the range of 300 to 500° C., a pressure in the range of 1 to 6500 p.s.i.g., a residence time in the range of 1 to 120 minutes, a solvent-to-coal ratio of 1/1 to 4/1 and, if desired, in the presence of a catalyst and/or up to 50 standard cubic feet of hydrogen per pound of MAF (moisture- and ash-free) coal.

Polycyclic, aromatic hydrocarbons which are liquid at the temperature and pressure of extraction are generally recognized to be suitable solvents for the coal in the extraction step. At least a portion of the aromatics may be partially or completely hydrogenated, whereby some hydrogen transfer from solvent to coal may occur to assist in the breakdown of the large coal molecules. Mixtures of the hydrocarbons are generally used and these may be derived from subsequent steps in the process of this invention. Other types of coal solvent, such as oxygenated aromatic compounds, may be added for special reasons, for example, to improve the solvent power, but the resulting mixture should be predominantly of the type mentioned.

The coal and the solvent are maintained in intimate contact at the elevated temperature until up to about 80 weight percent of the MAF feed coal has been converted, i.e. depolymerized, hydrogenated, etc., to a product soluble in the solvent at the temperature employed. The product, for want of a better term, is called "extract" even though more transpires in the conversion than simply dissolving the coal. Generally, in order to attain depths of extraction above 50 weight percent, hydrogen must be added to the coal during extraction. The hydrogen may be added by means of a hydrogen-transfer solvent of the type mentioned above, or simply as hydrogen gas.

Partial separation of the extraction product

The objective of the partial separation step is to provide (a) a low solids-containing product consisting essentially of extract and solvent, with such solids as may unavoidably be present, and (b) a high solids-containing product consisting essentially of extract, solvent and solids, with the solids in the predominant amount. The partial separation may be accomplished by sedimentation, use of hydrocyclones, filtration, centrifugation, or by a combination of two or more of these unit operations. If complete, or substantially complete separation is effected, as might

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be the case if filtration is used, then extract, and perhaps some high-boiling or non-distillable liquid, must be added to the solids to serve as binder, as will be more fully described later. In any case, separation is effected at elevated temperatures at or close to the temperature maintained in the extraction step.

Cooling of the extraction product may result in selective precipitation of some of the higher molecular weight portions of the extract. At times, this may be done deliberately to improve the ease of separation of the solids from the extract and to improve the quality of the extract produced. The above type of selective precipitation process may be further intensified, if desired, by addition of a saturated, i.e. paraffinic or naphthenic, solvent. The precipitated extract serves also as part of the binder required in the subsequent pelletizing step.

The low solids-containing product is separately recovered for use per se as a fuel, or as an intermediate in the production of liquid fuels by hydrogenation.

Adjustment of the relative proportions of solids, solvent and extract in the high solids-containing product

This step is the key step of my improved process. The primary objective of this step is to provide a high solids-containing product which is pelletizable in a pelletizing zone. The product, in order to be pelletizable, must contain sufficient binder to permit formation of the pellets. The extract itself is a viscous non-distillable material containing little or no material distillable at 400° C. and atmospheric pressure and having a softening point well above room temperature. It serves as the principal source of binder. However, the high molecular weight portion of the solvent may also serve as part of the binder. In addition, binder may be added extraneously to supplement the extract and solvent. For instance, high boiling residual oils may be used, or even coking coal, in limited amounts. When the term "extract" is used herein, it is intended to include extract itself and any extraneously added binder.

The composition of the high solids-containing product is adjusted with two objectives in mind; the first to provide a composition which is flowable and the second to provide a composition which is pelletizable in the pelletizing zone. If the conditions maintained in the pelletizing zone are such as to cause volatilization of the solvent, then the feed to the pelletizing zone may be richer in solvent. But if the conditions in the pelletizing zone do not cause volatilization of solvent, then the feed must be of the necessary composition for pelletization. The pelletizable composition, that is the composition excluding any solvent that may be vaporized in the pelletizing zone, is as follows:

	Weight percent
Extraction residue solids -----	55-75
Extract and solvent -----	25-45

where the extract is at least 30 weight percent of the extract-solvent mix, and is preferably greater than 50 weight percent. The pellets will, of course, have substantially the same composition unless the pelletization is conducted under carbonizing conditions which result in production of some gas and tar.

To obtain the desired proportions of solids, solvent and extract in the feed to the pelletizing zone generally requires adjustment of the composition of the high solids-containing product after it leaves the separation zone. However, part of the adjustment may be achieved in the separation zone itself if it is necessary to increase the amount of extract in the high solids-containing product. The necessary additional extract may be obtained by the addition of a precipitating solvent to the separation zone. Generally, the problem of adjustment is twofold, one of removal of extract, and the other of removal of solvent. The removal of solvent may be readily accomplished by distillation. The removal of extract to the extent desired may be effected by washing with solvent. Adjustment of

the relative proportions of the three ingredients may also be effected by adding recycled off-size pellets made in the pelletizing zone or from other sources. Generally, such pellets will have the same composition as the rest of the feed to the pelletizing zone except for losses in the pelletizing zone due to distillation. If pelletizing is conducted under carbonizing conditions, then the recycled pellets would constitute part of the solids fed to the pelletizing zone, and as such, would be considered as part of the extraction residue solids for the purpose of the above-mentioned formulation of solids and binder.

