



(12) **DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) **Date de dépôt PCT/PCT Filing Date:** 2018/02/02
(87) **Date publication PCT/PCT Publication Date:** 2018/08/09
(85) **Entrée phase nationale/National Entry:** 2019/08/01
(86) **N° demande PCT/PCT Application No.:** CA 2018/050123
(87) **N° publication PCT/PCT Publication No.:** 2018/141067
(30) **Priorité/Priority:** 2017/02/03 (US62/454,406)

(51) **Cl.Int./Int.Cl. C10G 1/04** (2006.01),
C02F 1/00 (2006.01), **C02F 1/26** (2006.01),
C02F 1/38 (2006.01), **C02F 1/48** (2006.01),
C10G 33/04 (2006.01), **C10G 75/02** (2006.01)
(71) **Demandeur/Applicant:**
ADJACENCY LABS CORP., CA
(72) **Inventeurs/Inventors:**
BRYANT, STEVEN, CA;
STEPHENSON, TYLER, CA;
ROGERS, ROBIN D., CA;
BERTON, PAULA, CA
(74) **Agent:** HICKS & ASSOCIATES

(54) **Titre : DECONSTRUCTION DE MATERIAUX EN SABLE BITUMINEUX A L'AIDE DE LIQUIDES IONIQUES**
(54) **Title: DECONSTRUCTION OF OILSAND MATERIALS USING IONIC LIQUIDS**

(57) **Abrégé/Abstract:**

In alternative aspects, the invention provides process for the use of ionic liquids in the remediation and amelioration of oilsand materials, including treatment of tailings products including but not limited to mature fine tailings (MFT), separation of bitumen from oilsand, bitumen transportation, remediation of spilled bitumen and dilbit, treatment (breakage) of steam assisted gravity drainage (SAGD) and heavy oil emulsions, solids removal from oil processing streams, in-situ bitumen recovery, in-situ extraction from mineral reservoirs, production well chemicals, CO2 sequestration and fracking fluids.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property
Organization

International Bureau



(10) International Publication Number

WO 2018/141067 A9

(43) International Publication Date
09 August 2018 (09.08.2018)

(51) International Patent Classification:

C10G 1/04 (2006.01) C02F 1/48 (2006.01)
C02F 1/00 (2006.01) C10G 33/04 (2006.01)
C02F 1/26 (2006.01) C10G 75/02 (2006.01)
C02F 1/38 (2006.01)

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/CA2018/050123

(22) International Filing Date:

02 February 2018 (02.02.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/454,406 03 February 2017 (03.02.2017) US

(71) Applicants: UTI LIMITED PARTNERSHIP [CA/CA];
Suite 130, 3553-31 Street N.W., Calgary, Alberta T2L 2K7
(CA). MCGILL UNIVERSITY [CA/CA]; Office of Tech-
nology Transfer, 845 Sherbrooke Street West, Unit 21,
Montreal, Québec H3A 0G4 (CA).

Published:

- with international search report (Art. 21(3))
- with information concerning authorization of rectification of an obvious mistake under Rule 91.3 (b) (Rule 48.2(i))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(48) Date of publication of this corrected version:

30 August 2018 (30.08.2018)

(15) Information about Correction:

see Notice of 30 August 2018 (30.08.2018)

(72) Inventors: BRYANT, Steven; c/o University of Calgary,
2500 University Drive NW, Calgary, Alberta T2N 1N4
(CA). STEPHENSON, Tyler; c/o University of Calgary,
2500 University Drive NW, Calgary, Alberta T2N 1N4
(CA). ROGERS, Robin D.; 845 Sherbrooke Street West,
Montreal, Québec H3A 0G4 (CA). BERTON, Paula; 845
Sherbrooke Street West, Montreal, Québec H3A 0G4 (CA).

(74) Agent: KINGWELL, Brian et al.; Gowling WLG (Can-
ada) LLP, 550 Burrard Street, Suite 2300, Bentall 5, Vancou-
ver, British Columbia V6C 2B5 (CA).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,

(54) Title: DECONSTRUCTION OF OILSAND MATERIALS USING IONIC LIQUIDS

(57) Abstract: In alternative aspects, the invention provides process for the use of ionic liquids in the remediation and amelioration of oilsand materials, including treatment of tailings products including but not limited to mature fine tailings (MFT), separation of bitumen from oilsand, bitumen transportation, remediation of spilled bitumen and dilbit, treatment (breakage) of steam assisted gravity drainage (SAGD) and heavy oil emulsions, solids removal from oil processing streams, in-situ bitumen recovery, in-situ extraction from mineral reservoirs, production well chemicals, CO2 sequestration and fracking fluids.



