

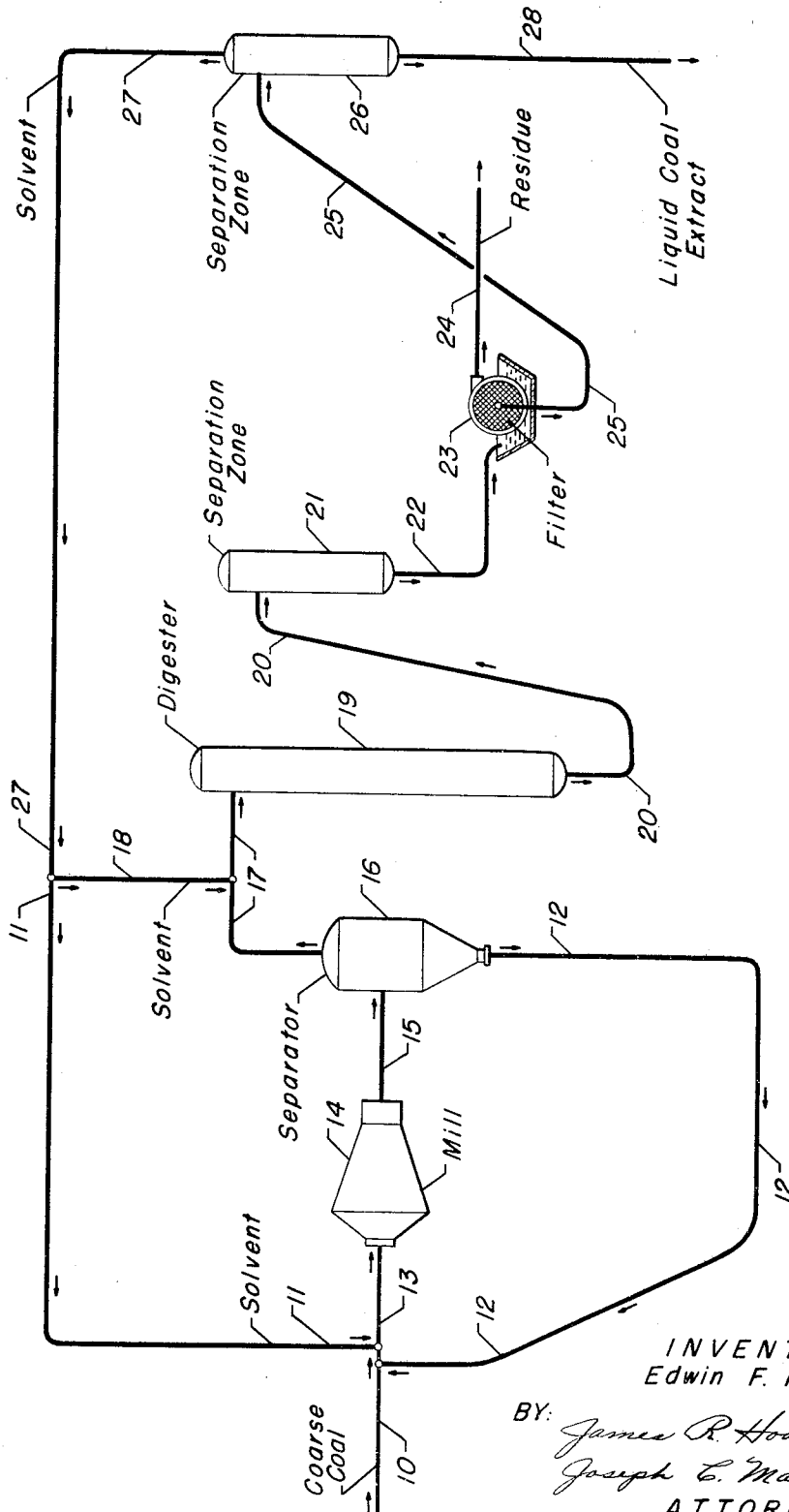
April 7, 1970

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3,505,202

SOLVENT EXTRACTION METHOD

Filed June 26, 1967



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3,505,202

SOLVENT EXTRACTION METHOD

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Filed June 26, 1967, Ser. No. 648,871

Int. Cl. C10g 1/00

U.S. Cl. 208—8

10 Claims

ABSTRACT OF THE DISCLOSURE

Method for the liquefaction of coal via solvent extraction using a hydrogen-donor selective solvent. The method contacts pulverized coal with a solvent, such as Tetralin, to produce a liquefied coal extract. Hydrocarbons useful as fuel and/or chemicals may be obtained from the liquid coal extract.