Formation of pellets

The primary objective of the pelletizing zone is to form pellets out of the flowable mass received from the separation zone after suitable adjustment of the composition as described above. The pellets may be made by any one of the many known pelletizing processes, for example, briquetting, extrusion, or agglomeration, under carbonizing or non-carbonizing conditions at a temperature above the softening point of the binder. The process selected should be one which is adapted to be used at an elevated temperature at which the extract is fluid. The size of the pellets is generally between 14 mesh Tyler Standard screen and two inches, suitable for use as a fuel or in subsequent treatments.

Induration of the pellets

To be useful as fuel or as reactant, the pellets must be sufficiently hard to permit handling without breakage or attrition. If the pellets are formed in the pelletizing zone under carbonizing conditions, that is at a temperature above 750° F., the resulting pellets will be sufficiently hard to permit handling for almost any use. However, if no carbonization occurs in the pelletizing zone, then congelation of the pellets subsequent to the pelletizing step is required. The extract will solidify upon cooling below the softening point of the solution of extract and solvent which is generally above 300° F. The resulting congealed pellets are of sufficient hardness to be handled for most uses as a fuel or reactant.

PREFERRED EMBODIMENT-PRODUCTION OF LOW-SULFUR LIQUID FUELS

For a better understanding of the present invention, its objects and advantages, reference should be had to the following description of the preferred embodiment of the present invention and to the accompanying drawing which illustrates schematically the preferred embodiment.

The preferred embodiment of the present invention comprises:

(1) a solvent extraction zone **10** (sometimes called Extractor) wherein a high-sulfur coal is extracted;

(2) a separation zone **20** (sometimes called Separator) wherein the extract (sometimes called "overflow") is partially separated from the residue (sometimes called "underflow");

(3) a distillation zone **30** (sometimes called a Still) wherein the overflow from the Separator **20** is distilled to recover solvent for recycle to the Extractor;

(4) a Washing Zone **40** and a Preheater **50** which, in combination, serve to adjust the composition of the underflow from the Separator **20** to make a pelletizable flowable mass;

(5) an agglomeration zone **60** (sometimes called Pelletizing Kiln) consisting essentially of a rotary kiln, usually slightly inclined from the horizontal, wherein pellets are formed from the suitably "adjusted" underflow;

(6) an Induration Zone **70** consisting of a water quench through which the pellets are passed to cool them and thereby congeal them to non-caking solids;

(7) a Gasifier **80** where a hydrogen-containing gas is produced from the pellets made in the Pelletizing Kiln; and

(8) a hydrogenation zone **90** (sometimes called Hydro Plant) wherein the extract is hydrogenated to yield low-sulfur liquid products suitable for use as liquid fuel.

Feed coal

A high-sulfur coal is preferably used in the process of this invention. Preferably, the coal fed to the process is one having a volatile matter content of at least 20 weight percent, for example, a high volatile bituminous coal such as Pittsburgh Seam coal. A typical composition of a Pittsburgh Seam coal suitable for use in the process is shown in Table I below.

TABLE I

15	Proximate analysis:	Wt. percent MF ¹ coal
	Volatile matter -----	39.3
	Fixed carbon -----	47.7
	Ash -----	13.0
20	Ultimate analysis:	Wt. percent MAF ² coal
	Hydrogen -----	5.5
	Carbon -----	80.8
	Nitrogen -----	1.4
	Oxygen -----	7.5
25	Sulfur -----	4.8
		100.0

¹ MF means moisture-free.

² MAF means moisture- and ash-free.

The feed coal is preferably ground to a finely divided state, for example, minus 14 mesh Tyler Standard screen, and is freed of substantially all extraneous water before introduction into the Extractor **10**.

(1) Solvent extraction zone

The high-sulfur coal is introduced into the Extractor **10** via a conduit **12**. Solvent is introduced into the Extractor via a conduit **14**. The coal and the solvent react therein to yield the desired coal extract.

The preferred solvent extraction process is a non-catalytic, continuous, countercurrent process conducted in a vertical cylindrical vessel, at a temperature in the range of 300 to 500° C., a pressure in the range of 1 to 6500 p.s.i.g., a residence time in the range of 1 to 120 minutes and a solvent-to-coal ratio of 1/1 to 4/1.

The preferred solvent for the coal is a polycyclic, aromatic hydrocarbon which is liquid under the temperature and pressure of extraction, and contains partially or completely hydrogenated aromatics. It is naturally derived from hydrogenation of the extract. It usually has a relatively wide distillation range with an initial atmospheric boiling point of about 450° F. and a final boiling point of 800° F. or even higher.

