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(54) **PRETREATMENT OF COAL**

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(57) **ABSTRACT**

The present invention is directed toward a method of solubilizing coal. The method includes providing coal and providing an oxoacid ester of phosphorus or a mixture of an oxoacid of phosphorus and an alcohol. A blend of the coal, the oxoacid ester of phosphorus or the mixture of the oxoacid of phosphorus and alcohol is formed. The blend is then treated under conditions effective to solubilize the coal.

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## PRETREATMENT OF COAL

[0001] This application claims benefit of the priority date of U.S. Provisional Patent Application Ser. No. 61/025,187, filed Jan. 31, 2008, which is hereby incorporated by reference in its entirety.

[0002] The subject matter of this application was made with support from the United States Government under Department of Energy, Grant No. DE-AC02-06CH11358. The U.S. Government has certain rights.

## FIELD OF THE INVENTION

[0003] The present invention relates to solubilization of coal.

## BACKGROUND OF THE INVENTION

[0004] In the study of coal structure, organic solvents are often used to extract coal components. These solvents include carbon disulfide, N-methyl-2-pyrrolidinone, pyridine, tetrahydrofuran, and tetracyanoethylene which are used separately or in combination (Shui, H. et al., *Fuel*, 85: 1798 (2006) and references therein; Larsen, J. *Energy & Fuels*, 4:107 (1990) and references therein; Takanohashi, T. et al. *Energy & Fuels*, 9: 788 (1995) and references therein; Liu, H.-T. et al. *Energy & Fuels*, 7: 1108 (1993) and references therein). The extraction of coals with pyridine is also an operation frequently used in the coal industry.

[0005] Early in the coalification process, formation of low-grade coals, such as lignite occurs. These coals have relatively high contents of partially coalified plant lignins compared with higher grade coals such as bituminous, sub-bituminous and anthracite coals which have higher carbon and lower oxygen contents.

[0006] Lignite deposits frequently harbor methanogenic bacteria which are able to convert the coal to methane. As is typical with bacterial processes, however, the production of methane is slow. It is desirable, therefore, that a solvent system be developed to solubilize coal in such a manner as to allow methanogenic bacteria greater access to the coal material, without causing significant toxicity to the bacteria.

[0007] Methods for the degradation of cellulosic materials to oligosaccharides and sugar alcohols aimed at facilitating ethanol production continue to be the subject of wide and intense interest. Such methods include cellulose treatment with enzymes, mainly cellulases and hemicellulases (Demain, A. L., et al., *Microbiol. Molec. Biol. Rev.* 69: 124 (2005); Fan, L. T., et al., *Cellulose Hydrolysis*, Springer, Berlin (1987); Zhang, Y. P., et al., *Biotechnol. Bioeng.*, 88: 797 (2004)), mineral acids (Mok. W. S., et al., *Ind. Eng. Chem. Res.*, 31: 94 (1992)), bases (Ishida, M., et al., *J. Chem. Technol. Biotechnol.*, 80: 281(2005)), supercritical water (Sasaki, M., et al., *Ind. Eng. Chem. Res.* 39: 2883 (2000)), hot water in the presence of a strongly acidic cation exchange resin (Kim, Y. M., et al., BIOT-323, Abstracts of Papers, 225<sup>th</sup> ACS national Meeting, New Orleans, La., Mar. 23-27(2003); and Ladisch, M. R., et al., AGFD-103, Abstracts of Papers, 225<sup>th</sup> ACS national Meeting, New Orleans, La., Mar. 23-27, 2003)), hot water solutions of lanthanide salts (Japanese Patent application JP 2002085100), and, more recently, platinum or ruthenium-supported catalysts that accomplish conversion to sugars (Fukuoka, A., et al., *Angew. Chem. Int. Ed.*, 45: 5161(2006)).

[0008] Approaches to simple disruption of the hydrogen bonds in cellulose have also been described. Examples include hot water treatment (Kobayashi, N., et al., World Congress of Chemical Engineering, 7<sup>th</sup>, Glasgow, United Kingdom, Jul. 10-14, 2005), pH controlled hot water treatment (Mosier, N., et al., *Biores. Technol.*, 96: 6, 673-686 (2005); and Mosier, N. S., et al., *Appl. Biochem. & Biotech.*, 125: 77-85 (2005)), extrusion/explosion processing of ammonia-impregnated fibers (AFEX) (Dale, B. E., et al., *Appl. Biochem. Biotechnol.* 77-79 (1999); and Liu, N., et al., "Research Progress of Converting Lignocellulose to Produce Fuel Ethanol", 25: 3, 19-22 (2005)), steam explosion (Sun, X. F., et al., *Carbohydr. Res.*, 340: 97-106 (2005); Josefsson, T., et al., *Holzforsch*, 56: 3, 289-297(2002); Jain, R. K., et al., CELL-041, Book of Abstracts, 218<sup>th</sup> ACS National Meeting, New Orleans, Aug. 22-26, 1999; and Wu, M. M., et al., *Appl. Biochem. Biotechnol.*, 77-79 (1999)), ultrasound treatment (Yang, K., et al., *Biotechnol. Prog.*, 20:1053 (2004)), and dissolution in ionic liquids (Zhu, S., et al., *Green Chem.* 8: 325 (2006)). The use of mixtures of electron-donor solvents with nitrogen oxides, lithium chloride, triethylamine oxide, methylmorpholine oxide, trifluoroacetic acid, orthophosphoric acid, and aqueous solutions of zinc chloride for dissolving cellulose, has been reviewed (see Grinshpan, D. D. B., "Novel Processes for Production and Processing of Cellulose Solutions", Editor: Sviridov, B. B. *Khimicheskie Problemy Sozdaniya Novykh Materialov I Tekhnologii*, 87, Belorusskii Gosudarstvennyi Universitet, Minsk (1998)).