BACKGROUND OF THE INVENTION

This invention relates to a solvent extraction method. It also relates to a method for liquefying coal using a selective solvent.

It has long been known that hydrocarbon gases, liquids, and pitch, and, the chemicals derived from or allied to these hydrocarbons, may be obtained in some form from coal which is mined from the earth. Usually, the prior art has employed destructive distillation or other gasification processes for the conversion of coal into these more valuable and useful products. Recently, the prior art has used high pressure hydrogenation of coal to make this conversion. Other satisfactory methods for the obtaining of useful fuels and chemicals from coal have involved the solvent extraction technique whereby the coal is contacted with a selective solvent which acts as a hydrogen donor for supplying sufficient hydrogen to the coal to aid in converting it into a liquid phase. Following the solvent extraction step, the prior art schemes have utilized various recovery procedures, such as hydrogenation of the liquid coal extract for increasing its value and utility together with retorting or coking of the residual materials obtained from the solvent extraction step to still further convert these coal-derived products into more valuable products.

Since it is clear to those skilled in the art that the vast mineral reserves of bituminous coal represent an extremely important supply of energy, it would be desirable to improve upon the prior art processes in order to reduce the cost of obtaining typically petroleum-type products from coal.

SUMMARY OF THE INVENTION

Therefore, it is an object of this invention to provide a method for the liquefaction of coal whereby valuable hydrocarbon products may be obtained therefrom.

It is a specific object of this invention to provide an improved method for subjecting pulverized coal to solvent extraction using, for example, Tetralin as the solvent.

Therefore, in accordance with the practice of one embodiment of this invention, there is provided a method for the liquefaction of coal which comprises admixing lump bituminous coal with solvent and then subjecting the admixture to coal pulverization conditions.

It is another embodiment of this invention to utilize the method hereinabove wherein the solvent comprises an at least partially hydrogenated polycyclic hydrocarbons.

Still another embodiment of this invention includes the method for the liquefaction of coal which comprises the steps of: (a) admixing lump bituminous coal with a solvent comprising an at least partially hydrogenated polycyclic hydrocarbon; (b) subjecting said admixture to

coal pulverization conditions including a relatively high temperature sufficient to at least partially dissolve coal into the solvent; (c) passing the pulverized coal-solvent product into a digestion zone maintained under conditions sufficient to substantially dissolve the pulverized coal; and (d) recovering liquid coal extract from the digestion zone in high concentration.

Thus, it is to be noted from the description of the invention presented thus far that the benefits to be derived from the practice thereof are predicated on the theory that having the presence of the solvent during the pulverization step of the coal results in a substantial increase in the efficiency of the operation and, as will be more fully developed hereinbelow, results in a decreased use of solvent for obtaining the same amount of liquid coal extract.

It is believed that the benefits obtained from the practice of this invention are predicated on the hypothesis that at the point of shear for the crushing and grinding of the coal, the shear site is extremely reactive and hydrogen, therefore, can be transferred into that site more easily than if the coal is pulverized prior to contact with the solvent. In addition, the small particles of coal which are sheared away from a large lump immediately expose not only the highly reactive shear site to the solvent, but also exposes an extremely large surface area to the solvent, thereby enabling these small particles of coal to almost immediately dissolve in the solvent and become a part of the liquid coal extract. While not desiring to be limited by this theory, the practice of this invention is at least explained to those skilled in the art so that future work may be used along these lines to even further improve upon the inventive concepts contained herein.

Additionally, there has been some discussion in the prior art that the presence of oxygen or oxygen compounds on the surface of the coal makes it difficult for the coal to react properly with the suitable solvents for the conversion thereof into liquid coal extract. Therefore, by pulverizing or crushing the coal in the presence of a liquid solvent, oxygen compounds or the presence of oxygen have been excluded from the highly reactive shear sites along the coal thereby enabling the transfer of the hydrogen from the solvent to the coal to become of significantly increased efficiency.