The coal and the solvent are maintained in intimate contact within the Extractor **10** until the solvent has extracted, i.e. converted or dissolved, 50 to 80 weight percent of the MAF feed coal. In order to attain such depths of extraction, hydrogen must be added to the coal during extraction. In this preferred embodiment, hydrogen is added by means of the solvent described above which is hydrogenated from time to time as needed.

(2) Separation zone

Following extraction, the mixture of solvent, extract and residue is conducted rapidly, so as to avoid excessive cooling of the mixture, through a conduit **16** to the Separator **20**. The preferred separation system is sedimentation (settling). Settling is conducted at or about 600° F. While settling may be conducted so as to effect substantially complete separation of liquid and solids, it is preferred, for the purpose of this invention, to assure an underflow which is a flowable slurry, that is, one having about 45 to 55 weight percent solids. This flowable slurry is withdrawn from the Separator **20** through

I claim:

1. In a coal conversion process which includes partial extraction of the coal by a solvent to yield a mixture of coal extract, solvent and undissolved carbonaceous residue, the improvement which comprises:
 - (a) effecting separation of said mixture into at least two parts, the first part being a low solids-containing product containing said coal extract and solvent, and the second part being a high solids-containing product containing said coal extract, solvent, and undissolved carbonaceous residue;
 - (b) adjusting the relative proportions of said solid residue, solvent, and coal extract in said second part to yield a flowable mass which is pelletizable in a pelletizing zone wherein said extract and solvent serve as the principal source of liquid binder;
 - (c) forming pellets from said pelletizable mass in a pelletizing zone; and
 - (d) subjecting said pellets to induration.
2. The process according to claim 1 wherein said second part produced in the separation step (a) is a flowable slurry.
3. The process according to claim 1 wherein the feed coal has a size less than 14 mesh Tyler Standard screen, and the pellets formed in the pelletizing zone are between 14 mesh Tyler Standard screen and two inches.
4. The process according to claim 1 wherein the pellets are subjected to gasification in a fixed bed gasifier by reaction with steam to form CO and H₂, and the hydrogen produced thereby is used to hydrogenate at least a portion of the coal extract contained in said first part produced in step (a).
5. The process according to claim 1 wherein said induration is effected by conducting pelletization under carbonizing conditions.
6. The process according to claim 1 wherein said induration is effected by congelation following pelletization in said pelletizing zone.
7. In a coal conversion process which includes partial extraction of the coal by a solvent to yield a mixture of coal extract, solvent and undissolved carbonaceous residue, the improvement which comprises:
 - (a) effecting separation of said mixture into at least two parts, the first part being a low solids-containing product containing said coal extract and solvent, and the second part being a high solids-containing product containing said coal extract, solvent and undissolved carbonaceous residue;
 - (b) adjusting the relative proportions of said coal extract, solvent and residue in said second part to yield a flowable mass which is pelletizable in a pelletizing zone, the composition of said mass in said pelletizing zone being 55-75 weight percent of solids and 25-45 weight percent of liquids, wherein said coal extract is at least 30 weight percent of said liquids;
 - (c) forming pellets from said pelletizable mass in said pelletizing zone; and
 - (d) subjecting said pellets to induration.
8. The process according to claim 7 wherein the pellets are formed by tumbling said pelletizable mass in a rotating kiln.

9. The process according to claim 7 wherein said induration is effected by conducting pelletization under carbonizing conditions in said pelletizing zone.
10. The process according to claim 7 wherein said induration is effected by congelation following pelletization in said pelletizing zone.
11. A process for making liquid fuels from coal which comprises:
 - (a) subjecting the coal to treatment with a solvent, whereby a mixture of extract and undissolved hydrocarbonaceous solid residue is obtained;
 - (b) effecting separation of said mixture into at least two parts, the first part being composed principally of extract in solvent, and the second part being composed principally of solid residue, extract, and solvent;
 - (c) subjecting at least a portion of the extract in said first part to hydrogenation, whereby a liquid fuel is obtained;
 - (d) adjusting the composition of said second part to have the following relative proportions of solid residue, extract and solvent,

	Weight percent
Residue -----	55-75
Extract plus solvent -----	25-45
Solvent -----	35-30

- wherein the extract is at least 30 weight percent of the extract-solvent mix;
- (e) forming pellets from said adjusted second part under non-carbonizing conditions;
 - (f) cooling said pellets to effect congelation, and thereby induration;
 - (g) subjecting said pellets to gasification by treatment with steam to form CO and H₂, and
 - (h) recovering H₂ from the gaseous product of step (e) and using at least a portion thereof to effect hydrogenation in step (c).
12. The process according to claim 11 wherein the adjustment in step (d) is effected, in part at least, by selective removal of extract and solvent.
 13. The process according to claim 11 wherein the pellets are formed by tumbling the adjusted second part in a rotating kiln.
 14. The process according to claim 13 wherein the pellets are formed in the rotary kiln at a temperature between 400 and 700° F.
 15. The process according to claim 14 wherein the pellets are thereafter subjected to carbonization in a separate zone.

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