WO 2018/141067 A9

CLAIMS

1. A process for the use of an ionic liquid to treat liquid waste streams in the form of slurries from industrial processes such that a solid, finely dispersed particulate phase is separated from said liquid waste stream, wherein said waste stream is tailings from the processing of oilsand, and said tailings are composed of an intimate mixture of water, bitumen, and particles which are dispersed to form the slurry.

2. The process of claim 1, where the particles comprise fine clay particles.

3. The process of claim 1, where said particles are under a particle size of 44 μm and said waste stream is comprised of 20-50 wt% solids, and 1-2 wt% bitumen, with the balance being water.

4. The process of claim 1, 2 or 3, where said waste stream has been gravity settled in a tailings pond, such that its solids content is greater than 40 wt% to form mature fine tailings (MFT).

5. The process of any one of claims 1-4, where an ionic liquid is mixed with said slurry to cause aggregation and/or gelation of the mixture.

6. The process of claim 5, where the ionic liquid is a surface active ionic liquid.

7. The process of claim 5 or 6, where said slurry is first diluted with a saline solution prior to the addition of the ionic liquid.

8. The process of claim 7, where said saline solution is an aqueous solution of NaCl or another salt with a concentration of 0-2.57 mol/L.

9. The process of claim 7 or 8, where said mixture comprising said slurry, saline solution, and ionic liquid is allowed to gravity settle to promote the separation of the solid phase that is a mixture of clay particles, ionic liquid, and bitumen.

10. The process of any one of claims 1-9, where said mixture is centrifuged from 0-14,000 rpm to promote the separation of said solid phase.

11. The process of any one of claims 1-10, where said ionic liquid is first mixed with (nano)particles to form a nanoparticle- ionic liquid dispersion prior to its addition to said slurry.

12. The process of claim 11, where said (nano)particles are magnetic and/or superparamagnetic.

13. The process of claim 12, where said superparamagnetic nanoparticles are a phase of iron oxide, a magnetite (Fe_3O_4), or a maghemite ($\gamma\text{-Fe}_2\text{O}_3$), with a particle size from 1-100 nm.

14. The process of claim 13, where said superparamagnetic iron oxide nanoparticles (SPIONs) are added to said slurry and mixed so as to promote aggregation of said clay particles with the SPIONs whereby said solid phase is rendered magnetic.

15. The process of claim 14, where a magnetic field from a permanent or electromagnet is used to separate said solid phase which has been rendered magnetic and is comprised of clay particles, ionic liquid, bitumen, and SPIONs.

16. The process of any one of claims 1-15, where the ionic liquid is recovered from said solid phase by solvent extraction to form a solvent loaded with ionic liquid.

17. The process of claim 16, where said solvent is a volatile organic solvent or a fatty acid.

18. The process of claim 16, where said solvent is acetone, isopropyl alcohol, ethyl acetate, octylamine, or oleic acid.

19. The process of any one of claims 16-18, wherein the content of volatile organic solvents is within the range 0-30 wt%.

20. The process of any one of claims 16-19, where said ionic liquid is recovered by a thin film treatment or pervaporation.

21. The process of any one of claims 1-20, wherein the process is carried out at 0-200 °C and 0-4 atm.

22. The process of any one of claims 1 to 21, further comprising treating the MFT with CO₂ so as to lower pH, wherein the CO₂ is transported for MFT treatment at least in part as a dissolved gas in the ionic liquid.

23. The process of any one of claims 1-22, wherein the ionic liquid has a melting point below 200 °C.

24. The process of any one claims 1-22, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more amines with at least one alkyl chain.

25. The process of any one of claims 1-22, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more primary ammonium cation.

26. The process of any one of claims 1-22, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more secondary, tertiary, quaternary amine, or cyclic amines.

27. The process of any one of claims 1-22, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid.

28. The process of any one of claims 1-22, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid, saturated or unsaturated.

29. The process of any one of claims 1-22, wherein the ionic liquid is octylammonium oleate ($[C_8NH_3][Oleate]$), butylammonium acetate ($[C_4NH_3][OAc]$), 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$), hexylammonium butyrate ($[C_6NH_3][Butyrate]$), or choline acetate ($[Cho][OAc]$).

30. The process of any one of claims 16-18, wherein the content of volatile organic solvents is within the range 0-30 wt%.

31. A process for the use of an ionic liquid as a bitumen diluent, to provide a stable ionic liquid-dilbit having very low vapour pressure and a density below that of water.