[0009] In addition to dissolution of cellulosic materials in some of the aforementioned media, some chemical derivatization can and probably does occur, as in the cases of trifluoroacetic and orthophosphoric acids to form trifluoroacetate and phosphate esters, respectively. Dissolving cellulose in an acid anhydride can lead to regioselectively functionalized polymers (El Seoud, O. A., et al., *Adv. Polymer Sci.*, 186: 103 (2005)), and regioselective esterification and etherification of glucose has been demonstrated to influence the processing and use of these products (Burkart, P., et al., *Polym. News*, 21: 155 (1996)). The synthesis of cellulose sulfonates (e.g., tosylates and mesylates) provides polymers with interesting properties as well as intermediates to new cellulosic products (Siegmond, G., et al., *Polym. News*, 27: 84 (2002)). Fatty acid esters of cellulose lead to novel bioplastics and films (Song, L., et al., *Gaofenzi Cailiao Kexue Yu Gongcheng*, 18: 11 (2002); and Satge, C., et al., *Comptes Rendus Chimie*, 7:135 (2004)). Such esters also open new synthetic possibilities for introducing functional groups into cellulose providing pathways to cellulose esters and ethers and their derivatives, as well as biologically active molecules covalently bound to cellulose (Bojanic, V., et al., *Hemisjska Industrija*, 52:191 (1998)). The reaction kinetics of the production of cellulose ethers (e.g., methyl, hydroxyethylmethyl and hydroxyethyl) have also been reviewed (see Doenges, R., *Brit. Polym. J.*, 23: 315-26 (1991)).

[0010] As a percentage of the approximately 89% dry matter in Distillers Dry Grains and Solubles (DDGS) obtained from Big River Resources, LLC, Burlington, Iowa, cellulose and starch (polyglucoses) comprise ca 16 and 5%, respectively, and the hemicelluloses (polypentoses) xylan, and arabinan comprise a total of about 13.5%.

[0011] None of these polysaccharides have appreciable solubility in water, and so it is desirable to develop reasonably mild methods for degrading and/or derivatizing these materials in such a way as to solubilize them in water, since water

is the solvent of choice for the commercial production of ethanol by enzymatic means. Thus, water solubilization of these polysaccharides and heteropolysaccharides facilitate access to them by cellulases and fermentation enzymes. A recent review (Mosier, N., et. al., *Biores. Technol.*, 96(6): 673-686 (2005)) describes desired traits in a pretreatment, including its effect on biomass surface area, cellulose crystallinity, and hemicellulose and lignin processability. A review of current pretreatment technologies is also given (Mosier, N. S., et. al., *Appl. Biochem. & Biotechnol.*, 125: 77-85 (2005)). A coordinated effort to develop leading pretreatment technologies was also reported (Wyman C. E., et al., *Biores. Technol.*, 96: 1959-1966 (2005)).

**[0012]** Phosphitylation has been developed in recent years as a technique for derivatizing carbohydrates, nucleosides, and nucleotides (Dabkowski, W., *Chem. Nucl. Acid Comp.: Collect. Symp. Series*, 7: 39-46 (2005); Dabkowski, W., et. al., *N. J. Chem.*, 29: 11 (2005); Laneman, Scott A., *Spec. Chem. Mag.*, 25(1): 30-32 (2005); Ahmadibeni, Y., et. al., *J. Org. Chem.*, 70(3): 1100-1103 (2005); Oka, N., et. al., *J. Am. Chem. Soc.*, 125(27): 8307-8317 (2003); and Parang, K., et. al., *Org. Letters*, 3(2): 307-309 (2001), although this technique has been known longer for simple alcohols (Dabkowski, W., *Chem. Nucl. Acid Comp.: Collect. Symp. Series*, 7: 39-46 (2005); Dabkowski, W., et. al., *N.J. Chem.*, 29: 11 (2005); and Watanabe, Y., et. al., *Tetrahed. Letters*, 31(2): 255-6 (1990)).

**[0013]** The present invention is directed to overcoming these and other deficiencies in the art.

#### SUMMARY OF THE INVENTION

**[0014]** One aspect of the present invention is directed toward a method of solubilizing coal. The method includes providing coal and providing an oxoacid ester of phosphorus or a mixture of an oxoacid of phosphorus and an alcohol. A blend of the coal and the oxoacid ester of phosphorus or the mixture of the oxoacid of phosphorus and alcohol is formed. The blend is then treated under conditions effective to solubilize the coal.

**[0015]** Another aspect is directed toward a method of solubilizing coal. The method includes treating coal with a mixture of (i) water and (ii) at least one member selected from the group consisting of an oxoacid ester and a thioacid ester of phosphorous under conditions effective to solubilize the coal.

**[0016]** Another aspect of the present invention is directed toward a method of solubilizing coal. The method includes treating coal with at least one of an oxoacid ester of phosphorus, a mixture of an oxoacid of phosphorus and an alcohol, or a thioacid ester of phosphorus or a mixture of an thioacid of phosphorus and an alcohol under conditions effective to solubilize at least a portion of the coal.

**[0017]** Yet another aspect of the present invention is directed toward a composition comprising solubilized organophosphorus ester derivatives of coal.

**[0018]** A further aspect of the present invention is directed toward a bioconversion method. The method includes providing the composition as described above and providing a bioconversion agent. The composition is treated with the bioconversion agent under conditions effective to bioconvert the composition.

**[0019]** The solubilizing solvent system of the present invention could be injected into the coal bed, thus avoiding conventional mining costs. For example, in a process for bioconverting coal by bacterial bioconversion, partially

“etching” away the coal surfaces in coal bed cracks would expose relatively huge coal surface areas for methanogenic bacteria to multiply, thereby considerably raising the volume of bioconversion per unit time.

**[0020]** Relatively deep coal mines can have temperatures near the boiling point of water. The solvent systems of the present invention would be very compatible with such temperatures, since the solubilizing agent operates well at elevated temperatures.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0021]** One aspect of the present invention is directed toward a method of solubilizing coal. The method includes providing coal and providing an oxoacid ester of phosphorus or a mixture of an oxoacid of phosphorus and an alcohol. A blend of the coal and the oxoacid ester of phosphorus or the mixture of the oxoacid of phosphorus and alcohol is formed. The blend is then treated under conditions effective to solubilize the coal.

