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(54) Title: RECOVERY OF HYDROCARBONS FROM ASPHALTENE-CONTAINING MATERIALS

(57) Abstract: In the recovery of liquid hydrocarbon from an asphaltene-containing starting material such as oil sands or tar sands, the use of a laccase and oxygen may reduce the viscosity of the liquid hydrocarbon, increase the hydrophilicity of the asphaltene, and improve the removal of heavy metals, nitrogen and sulfur from the liquid hydrocarbon.

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RECOVERY OF HYDROCARBONS FROM ASPHALTENE-CONTAINING MATERIALS

FIELD OF THE INVENTION

The present invention relates to a process for recovering hydrocarbons from an asphaltene-containing material such as oil sands or tar sands.

BACKGROUND OF THE INVENTION

Bituminous deposits such as the oil sands or tar sands found in the Athabasca region of northeastern Alberta, Canada, constitute a very significant energy resource, but their recovery presents serious problems in processing and transportation due to a high content of asphaltene which gives rise to an extremely high viscosity and to a high content of metals such as vanadium and nickel.

One method of recovery hydrocarbons from tar sands involves crushing, adding water or steam to form a slurry, for transportation to an extraction plant where asphaltene or bitumen is removed. It may be desirable to reduce the viscosity or the metal ions content to facilitate further processing and/or to increase the total value of fractions made from the starting material.

Fedorak et al., 1993, *Enzyme Microb. Technol.* 15(5): 429-437, reports that chloroperoxidase can alter components in the asphaltene fraction of petroleum and is effective for metal removal, but concludes that this would yield chlorinated products which would be undesirable as a refinery feedstock.

Mogollon et al., 1998, *Applied Biochemistry and Biotechnology* 70-72: 765-777 reports that CPO (chloroperoxidase) was able to alter asphaltene fractions and remove heavy metals (Ni and V), but that no biocatalytic modifications of asphaltenes was observed with Cit-C (cytochrome C peroxidase) or LPO (lignin peroxidase).

CA 940853, CA 2232929 (Shell Canada) and U.S. Patent No. 5,876,592 (to Alberta Energy et al.) disclose processes for bitumen separation.

Vazquez-Duhalt et al., 1992, *Enzyme Microb. Technol.* 14: 837-841 mentions investigations to determine the effect of peroxidase on asphaltenes in organic solvents.

SUMMARY OF THE INVENTION

The inventors have found that in the recovery of liquid hydrocarbons from an asphaltene-containing starting material, the use of a laccase and oxygen may reduce the viscosity of the liquid hydrocarbon, increase the hydrophilicity of the asphaltene.

In the case of a high-asphaltene starting material, the treatment may lead to a liquid hydrocarbon with lower density and/or lower viscosity and hence more amenable to pipeline transportation and/or lead to a higher yield of high-value fractions such as naphtha and diesel fuel. When the liquid hydrocarbon is to be diluted and pumped through a pipeline, the enzymatic treatment may reduce the consumption of diluent for meeting pipeline specifications may be reduced, and/or the pumping costs may be reduced. The enzyme treatment may lead to a reduced consumption of energy and hydrogen for upgrading the liquid hydrocarbons to synthetic crude oil (SCO) by a treatment with hydrogen for refining the SCO. The enzyme treatment may increase the yield in the extraction of bitumen with separation from sand and clay. Further, the losses of solvent to tailings may be reduced, and fine solids in the SCO may be reduced.

In the case of a low-asphaltene starting material, the treatment may reduce the precipitation of asphaltenes during pipeline transportation or in the refinery.

Accordingly, the invention provides a process of recovering hydrocarbons, comprising

- a) mixing a hydrocarbon starting material comprising asphaltene with water to form a slurry,
- b) mixing the slurry with an oxidoreductase which acts with molecular oxygen and a phenol as substrates,
- c) incubating the mixture in the presence of oxygen, and
- d) removing a high-asphaltene fraction to obtain a hydrocarbon with a lower asphaltene content.