The coal preferred for use in the practice of the present inventive method is of the bituminous type, such as Pittsburgh Seam Coal. More preferably, however, the bituminous coal is a high volatile content coal having a volatile content greater than about 20% by weight of the m.a.f. coal (moisture and ash-free coal).

The extraction of coal by means of solvent has been proposed by definition as partial conversion of the coal since not only is the coal reacted with the hydrogen which is transferred from the solvent but there is also a solution phenomenon which actually dissolves the coal, which has accepted the hydrogen into the solvent. Therefore, as used herein, the term "liquid coal extract" and "liquefied coal fraction" is intended to include the liquid product which is obtained from the solvent extraction of the coal with the selective solvent, and will be generally described on the basis of being "solvent-free," even though a portion of extract comprises hydrocarbons suitable for use as the solvent. The practice of the present invention is performed under conditions which increase the kinetics of the reaction while maintaining the components therein in primarily liquid phase; although, in some cases, it may be desirable to practice this invention in the presence of a vaporized solvent by using a vaporous pulverization technique.

Suitable solvents for use in the practice of this invention in the extraction step are those which are of the hydrogen donor type and are at least partially hydrogenated

and include naphthenic hydrocarbons. Preferably, the solvent is one which is in liquid phase at the recommended temperature and pressure for the extraction and pulverization step. Mixtures of the hydrocarbons are generally employed and, preferably, are derived from intermediate or final products obtained from subsequent processing following the practice of this invention. Typically, these solvent hydrocarbons or mixture of hydrocarbons boil between about 260° C. and 425° C. Examples of suitable solvents are tetrahydronaphthalene (Tetralin), decahydronaphthalene (Decalin), biphenyl, methylnaphthalene, dimethylnaphthalene, etc. Other types of solvents which may be added to the preferred solvents of this invention for special reasons include phenolic compounds such as phenols, cresols, and xylenols. It is also to be recognized that in some cases it may be desirable during a subsequent separation step prior to the removal of the solvent from the liquid coal extract to add an anti-solvent, such as a saturated paraffinic hydrocarbon like hexane, to aid in the precipitation of tarry and solid residues from the coal extract of the invention.

Apparatus for use in pulverizing the lump or coarse coal feed to the present invention may be of any type known to those skilled in the art. Conventional ball mills or rod mills may be used with satisfactory results. The only requirement for the apparatus in the practice of this invention is that the apparatus must be able to pulverize lump or coarse coal in the presence of significant quantities of liquid solvent without difficulty. Those skilled in the art are familiar with the kinds of apparatus for processing wet solids and the crushing and grinding thereof such that no detailed discussion of the apparatus need be presented herein. The primary requirement for crushing and grinding of the lump coal in the presence of the selective solvent is that coarse coal usually having an average particle diameter in excess of 0.08 inch and, typically, between about 0.25 and 2.0 inches must be processed thereto and reduced in size to an average particle diameter which would be of at least a —8 Tyler screen size, and preferably, would be reduced to an average particle size for —14 Tyler screen size. As used herein, the term "Tyler screen" refers in all instances to the commercial Tyler Standard Screens. The correlation between Tyler screen mesh and average particle diameter is as follows:

Tyler screen mesh:	Average diameter of particles D_{avg} in.
—8+10	0.0791
—10+14	0.0555
—14+20	0.0394
—20+28	0.0280
—28+35	0.0198
—35+48	0.0140
—48+65	0.0099
—65+100	0.0070
—100+150	0.00496
—150+200	0.0035

The conditions during the pulverization step may be varied widely according to the desires of those skilled in the art and practicing this invention. The temperature, of course, may be varied over a relatively broad range from essentially atmospheric temperature to a relatively high temperature. It is distinctly preferred in the practice of this invention that the temperature of the coal and the solvent be maintained at a relatively high temperature, say, from 300° C. to 500° C. The pressure, in similar manner, may be varied over an extremely wide range from atmospheric pressure to, say, 10,000 p.s.i.g. with a preferred pressure being about 100 p.s.i.g. or typically about 70 p.s.i.g.