**[0022]** In certain embodiments, the oxoacid ester of phosphorus is provided. In some embodiments, the mixture of the oxoacid of phosphorus and the alcohol is provided. The coal may be fully solubilized or may be partially solubilized as a result of the treating.

**[0023]** The coal may be lignite or any form or rank of coal, ranging from brown coal to anthracite.

**[0024]** The treating step may be carried out at a temperature of 0 to 200° C., preferably at a temperature of 80 to 100° C.

**[0025]** The treating step may be carried out at any pH, preferably in the range of 6 to 9. The treating step may be carried out at any pressure ranging from with a vacuum to greater than 5,000 psig.

**[0026]** The oxoacid ester of phosphorus may be an ester of phosphorous acid, phosphoric acid, hypophosphorous acid, polyphosphoric acid, or mixtures thereof.

**[0027]** The oxoacid of phosphorus may be phosphorous acid, phosphoric acid, hypophosphorous acid, polyphosphoric acid, or mixtures thereof.

**[0028]** Suitable alcohols include methanol, ethanol, ethylene glycol, propylene glycol, glycerol, pentaerythritol, trimethylol ethane, trimethylol propane, trimethylol alkane, benzyl alcohol, resorcinol, phenol, catechol, alkanol, polyol, or mixtures thereof. In a preferred embodiment the ester is a mono-acid and/or di-ester of an acid of phosphorous.

**[0029]** The blend may have any ratio of the oxoacid of phosphorus to the alcohol. Preferably, the ratio of the oxoacid of phosphorus to the alcohol is from 10:1 to 1:10.

**[0030]** The methods of the present invention can include regulating the water content of the blend before or during treating. Regulation of the water content can be carried out by removing water. Suitable techniques for doing so include molecular sieving, distillation, or adding a dehydrating agent to the blend.

**[0031]** The methods of the present invention may also include sonicating the blend during or after the treating. The methods of the present invention may also include adding a bioconversion agent to the blend after treating. Suitable bioconversion agents include methanogens.

**[0032]** Another aspect is directed toward a method of solubilizing coal. The method includes treating coal with a mixture of (i) water and (ii) at least one member selected from the group consisting of an oxoacid ester and a thioacid ester of phosphorous under conditions effective to solubilize the coal.

[0033] The oxoacid or thioacid ester of phosphorous may be formed in situ from a mixture of the appropriate acid and alcohol, i.e., alcohol and acid in the appropriate amounts are added to water to produce the ester and used for the treatment.

[0034] In certain embodiments the member is an oxoacid ester of phosphorus. In some embodiments the mixture includes an oxoacid of phosphorus and an alcohol.

[0035] The method of the present invention can include sonicating the mixture during or after said treating. The method of the present invention can also include bioconverting solubilized coal.

[0036] In certain embodiments, the bioconverting is effected with a bioconversion agent. The bioconversion agent can be a methanogen.

[0037] Another aspect of the present invention is directed toward a method of solubilizing coal. The method includes treating coal with at least one of an oxoacid ester of phosphorus, a mixture of an oxoacid of phosphorus and an alcohol, or a thioacid ester of phosphorus or a mixture of an thioacid of phosphorus and an alcohol under conditions effective to solubilize at least a portion of the coal.

[0038] In certain embodiments, the coal is treated with an oxoacid ester of phosphorus. In certain embodiments, the oxoacid ester of phosphorous is formed by mixing an oxoacid of phosphorus and an alcohol.

[0039] In certain embodiments, the coal is partially or fully solubilized as a result of the treating.

[0040] In certain embodiments, the coal is selected from the group consisting of lignite, brown coal, sub-bituminous coal, bituminous coal, anthracite, and combinations thereof.

[0041] In certain embodiments, the treating is carried out at a temperature of 0 to 200° C. In a preferred embodiment, the treating is carried out at a temperature of 80 to 100° C.

[0042] In certain embodiments, the treating is carried out at a pH range of 6 to 9.

[0043] In certain embodiments, the oxoacid ester of phosphorus is selected from the group consisting of esters of phosphorous acid, phosphoric acid, hypophosphorous acid, polyphosphoric acid, and mixtures thereof. In certain embodiments, the oxoacid of phosphorus is selected from the group consisting of phosphorous acid, phosphoric acid, hypophosphorous acid, polyphosphoric acid, and mixtures thereof. In certain embodiments, the alcohol is selected from the group consisting of methanol, ethanol, ethylene glycol, propylene glycol, glycerol, pentaerythritol, trimethylol ethane, trimethylol propane, trimethylol alkane, alkanol, polyol, and mixtures thereof.

[0044] In certain embodiments, the mixing has a ratio of the oxoacid of phosphorus to the alcohol of from 10:1 to 1:10. In certain embodiments, the methods include regulating the water content of the blend before or during said treating. In a preferred embodiment, the regulating of the water content comprises removing water. The water may be removed, for example, by molecular sieving, distillation, or addition of a dehydrating agent.

[0045] In certain embodiments, the methods include sonicating the blend during or after said treating.

[0046] In certain embodiments, the methods include treating the coal with a bioconversion agent. The bioconversion agent may be a methanogen.

[0047] Certain embodiments of the invention are treated product produced by of the methods described herein. Certain embodiments provide a composition comprising solubilized organophosphorus ester derivatives of coal.

[0048] In certain embodiments, the coal is present in a subterranean coal deposit.

[0049] In certain embodiments, the treated coal in the coal deposit is bioconverted with a bioconverting agent. The bioconversion agent is a consortium of bacteria, the consortium may include methanogens.

[0050] In certain embodiments, an aqueous solution containing at least one oxoacid ester of phosphorous is introduced into the coal bed. In certain embodiments, the oxoacid ester of phosphorus is produced in the solution from the corresponding oxoacid of phosphorus and the corresponding alcohol. The solution may contain a phosphite ester. The phosphite ester may be a diester or a monoester. In certain embodiments, the solution contains a phosphite monoester and a phosphite diester.