The invention further provides a process of recovering hydrocarbons, comprising

- a) providing a starting material comprising asphaltene and liquid hydrocarbon,
- b) preparing a slurry comprising the starting material, water and a laccase,
- c) incubating the slurry in the presence of oxygen, and
- d) removing a high-asphaltene fraction to obtain a hydrocarbon with a lower asphaltene content.

The invention further provides a process of recovering hydrocarbons, comprising

a) providing a starting material comprising asphaltene and liquid hydrocarbon,

b) preparing a slurry comprising the starting material, water, a laccase and a mediator for the laccase, wherein the laccase and the mediator are added in amounts effective to reduce the asphaltene content of the starting material,

c) incubating the slurry in the presence of oxygen, and

d) removing a high-asphaltene fraction to obtain a hydrocarbon with a lower asphaltene content.

DETAILED DESCRIPTION OF THE INVENTION

Starting material

The process of the invention is applied to a starting material which contains asphaltene and liquid hydrocarbon, particularly materials with a high viscosity and or a high metal ions content due to a high content of asphaltenes.

Examples of such starting materials are heavy crude oil (typically with a viscosity >1 cP and a density <20 API), high asphaltene crude such as Venezuelan heavy crude from the Orinoco Belt, crude from Baxterville oilfield in Mississippi on the US Gulf Coast, bitumen, oil sands, tar sands (as found, e.g., in the Athabasca region of Alberta, Canada), oil shale, or processed refinery oil streams, such as vacuum distillation residue and oil processed in the desalting unit.

Oxidoreductase

The process uses an oxidoreductase which acts with oxygen and a phenol as substrates. It may be a diphenol oxidase or a benzenediol:oxygen oxidoreductase acting on *o*- or *p*-diphenol (catechol or hydroquinone) such as a laccase or a tyrosinase. The oxidoreductase may act on any condensed aromatic structure with a sufficiently low redox potential.

The tyrosinase or catechol oxidase may be classified as EC 1.10.3.1. It may be derived from bacteria, fungi (e.g., mushrooms), plants and animals. Some examples are described in Matoba et al., 2006, J. Biol. Chem. 281(13): 8981-90; Mayer, 2006, Phytochemistry 67: 2318-2331; and Jaenicke et al., 2003, Biochem. J. 371(2): 515-23.

The laccase is a transition metal ion containing oxidase which catalyzes one-electron oxidation of a substrate with molecular oxygen as electron acceptor. The laccase typically has a wide substrate specificity acting on phenolic and other compounds such as oxidation labile heterocyclic, aromatic compounds, and the laccase activity may be detected in a

reaction with benzenediol (which is oxidized to benzosemiquinone), *o*- and *p*-quinols, aminophenols, phenylenediamine or asphaltene as test substrate. One-electron oxidation leads to the formation of free radicals with unpaired electrons which may be detected by ESR (electron spin resonance) or EPR (electron paramagnetic resonance). The laccase may be classified as EC 1.10.3.2 in the IUBMB Enzyme Nomenclature, also known as urushiol oxidase or *p*-diphenol oxidase. The transition metal is typically copper, and the laccase is typically a multi-copper protein. The laccase may be derived from fungi such as *Trametes*, e.g., *T. villosa* or *T. versicolor*, *Collybia*, *Fomes*, *Lentinus*, *Pleurotus*, *Rhizoctonia*, e.g., *R. solani*, *Aspergillus*, *Neurospora*, *Podospora*, *Phlebia*, e.g., *P. radiata* (WO 92/01046), *Coriolus*, e.g., *C. hirsutus* (JP 2-238885), *Myceliophthora*, e.g., *M. thermophila* or *Botrytis*. Particular examples are *Myceliophthora thermophila* laccase (MtL) described in WO 95/33836; *Streptomyces coelicolor* laccase (ScL) described by Machczynski et al., 2004, Protein Science 13: 2388-2397; *Polyporus* laccase (WO 96/00290); and *Coprinus* laccase (WO 97/08325). The laccase may also be derived from plants such as *Rhus*, e.g., *R. vernificera* or *R. succedana*.

The laccase may be added at a concentration of 0.001-10 mM, particularly 0.05-1 mM, or 10-100 laccase units.