32. The process of claim 31, where the ionic liquid is a surface active ionic liquid.

33. A process for the use of an ionic liquid to extract bitumen from an oilsand, wherein the bitumen is extracted into a phase comprising a mixture of the ionic liquid and bitumen.

34. The process of claim 33, wherein the ionic liquid is a surface active ionic liquid.

35. The process of claim 33 or 34, where bitumen is separated from mineral solids upon addition of aqueous solution, in a process that uses oilsand, tarsand, oil shale, oil contaminated sand or oil contaminated earth, tailings pond material and/or sand containing crude oil as a raw material.

36. The process of claim 33 or 34, wherein one layer predominantly comprises ionic liquid and bitumen, another layer predominantly comprises clay, and another layer predominantly comprises sand, wherein when water is added in the separation process, a fourth layer consisting essentially of water forms.

37. The process of any one of claims 31-36, wherein the ionic liquid has a melting point below 200 °C.

38. The process of any one of claims 31-36, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more amines with at least one alkyl chain.

39. The process of any one of claims 31-36, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more primary ammonium cation.

40. The process of any one of claims 31-36, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more secondary, tertiary, quaternary amine, or cyclic amines.

41. The process of any one of claims 31-36, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid.

42. The process of any one of claims 31-36, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid, saturated or unsaturated.

43. The process of any one of claims 31-36, wherein the ionic liquid is octylammonium oleate ($[C_8NH_3][Oleate]$) or choline formate.

44. The process of any one of claims 30-33, wherein the content of volatile organic solvents is within the range 0-30 wt%.

45. The process of any one of claims 30-33 which is carried out at 0-200 °C and 0-4 atm.

46. The process of any one of claims 30-33, where said mixture is separated by freeze-thawing between -10 and 80 °C.

47. The process of any one of claims 30-33, where said mixture is separated by heating, filtration, centrifugation, and/or gravity settling.

48. The process of any one of claims 30-33, which is carried out at ambient temperature and pressure.

49. A process comprising use of an ionic liquid to break an oil-water emulsion.

50. The process of claim 49, wherein the ionic liquid has a melting point below 200 °C.

51. The process of claim 49, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more amines with at least one alkyl chain.

52. The process of claim 49, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more primary ammonium cation.

53. The process of claim 49, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more secondary, tertiary, quaternary amine, or cyclic amines.

54. The process of claim 49, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid.

55. The process of claim 49, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid, saturated or unsaturated.

56. The process of claim 49 wherein the ionic liquid is a surface active ionic liquid.

57. The process of claim 49 wherein the ionic liquid is octylammonium oleate ($[C_8NH_3][Oleate]$).

58. A process comprising the use of an ionic liquid to elicit a miscible displacement of oil from a porous mineral reservoir.

59. The process of claim 58, wherein the ionic liquid has a melting point below 200 °C.

60. The process of claim 58, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more amines with at least one alkyl chain.

61. The process of claim 58, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more primary ammonium cation.

62. The process of claim 58, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more secondary, tertiary, quaternary amine, or cyclic amines.

63. The process of claim 58, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid.

64. The process of claim 58, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid, saturated or unsaturated.

65. The process of claim 58, wherein the ionic liquid is a surface active ionic liquid.

66. The process of claim 58, wherein the ionic liquid is octylammonium oleate ($[C_8NH_3][Oleate]$).

67. The process of claim 58, where the ionic liquid is pumped into the reservoir, allowed to become loaded with oil, and then produced from the reservoir.

68. A process comprising use of an ionic liquid as a corrosion inhibitor for steel infrastructure.

69. The process of claim 68, wherein the ionic liquid has a melting point below 200 °C.

70. The process of claim 68, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more amines with at least one alkyl chain.

71. The process of claim 68, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more primary ammonium cation.

72. The process of claim 68, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more secondary, tertiary, quaternary amine, or cyclic amines.

73. The process of claim 68, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid.

74. The process of claim 68, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid, saturated or unsaturated.

75. The process of claim 68 wherein the ionic liquid is a surface active ionic liquid.

76. The process of claim 68, wherein the ionic liquid is octylammonium oleate ($[C_8NH_3][Oleate]$).

77. A process comprising use of an ionic liquid to transport CO_2 .

78. The process of claim 77, which is carried out at 0-200 °C and 0-4 atm.

79. The process of claim 77, wherein the CO_2 reacts with one of the ions of the ionic liquid, or the CO_2 dissolves in the ionic liquid.

80. The process of claim 77, wherein the ionic liquid has a melting point below 200 °C.

81. The process of claim 77, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more amines with at least one alkyl chain.