[0051] Yet another aspect of the present invention is directed toward a composition comprising solubilized organophosphorus ester derivatives of coal.

[0052] A further aspect of the present invention is directed toward a bioconversion method. The method includes providing the composition as described above and providing a bioconversion agent. The composition is treated with the bioconversion agent under conditions effective to bioconvert the composition to hydrocarbons and carbon dioxide. Useful bioconversion agents include methanogens. Suitable bioconversion includes formation of hydrocarbons such as methane, ethane, propane, and others, as well as carbon dioxide.

[0053] A further aspect of the present invention is directed toward solubilizing the coal as part of a process for bioconverting coal. Suitable bioconversion includes formation of hydrocarbons such as methane, ethane, propane, and others, as well as carbon dioxide. Suitable bioconversion includes formation of hydrocarbons such as methane, ethane, propane, and others, as well as carbon dioxide.

[0054] In one aspect, as known in the art, coal may be bioconverted by an appropriate consortium of bacteria that includes for example, methanogens and acetogens. Such consortium may be inherently present in the coal deposit and/or may be added to the coal seam. In addition, appropriate nutrients may be provided to the coal seam to promote the growth the bacteria present and/or added to the coal.

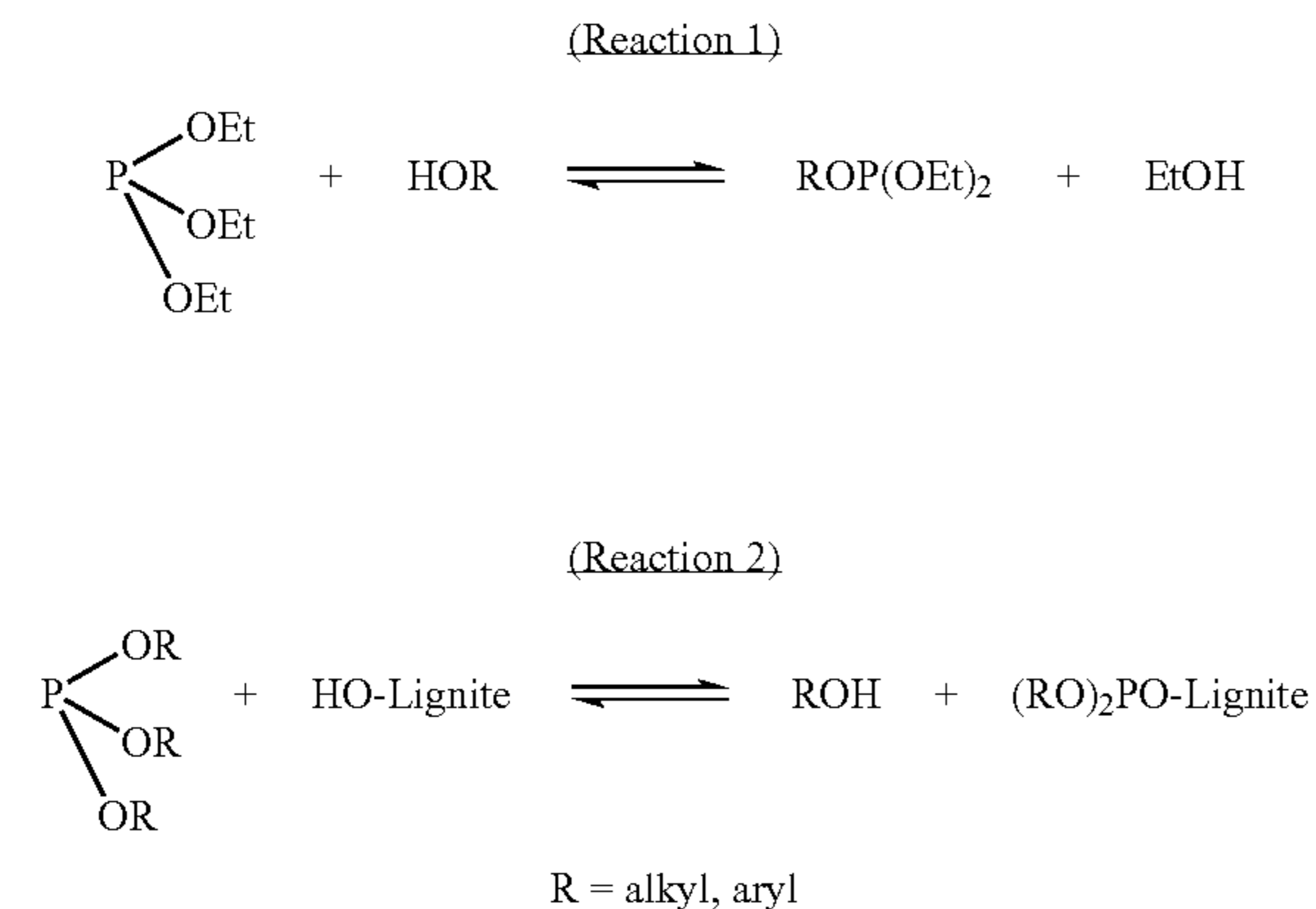
[0055] Thus, in accordance with an aspect of the invention, the solubilization solvent used in the invention is injected into a coal bed as part of the overall procedure for bioconverting coal.

[0056] The method of the present invention is useful in treating coal which renders the water-soluble product suitable, for example, for further processing such as bioconversion including formation of methane.

[0057] As used herein, coal refers to any of the series of carbonaceous fuels ranging from lignite to anthracite. The members of the series differ from each other in the relative amounts of moisture, volatile matter, and fixed carbon they contain. Of the coals, those containing the largest amounts of fixed carbon and the smallest amounts of moisture and volatile matter are the most useful to humans. The lowest in carbon content, lignite or brown coal, is followed in ascending order by subbituminous coal or black lignite (a slightly higher grade than lignite), bituminous coal, semibituminous (a high-grade bituminous coal), semianthracite (a low-grade anthracite), and anthracite.