The laccase may be chemically modified to increase its superficial hydrophobicity, e.g., as described by Magdassi et al., 2001, Journal of Dispersion Science and Technology 22(4): 313-322; Vazquez-Duhalt et al., 1995, Applied Microbiology and Biotechnology 42(5): 675-681; or Vazquez-Duhalt et al., 1992, Enzyme Microb. Technol. 14: 837-841.

The laccase may be immobilized, e.g., as described by Ruggiero et al., 1989, Soil Science 147(5): 361-370; Yinghui et al., 2002, Letters in Applied Microbiology 35(6): 451-456; and Dodor et al., 2004, Enzyme and Microbial Technology 35(2-3): 210-217.

Optional mediator

The oxidoreductase may optionally be used together with a mediator for single-electron transfer. Suitable mediators (also referred to as enhancing agents or enhancers) include, for example, acetosyringon, an alkyl syringate such as methylsyringate (MS), ethylsyringate, butylsyringate, laurylsyringate, 10-propionic acid-phenothiazine (PPT), 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS), chlorpromazine (CPZ), or 1-hydroxybenzotriazole (HOBT). Other suitable mediators are described in WO 01/48304 and US 20030096394. The mediator is preferably a mediator effective for promoting the precipitation of asphaltenes from the hydrocarbon starting material. Effective mediators may be identified as described, for example, in Example 1.

The mediator may be used at a concentration of 0.2-5 mM.

Mixing and incubation

The starting is mixed with water or steam to form a slurry, e.g., at a temperature of
5 20-60°C, particularly 30-50°C. A caustic such as sodium hydroxide may be added to
achieve a near-neutral pH suitable for laccase, e.g., a pH in the range pH 4-9, e.g., pH 5.0-
8.0, such as pH 6.0-7.5.

The ratio of water to starting material dry matter may generally be in the range
0.001:1 to 10:1. Conveniently, the enzyme treatment may generally be done at a water
10 content which is already found in the existing process. Thus, oil sands (tar sands) may be
treated at a ratio of 1:4 to 4:1, particularly 1:2 to 2:1, and refinery oil streams may be treated
at a ratio of water to starting material in the range 0.001:1 to 0.03:1.

The oxidoreductase is added, e.g., in the form of a microemulsion as described by
Michizoe et al., 2005, Journal of Bioscience and Bioengineering 99(6): 642-647; Levashov,
15 1992, Pure & Appl. Chem. 64(8): 125-1128; and Michizoe et al., 2001, Journal of Bioscience
and Bioengineering 92(1): 67-71.

The slurry is incubated in the presence of an oxidant. Conveniently, this may occur
during pipeline transportation of the slurry (hydrotransport) from the ore preparation to the
extraction plant. The incubation may be done at a temperature of 20-60°C, particularly 30-
20 50°C. The incubation may last 10 minutes to 48 hours, particularly 1-6 hours.

Asphaltene removal

A fraction with a relatively high asphaltene content is separated and removed to
obtain liquid hydrocarbon with a relatively lower asphaltene content. The separation may be
25 done by a process comprising the following steps, e.g., as described in CA 940853, CA
2232929 (Shell Canada) or U.S. Patent No. 5,876,592 (to Alberta Energy et al.). The
solvent uses a paraffinic solvent, e.g., C₃-C₇ alkane or natural gas condensate.

- adding air to form a bitumen-rich froth,
- mixing with a paraffinic solvent to precipitate asphaltenes, and
- 30 • removing precipitated asphaltenes to obtain a hydrocarbon product with a reduced
asphaltene content.