The operation of the pulverizing equipment is preferably performed so that the oversized material; that is, greater in size than the minus (—) 8 Tyler screen size, be separated and returned to the apparatus for further

pulverizing. The utilization of the closed circuit technique is well known to those skilled in the art, and is preferred in the practice of this invention. Unless otherwise stated, closed circuit operation of the pulverization equipment will be deemed inherent in the practice of this invention.

The amount of solvent which is used during the pulverization step generally will range from 0.2 to 10 pounds of solvent per pound of coal. Satisfactory results may be obtained in the practice of this invention in utilizing approximately equal amounts of solvent to coal on a weight basis. The conditions during the pulverization step should be chosen such that the coarse coal is reduced in size to at least a —8 Tyler screen size and the solvent has a chance to react and dissolve the coal to an extent such that the coal particles are at least partially dissolved in the solvent.

It is an essential feature of this invention that the pulverization step be not only a mechanism for reducing the size of the coal, but also be used to at least partially dissolve the coal in the solvent. In other words, as will be more fully evident from the discussions presented hereinafter, the present invention is in some respects a two-stage solvent extraction step. In the practice of this invention the conditions chosen in the pulverization step will be such that from 10% to 40% by weight of the m.a.f. coal is dissolved in the solvent with at least an additional 50% by weight being dissolved during the subsequent digestion zone, more fully discussed hereinafter.

Following the size reduction step wherein at least part of the coal has been dissolved in the solvent and the oversized solid materials have been separated, the effluent product comprising solvent, having dissolved therein liquid coal extract, and undissolved solid coal is passed into a digestion zone which is a reaction zone for the substantial conversion of the coal into liquid coal extract. The operating conditions for the digestion zone include a temperature from 300° C. to 500° C., a pressure from atmospheric to 10,000 p.s.i.g., a solvent to coal weight ratio from 0.2 to 10, and a residence time from 30 second to 5 hours, sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal has been liquefied. It is to be noted that the temperature and pressure conditions during the digestion zone may be the same, may be higher, may be lower, or may be any different conditions during the digestion zone may be the same, may be higher, may be lower, or may be any different configuration desired by those skilled in the art over those conditions maintained in the pulverization zone. It has been found satisfactory in the practice of this invention that the temperature and pressure in the digestion zone be maintained essentially at the same level as the temperature and pressure maintained in the pulverization zone.

Since the purpose of the digestion zone is to substantially complete the conversion of the coal into a liquid coal extract, it may be desirable to add additional solvent to the zone, add a hydrogen-containing gas to the zone, and/or utilize a catalyst in the digestion zone. The catalyst used may be conventional, may be homogenous or heterogenous and may be introduced in the pulverization zone and/or digestion zone in admixture with the liquid solvent or with the solid coal. Those skilled in the art from a knowledge of the characteristics of the coal, the solvent, and the properties desired for the end-product will know whether or not it may be desirable to use any or all of these additional features in the digestion zone. Conventional hydrogenation catalyst may be desirable; such as palladium on an alumina support, or a cobalt-molybdate catalyst or any other hydrogenation catalyst known to those skilled in the art and applicable to the solvent-coal system environment maintained in the digestion zone including the use of a slurry-catalyst system.

After separation of the solvent and undissolved coal residue (and catalyst, if any from the total effluent of the digestion zone, the liquid coal extract is further processed by means known to those skilled in the art such as conventional hydrogenation treatment to convert the liquid coal extract into more valuable products, such as fuel, e.g. gasoline boiling range products, and/or chemicals, such as aromatic hydrocarbons, the utility of which is well known.

The invention may be more fully understood with reference to the appended drawing which is a schematic representation of apparatus for practicing one embodiment of the present invention.

DESCRIPTION OF THE DRAWING

Referring now to the drawing, coarse coal having an average particle diameter, generally, in excess of 0.08 inch is introduced into the system via line 10. A suitable selective solvent for the coal is introduced into admixture with the coarse coal from line 11, by means more fully hereinafter discussed; the oversized solid material from the pulverizing zone is also preferably returned to the pulverizing zone via line 12. The entire admixture of coarse coal and solvent is passed via line 13 into mill 14 which conventionally may be of the ball mill type.