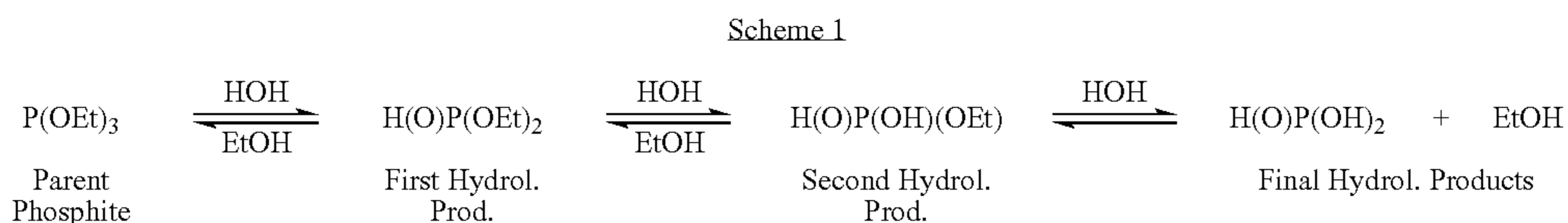
[0058] While not wishing to be bound by theory, transesterification can be driven by the release of a more volatile alcohol as in reaction 1 (below), where R is larger than an

ethyl group. However, it has been observed that phosphite esters are also capable of dissolving coal to varying degrees (depending on the source) via conversion of at least some of the hydroxyl groups to phosphite ester groups in a phosphitylation reaction (e.g., reaction 2, below).



**[0059]** There are two independent variables at work in the technology, namely, coal solubility and the degree of CO—H bond cleavage in the coal matrix. The first depends in large measure on how well the phosphite ester system cleaves the relatively weak van der Waals interactions and London forces operating to bind carbon layers together, and the second depends on how well the phosphite ester system cleaves CO—H chemical bonds for better methanogenic bacterial access. The harsher conditions proposed will be generated by employing high-power sonication, a technique increasingly used in industry.

**[0060]** It is well known that hydrolysis equilibria are reversible for many chemicals. Phosphite esters are no exceptions (see Scheme 1 for an example). Thus, this process can proceed from left to right in each equilibrium step starting with  $\text{P(OEt)}_3$  and water, or from right to left starting from phosphorous acid and ethanol at the lower right of the Scheme. Starting with 3 equivalents of EtOH and an equivalent of phosphorous acid and then removing the water (e.g., with molecular sieves) produces mainly  $\text{P(OEt)}_3$ .