EXAMPLES**Example 1: Laccase treatment of Athabasca bitumen**

To a 125 mL Erlenmeyer flask was added 50 mM sodium acetate buffer (6 mL, pH 5.5) containing 48 Units of laccase and mediator (mediator concentration of 1 mM in aqueous layer) followed by 6 grams of a 1:1 (w/w) mixture of Athabasca bitumen dissolved in toluene. The flask was sealed with a teflon-lined screw cap and immersed into a shaker style water bath with a temperature set point of 40°C. The resulting dark emulsion was shaken at about 200 rpm for 18 hours at which time the contents of the flask were transferred to a Teflon centrifuge tube, quantitatively, using dichloromethane. The emulsion was mostly broken with the aid of a centrifuge (3,000 rpm, 10 minutes) and the layers were separated using a separatory funnel. The aqueous layer was rinsed multiple times with small amounts of dichloromethane and the rinsings were combined with the original organic layer. The dichloromethane was removed using a rotary evaporator (bath temperature at 70°C) and the resulting bitumen / toluene residue was taken up in 20 mL of dichloromethane followed by 100 mL of pentane and the solution was allowed to stand at room temperature in the stoppered flask for 18 hours. The resulting (asphaltene) precipitate was isolated via suction filtration, dried, and weighed.

The accompanying Table shows the results obtained versus control experiments run alongside in the absence of laccase and / or mediator.

Experiment #	Description of experiment	Mass Asphaltene collected from precipitation	% Asphaltene collected vs original bitumen sample
1	Laccase / ABTS	0.2766 g	9.22%
2	Laccase / ABTS	0.2799 g	9.32%
3	Laccase / HOBT	0.2264 g	7.61%
4	Laccase alone	0.2152 g	7.17%
5	ABTS alone	0.2323 g	7.72%
6	HOBT alone	0.2323 g	7.73%
7	Laccase / ABTS and HOBT	0.2749 g	9.16%
8	No laccase nor mediator	0.2277 g	7.57%
9	No laccase nor mediator	0.2296 g	7.65%
10	No laccase nor mediator	0.2413 g	8.01%

The data indicates that 20% more precipitate is formed in the experiment run with laccase and ABTS mediator. Although it is not clear why HOBT apparently showed no reaction, whereas the mediator ABTS did, it is believed that these two mediators operate via two different mechanisms: HOBT via a radical mechanism and ABTS via an electron transfer mechanism.

CLAIMS

1. A process of recovering hydrocarbons, comprising
 - a) providing a starting material comprising asphaltene and liquid hydrocarbon,
 - 5 b) preparing a slurry comprising the starting material, water, a laccase and a mediator,
 - c) incubating the slurry in the presence of oxygen, and
 - d) removing a high-asphaltene fraction to obtain a hydrocarbon with a lower asphaltene content.
- 10 2. The process of claim 1, wherein the laccase is *Myceliophthora thermophila* laccase or *Streptomyces coelicolor* laccase.
3. The process of claim 1 or 2, wherein the laccase is present at concentration of 0.001-
15 10 mM.
4. The process of any of claims 1-3, wherein the laccase is present at concentration of 0.05-1 mM.
- 20 5. The process of any of claims 1-4, wherein the mediator is 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS), methyl syringate (MS) or chlorpromazine (CPZ).
6. The process of any of claims 1-5, wherein the hydrocarbon material comprises oil
25 sands, tar sands, or bitumen.
7. The process of any of claims 1-6, wherein the incubation occurs at a temperature of 20-60°C.
- 30 8. The process of any of claims 1-7, wherein the incubation occurs at a temperature of 30-50°C.
9. The process of any of claims 1-8, wherein the slurry contains the water and the starting material at a weight ratio of 1:4 to 4:1.

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10. The process of any of claims 1-9, wherein the slurry contains the water and the starting material at a weight ratio of 1:2 to 2:1.
11. The process of any of claims 1-10, wherein the incubation occurs for a duration of 10
5 minutes to 48 hours.
12. The process of any of claims 1-11, wherein the incubation occurs for a duration of 1-6 hours.
- 10 13. The process of any of claims 1-12, wherein the laccase is added in the form of a microemulsion.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/066663

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G1/00 C10G32/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2 742 398 A (ZOBELL CLAUDE E) 17 April 1956 (1956-04-17) column 1, line 68 - column 2, line 69 column 3, line 18 - line 25 column 4, line 21 - line 74; claims 2,5 -----	1-13
X	US 4 349 633 A (WORNE HOWARD E ET AL) 14 September 1982 (1982-09-14) column 1, line 5 - line 23; claims 1,10-16 ----- -/--	1-13

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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