Suitable pulverization conditions including a temperature from 300° C. to 500° C. is maintained in mill 14 such that the coarse coal is reduced to an average particle diameter between 0.08 and 0.04 inch and at least a portion of the coal, say from 10% to 40% by weight is dissolved into the solvent.

The effluent from mill 14 containing solvent having dissolved therein the liquid coal extract, undissolved coal of proper small particle size, and undissolved coal of oversize is passed via line 15 into separator 16 which may be of the cyclone type. Conditions are maintained in separator 16 whereby the oversize coal particles, preferably in admixture with at least a portion of the liquid material, is removed via line 12 and returned to mill 14 in a manner previously discussed.

The solvent having dissolved therein the liquid coal extract plus undissolved pulverized coal is passed via line 17 into digestion zone 19 which may be of a jacketed, stirred-type vessel. Added solvent, if any, may be introduced to the system via line 18 in an amount sufficient to maintain the solvent to coal ratios at the desired levels both in digester 19 and mill 14. Control of the solvent dosage to mill 14 will be more fully discussed hereinafter.

The entire effluent from digestion zone 19 is passed via line 20 into first separation zone 21 wherein conditions are maintained sufficient to begin settling and agglomerating the coal residues and solid materials. As previously mentioned, if desired, by means not shown, an anti-solvent such as hexane may be added to zone 21 in an effort to further aid in removing tars and solid materials from the desired solvent and liquid coal extract. An effluent stream from zone 21 is removed via line 22 and passed into filtration zone 23 which is operated in such a manner that the solid coal residue may be withdrawn via line 24 and the solvent-liquid coal extract stream may be withdrawn via line 25.

The mother liquor from the filter 23 is passed via line 25 into second separator 26 which may be of a conventional distillation column type. Suitable conditions are maintained therein such that a distillate fraction comprising lean solvent may be withdrawn via line 27 and preferably is returned to admixture with the incoming coarse coal feed from line 10, as previously mentioned. The remaining liquid coal extract is removed from separator 26 via line 28 for further processing in accordance with practices known to those skilled in the art including hydrogenation techniques for upgrading the liquid coal extract to the desired valuable product of motor fuel and/or chemicals. Means (not shown) for removing the

anti-solvent, if any, may also be incorporated in separation zone 26.

The following examples are presented to illustrate some of the advantages which may be achieved in the practice of the present invention, particularly when compared to the prior art processing scheme which in every case pulverizes the coal prior to admixture thereof with any solvent.

Example 1

10 Illustrative of a prior art scheme, a Pittsburg Seam Coal was first pulverized to an average particle diameter of -14 Tyler mesh size. The pulverized coal was treated in a solvent extraction zone with Tetralin solvent under the following conditions:

15 Temperature—380° C.
Pressure—70 p.s.i.g.
Solvent/coal—1.0
Residence time—1.0 hour

20 The yield from this extraction treatment was 57.8% by weight of liquid coal extract (solvent-free) based on the original m.a.f. coal. Thus, based on a use of 100 pounds of solvent per 100 pounds of pulverized coal, the prior art obtained about 58 pounds of liquid coal extract.

Example 2

30 Illustrative of the instant inventive method, a Pittsburg Seam Coal, coarse size, was admixed with an equal weight of Tetralin solvent and the mixture subjected to crushing and grinding in a ball mill. After separation and recycle to the mill of the oversize particles, the entire product from the ball mill including solid coal particles of -14 Tyler mesh average particle diameter, liquid extract and solvent, was passed into a digester. The following conditions were maintained for each designated step:

	Ball mill	Digester
Temperature, ° C.....	380	380
Pressure, p.s.i.g.....	70	70
Solvent/coal ratio.....	1.0	1.0
Residence time, hours.....	1.0	1.0
Liquid coal extract, ¹ percent.....	17	² 50

¹ Solvent-free basis.

² Additional.

45 It is noted that the inventive method accomplishes a significant increase in liquid coal extract under substantially the same conditions including the same amount of solvent as used in Example 1. It is further believed that the liquid coal extract obtained from the inventive process contained no more benzene-insoluble material proportionately than the extract obtained from Example 1.