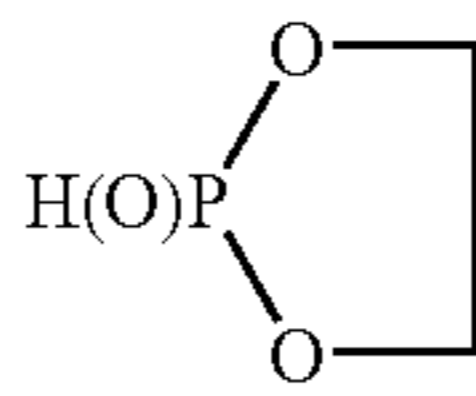
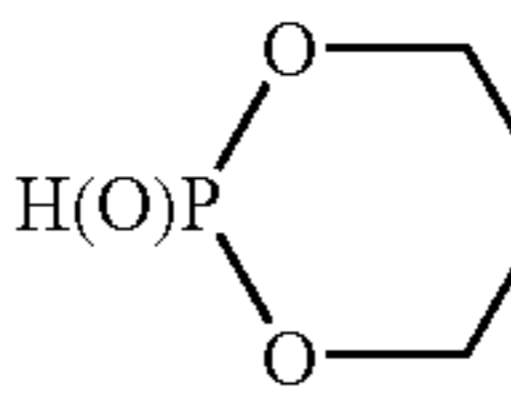
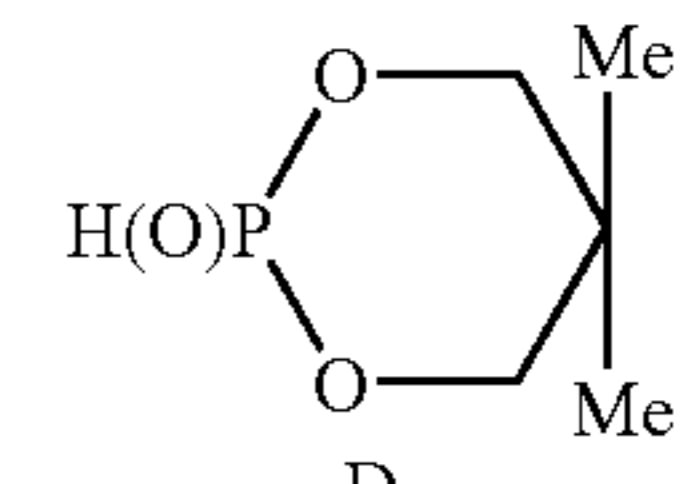
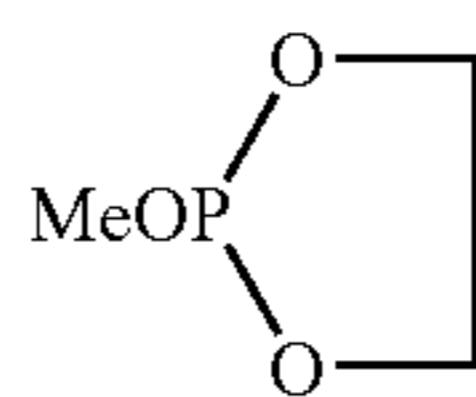
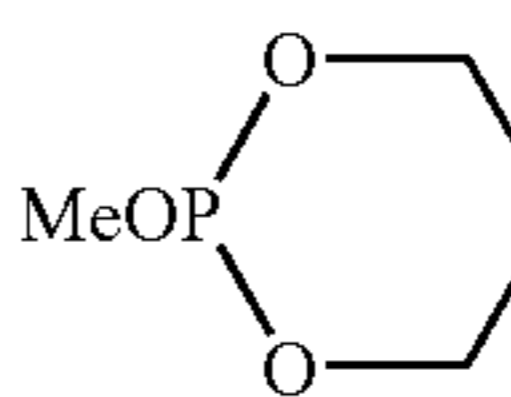
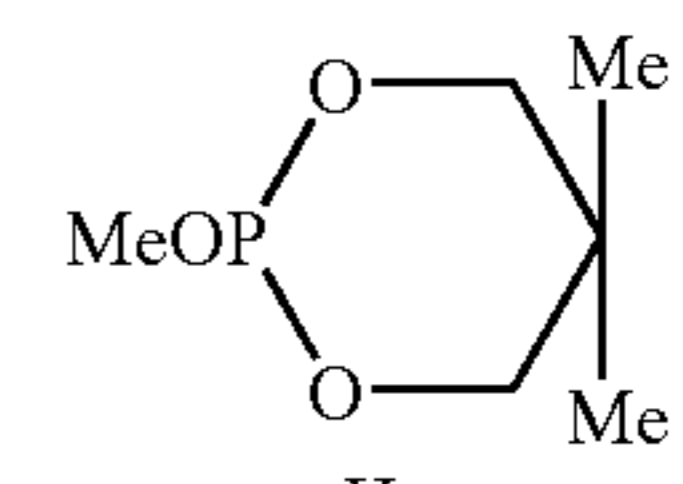
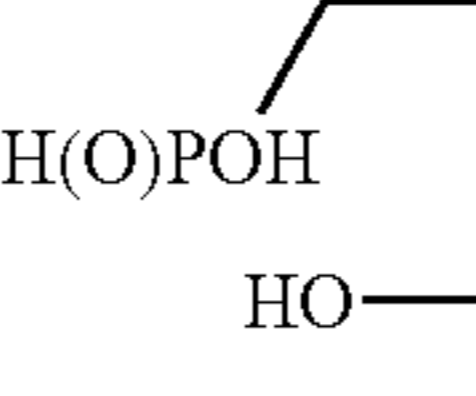
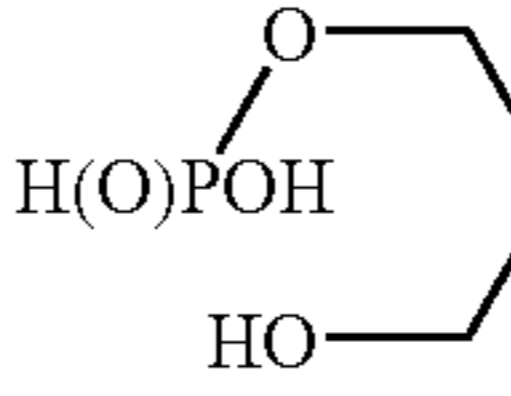
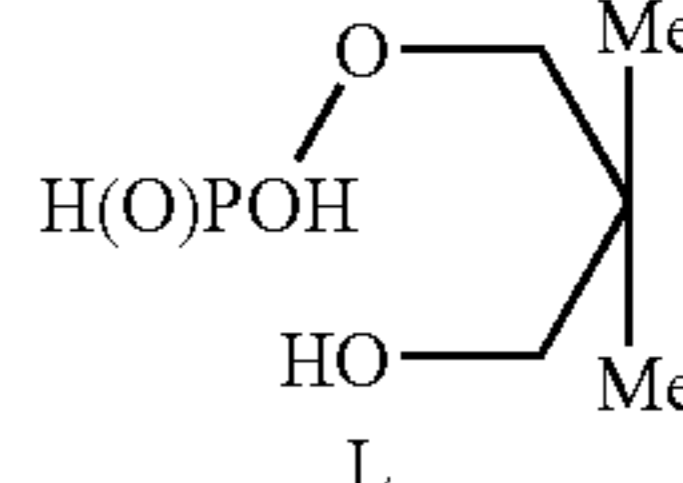
**[0061]** It is possible to start with phosphorous acid and the required alcohol to make a mixture of the first hydrolysis product and the second hydrolysis product for use as the active pretreatment medium or to start with the first hydrolysis product, and by adding the correct amount of water, make the same mixture as starting with phosphorous acid and the required alcohol.

**[0062]** It is generally possible to proceed in either direction of an equilibrium or sequence of equilibria. This process is governed by Le Chatelier's Principle.

**[0063]** It has been shown that the non-toxic first and second hydrolysis products of the toxic bicyclic phosphite  $\text{P(OCH}_2)_3\text{CEt}$  are the active species for effectively solubilizing lignins in a wide range of lignocellulosics (e.g., cellulose itself, corn stover, pine and poplar shavings, kenaf, and Distillers Dry Grains and Solubles (DDGS, which comes from the dry mill corn-to-ethanol process)).