82. The process of claim 77, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more primary ammonium cation.

83. The process of claim 77, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the cations comprise one or more secondary, tertiary, quaternary amine, or cyclic amines.

84. The process of claim 77, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid.

85. The process of claim 77, wherein the ionic liquid comprises one or more cations and one or more anions and wherein the anions comprise one or more primary carboxylic acid, saturated or unsaturated.

86. The process of claim 77, wherein the ionic liquid is a surface active ionic liquid.

87. The process of claim 77, wherein the ionic liquid is octylammonium oleate ($[\text{C}_8\text{NH}_3][\text{Oleate}]$).

88. A process for treating mature fine tailings (MFT) comprising mixing an ionic liquid (IL) with a MFT mixture comprising clay particles and bitumen contaminants suspended in saline MFT water to form an IL/MFT phase; and separating the IL/MFT phase into two phases, a first phase comprising the clay particles, bitumen contaminants and the IL, and a second aqueous phase comprising more than about 30% of the MFT water.

89. The process of claim 88, further comprising adding an aqueous saline MFT diluent to the MFT mixture prior to mixing with the ionic liquid.

90. The process of claim 88, wherein the saline MFT diluent is added to provide an MFT mixture diluted to 30 wt% solids, and the ionic liquid is added for mixing to provide 9 vol% IL.

91. The process of claim 89 or 90, wherein with the aqueous saline MFT diluents is approximately 1.7 mol/L NaCl.

92. The process of any one of claims 88 to 91, wherein water forms at least 50% by weight of the MFT mixture.

93. The process of any one of claims 88 to 92, wherein the clay particles comprise particles smaller than 44 μm .

94. The process of any one of claims 88 to 93, wherein separating the IL/MFT gel into two phases comprises centrifugation.

95. The process of any one of claims 88 to 94, further comprising adding magnetic particles to the IL, wherein separated the IL/MFT gel into two phases comprises magnetically separating the first and second phases.

96. The process of claim 95, wherein the magnetic particles are superparamagnetic iron oxide (Fe_3O_4) nanoparticles with a particle size of 20-30nm.

97. The process of any one of claims 88 to 96, further comprising removing ionic liquids from the first phase by solvent extraction to form a solvent loaded with ionic liquid.

98. The process of claim 97, further comprising recovering ionic liquids from the solvent loaded with ionic liquid by evaporation, a thin film treatment or pervaporation.

99. The process of any one of claims 88 to 98, wherein the process is carried out at 0-100°C and at atmospheric pressure.

100. The process of any one of claims 88 to 99, wherein the ionic liquid comprises an unsaturated fatty acid anion.

101. The process of claim 100, wherein the unsaturated fatty acid anion is an oleate or linoleate anion.

102. The process of any one of claims 88 to 101, wherein the ionic liquid comprises an ammonium cation.

103. The process of claim 102, wherein the ammonium cation is an alkylammonium cation.

104. The process of claim 102 or 103, wherein the ammonium cation is a primary ammonium cation.

105. The process of any one of claims 88 to 99, wherein the IL is a surface active ionic liquid.

106. The process of any one of claims 88 to 99, wherein the IL is $[C_8NH_3][Oleate]$.

107. The process of any one of claims 88 to 106, further comprising treating the MFT with CO_2 so as to lower pH, wherein the CO_2 is transported for MFT treatment at least in part as a dissolved gas in the ionic liquid.

108. Use of an ionic liquid as a bitumen diluent, to provide a stable IL-dilbit having a density below that of water.

109. Use of an ionic liquid to extract bitumen from an oilsand, wherein the bitumen is extracted into a phase comprising the ionic liquid.

110. The use according to claim 108 or 109, wherein the ionic liquid comprises an unsaturated fatty acid anion.

111. The use according to claim 110, wherein the unsaturated fatty acid anion is an oleate or linoleate anion.

112. The use according to any one of claims 108 to 111, wherein the ionic liquid comprises an ammonium cation.

113. The use according to claim 112, wherein the ammonium cation is an alkyl ammonium cation.

114. The use according to claim 112 or 113, wherein the ammonium cation is a primary ammonium cation.

115. The use according to claim 108 or 109, wherein the ionic liquid is a surface active ionic liquid.

116. The use according to claim 108 or 109, wherein the ionic liquid is [P₆₆₆₁₄][Cl] or [C₈NH₃][Oleate].

117. Use of [C₈NH₃][Oleate] to break an oil-water emulsion.

118. Use of [C₈NH₃][Oleate] to transport CO₂.