PREFERRED EMBODIMENT

55 A preferred embodiment of the present invention includes a method for the liquefaction of coal which comprises the steps of: (a) admixing coarse size bituminous coal with a solvent comprising at least partially hydrogenated polycyclic hydrocarbons boiling between about 260° C. and 425° C.; (b) introducing the solvent-coarse coal admixture into a pulverization zone under conditions including a temperature from 300° C. to 500° C., pressure from atmospheric to 10,000 p.s.i.g., solvent to coal weight ratio from 0.2 to 10 sufficient to reduce said coarse coal to at least a -8 Tyler screen size and to at least partially dissolve coal into said solvent; (c) passing the pulverized coal-solvent product including dissolved coal from the pulverization zone into a digestion zone maintained under conditions including a temperature from 300° C. to 500° C., pressure from atmospheric to 10,000 p.s.i.g., solvent to coal weight ratio from 0.2 to 10, and a residence time from 30 seconds to 5 hours sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal is liquefied; (d) introducing the total effluent from the digestion zone into a separation zone under conditions sufficient to produce a solvent fraction, a liquefied coal fraction, and a

solids fraction comprising undissolved coal; and, (e) recovering said liquefied coal fraction in high concentration.

Another preferred embodiment of the present invention includes a method for liquefying coal which involves size reduction of the feed coal and solvent extraction to dissolve pulverized coal particles, the improvement which comprises pulverizing coarse size feed coal in the presence of said solvent to an average particle diameter smaller than 0.08 inch.

The invention claimed:

1. Method for the liquefaction of coal which comprises the steps of:

- (a) admixing lump bituminous coal prior to pulverization thereof with a solvent comprising an at least partially hydrogenated polycyclic hydrocarbon;
- (b) subjecting said admixture to coal pulverization conditions including a relatively high temperature sufficient to at least partially dissolve coal into said solvent during shearing of the coal;
- (c) passing the pulverized coal-solvent product into a digestion zone maintained under conditions sufficient to substantially dissolve the pulverized coal; and
- (d) recovering liquid coal extract from the digestion zone in high concentration.

2. Method according to claim 1 wherein said solvent comprises tetrahydronaphthalene.

3. Method according to claim 1 wherein said pulverization conditions include a temperature from 300° C. to 500° C.

4. Method according to claim 1 wherein said digestion conditions include the presence of a catalyst.

5. Method for the liquefaction of coal which comprises the steps of:

- (a) admixing coarse size bituminous coal prior to pulverization thereof with a solvent comprising at least partially hydrogenated polycyclic hydrocarbons boiling between about 260° C. and 425° C.;
- (b) introducing the solvent-coarse coal admixture into a pulverization zone under conditions including a temperature from 300° C. to 500° C., pressure from atmospheric to 10,000 p.s.i.g., solvent to coal weight ratio from 0.2 to 10 sufficient to reduce said coarse coal to at least a -8 Tyler screen size and to at least partially dissolve coal into said solvent during shearing of said coal;
- (c) passing the pulverized coal-solvent product including dissolved coal from the pulverization zone into a digestion zone maintained under conditions includ-

ing a temperature from 300° C. to 500° C., pressure from atmospheric to 10,000 p.s.i.g., solvent to coal weight ratio from 0.2 to 10, and a residence time from 30 seconds to 5 hours sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal is liquefied;

(d) introducing the total effluent from the digestion zone into a separation zone under conditions sufficient to produce a solvent fraction, a liquefied coal fraction, and a solids fraction comprising undissolved coal; and

(e) recovering said liquefied coal fraction in high concentration.

6. Method according to claim 5 wherein said solvent fraction of step (d) is returned to step (a) for admixture with coarse size coal as specified.

7. Method according to claim 5 wherein said solvent comprises Tetralin.

8. Method according to claim 5 wherein said coarse coal is reduced in step (b) to an average particle diameter between 0.08 to 0.04 inch.

9. Method according to claim 8 wherein from 10% to 40% by weight of coal is dissolved in the pulverization zone and at least an additional 50% by weight is dissolved in the digestion zone.

10. Method according to claim 9 wherein at least a portion of the solvent is selected from the group consisting of tetrahydronaphthalene, decahydronaphthalene, biphenyl, methylnaphthalene, and dimethylnaphthalene.

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