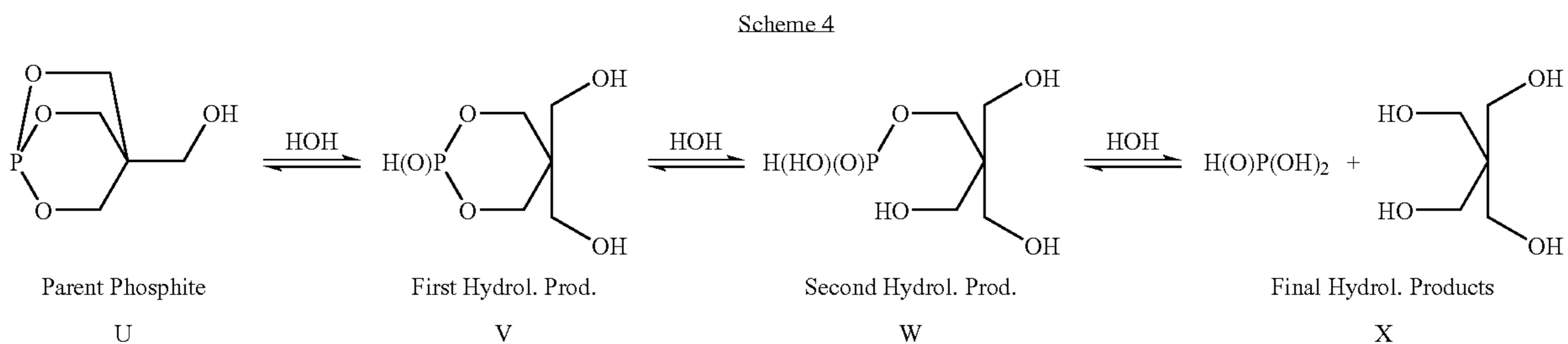
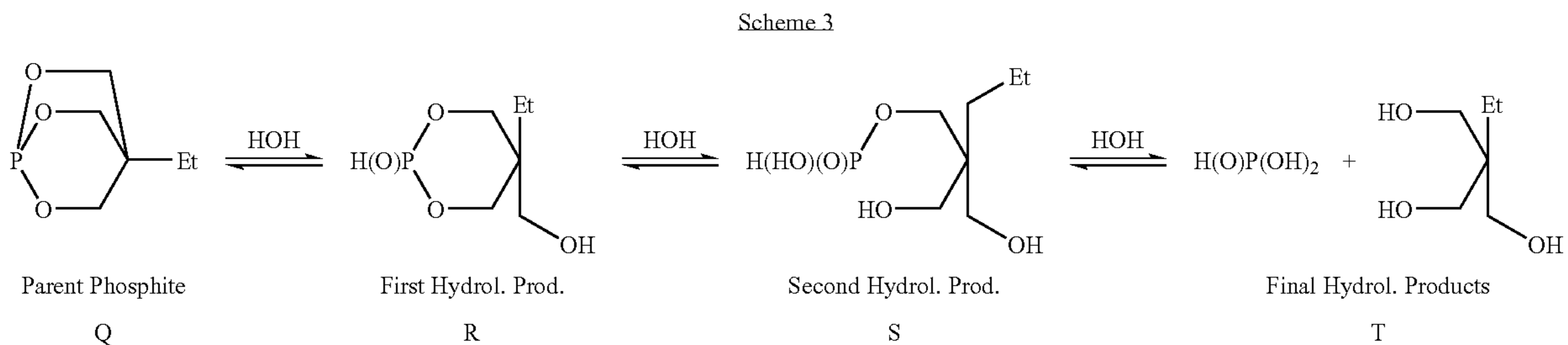
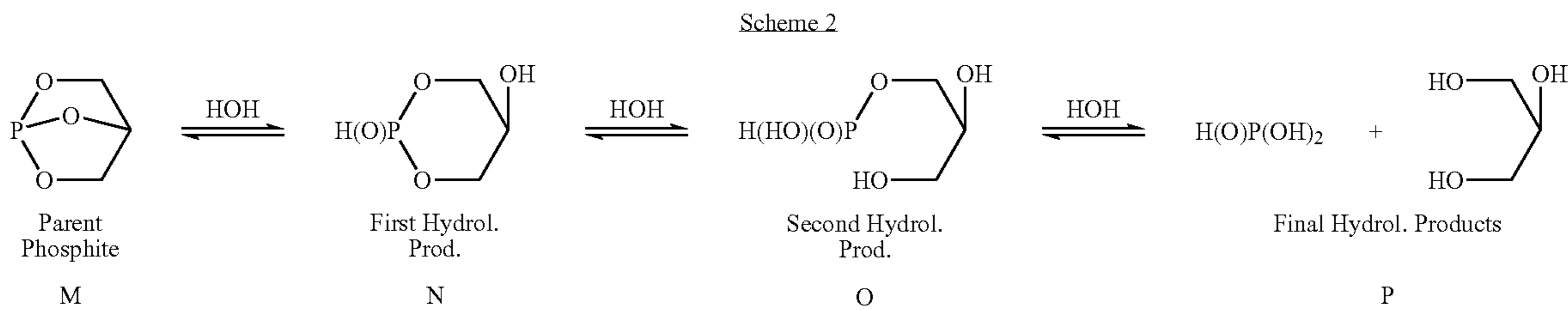
**[0064]** The alcohols (see Table 1, below) from which A, (ethanol), B (ethylene glycol), C (propylene glycol), and D (2,2-dimethylpropylene-1,3-diol) are commercially inexpensive, are manufactured in large volumes, and are of very considerable industrial importance.

TABLE 1

$\text{H(O)P(OEt)}_2$			
A	B	C	D
$\text{EtOP(OEt)}_2$			
E	F	G	H
$\text{H(O)POH(OEt)}$			
I	J	K	L

**[0065]** In Schemes 2, 3, and 4 (below), the polyols from which N, R, and V in these schemes are made are glycerol, trimethylol propane, and pentaerythritol, respectively (see Table 1, above). These polyols are very cheap and are made in large volumes (i.e. glycerol is an overly abundant byproduct of the biodiesel industry, trimethylol propane is used in polyurethane manufacture, and pentaerythritol is made in over 100 million pound quantities per year, most of which is used in alkyd resins and lubricants). Although the parent bicyclic

phosphite M in Scheme 2 is known, it would not form in the proposed reaction of glycerol and phosphorous acid, because of its strained bonds and the fact that its formation would require the presence of a catalyst. A catalyst is also required for the analogous formations of the toxic parent phosphite Q in Scheme 3 and the non-toxic parent phosphite U shown in Scheme 4. It should be noted that neither first nor second hydrolysis products for the phosphite esters in Schemes 2-4 are commercially available nor are there reports of their isolation to date.



**[0066]** Synthesis of parent phosphite esters for subsequent hydrolysis (to make the desired ratio of first to second hydrolysis products) requires expense, time and energy, which can be avoided by starting with phosphorous acid and the desired alcohol, diol, triol or tetraol, followed by removing the appropriate amount of water. Note that the parent phosphite esters by themselves are ineffective solubilizing agents. The mixture of active solubilizing agents is created by proceeding from the final hydrolysis products and working toward parent phosphites but not actually synthesizing them.

**[0067]** The first hydrolysis products A-D of the parent phosphites E-H, respectively, are effective solubilizing agents for coal. Compounds A, B, and D are commercially available, but C can be synthesized. It should be noted that A-D by themselves are also effective in the presence of some water to make a mixture of first and second hydrolysis products I-L.

**[0068]** One skilled in the art would recognize that thiophosphoryl compounds, those bearing the P=S functionality, may be substituted for related phosphoryl derivatives. Such substitution of a sulfur for one or more oxygens in a phosphorous oxoacid, oxoacid ester, a phosphoric oxoacid, or phosphoric acid ester would be possible as thiophosphorous and thiophosphoric compounds are well known. However, such sulfur containing compounds could be more expensive and pose environmental problems.

**[0069]** In one aspect of the present invention, coal is treated with an oxoacid or thioacid ester of phosphorous as part of a process for bioconverting the coal to produce one or more hydrocarbons, and in particular methane. Although the present invention is not limited thereby, it is believed that such treatment results in a more effective bioconversion as a result of (i) the breaking of bonds in the coal matrix resulting in chemical breakdown of portions of the coal and/or (ii) cleaving of bonds holding carbon layers together. Thus, the solubilization of the coal may involve one or more of a chemical break-down of the coal and/or cleaving of coal bonds. The coal that is treated and bioconverted may be part of a subterranean deposit, in which case, a solution containing the oxoacid and/or thioacid ester of phosphorus is introduced into such deposit through a suitable well. The bacterial consortia used in the bioconversion may be present in such deposit and/or added to the deposit. As previously indicated, the ester used in the treatment may be produced in the solution from the corresponding alcohol and acid.

#### EXAMPLES

##### Example 1

##### Solubility of Lignite in $P(OCH_2)_3Cet$

**[0070]** Lignite was mixed in a solution of  $P(OCH_2)_3Cet$ /water and reacted at 150 deg C. The sample was found to be

66% soluble in  $P(OCH_2)_3CEt$ /water compared to a similar sample that was found to be only 12% soluble in pyridine.

[0071] Although preferred embodiments have been depicted and described in detail herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions, and the like can be made without departing from the spirit of the invention and these are therefore considered to be within the scope of the invention as defined in the claims which follow.

What is claimed:

1. A method of solubilizing coal comprising: treating coal with at least one of an oxoacid ester of phosphorus, a mixture of an oxoacid of phosphorus and an alcohol, or a thioacid ester of phosphorous, or a mixture of a thioacid of phosphorus and an alcohol under conditions effective to solubilize at least a portion of the coal.
2. The method of claim 1, wherein the coal is treated with an oxoacid ester of phosphorus.
3. The method of claim 2, wherein the oxoacid ester of phosphorous is formed by mixing an oxoacid of phosphorus and an alcohol.
4. The method of claim 2, wherein the coal is fully solubilized as a result of said treating.
5. The method of claim 2, wherein the coal is partially solubilized as a result of said treating.
6. The method of claim 2, wherein the coal is selected from the group consisting of lignite, brown coal, sub-bituminous coal, bituminous coal, anthracite, and combinations thereof.
7. The method of claim 2, wherein said treating is carried out at a temperature of 0 to 200° C.
8. The method of claim 2, wherein said treating is carried out at a temperature of 80 to 100° C.
9. The method of claim 2, wherein said treating is carried out at a pH range of 6 to 9.
10. The method of claim 2, wherein the oxoacid ester of phosphorus is selected from the group consisting of esters of phosphorous acid, phosphoric acid, hypophosphorous acid, polyphosphoric acid, and mixtures thereof.
11. The method of claim 3, wherein the oxoacid of phosphorus is selected from the group consisting of phosphorous acid, phosphoric acid, hypophosphorous acid, polyphosphoric acid, and mixtures thereof.
12. The method of claim 3, wherein the alcohol is selected from the group consisting of methanol, ethanol, ethylene glycol, propylene glycol, glycerol, pentaerythritol, trimethylol ethane, trimethylol propane, trimethylol alkane, alkanol, polyol, and mixtures thereof.
13. The method of claim 3, wherein the mixing has a ratio of the oxoacid of phosphorus to the alcohol of from 10:1 to 1:10.

14. The method of claim 2 further comprising: regulating the water content of the blend before or during said treating.
15. The method of claim 14, wherein said regulating the water content comprises removing water.
16. The method of claim 15, wherein said removing water comprises molecular sieving.
17. The method of claim 15, wherein said removing water comprises distillation.
18. The method of claim 15, wherein said removing water comprises adding a dehydrating agent to the blend.
19. The method of claim 1 further comprising: sonicating the blend during or after said treating.
20. The method of claim 1 further comprising: treating the coal with a bioconversion agent.
21. The method of claim 20, wherein the bioconversion agent is a methanogen.
22. The treated product produced by of the method of claim 1.
23. The bioconverted, treated product of the method of claim 20.
24. A composition comprising solubilized organophosphorus ester derivatives of coal.
25. The method of claim 1 wherein the coal is present in a subterranean coal deposit.
26. The method of claim 25 wherein treated coal in said coal deposit is bioconverted with a bioconverting agent.
27. The method of claim 26 wherein the bioconversion agent is a consortium of bacteria.
28. The method of claim 27 wherein the consortium includes methanogens.
29. The method of claim wherein 28 a bacteria consortium is added to the coal deposit as a bioconversion agent.
30. The method of claim 28 wherein the coal deposit includes a consortium of bacteria.
31. The method of claim 28 wherein the coal is treated with at least one oxoacid ester of phosphorous.
32. The method of claim 31 wherein an aqueous solution containing at least one oxoacid ester of phosphorous is introduced into the coal bed.
33. The method of claim 32 wherein said oxoacid ester of phosphorus is produced in said solution from the corresponding oxoacid of phosphorus and the corresponding alcohol.
34. The method of claim 31 wherein the solution contains a phosphite ester.
35. The method of claim 34 wherein the phosphite ester is a diester.
36. The method of claim 34 wherein the phosphite ester is a monoester.
37. The method of claim 34 wherein the solution contains a phosphite monoester and a phosphite diester.

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