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(54) Title: METHODS FOR PRODUCING SILICON TETRAFLUORIDE

(57) Abstract: Methods for producing silicon tetrafluoride by acid digestion of fluoride salts of alkali metal or alkaline earth metal and aluminum, optionally, in the presence of a source of silicon; methods for producing silane that include acid digestion of by-products of silane production to produce silicon tetrafluoride.

AMENDED CLAIMS
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1. A method for producing silicon tetrafluoride, the method comprising:

contacting a fluoroaluminate feed comprising at least about 30% by weight fluoride salts of alkali metal or alkaline earth-metal and aluminum, an acid gas and a source of silicon to produce silicon tetrafluoride and at least one by-product.

2. The method as set forth in claim 1 wherein the feed is a by-product of silane production.

3. The method as set forth in claim 1 or claim 2 wherein silicon tetrafluoride is separated from the by-product to recover silicon tetrafluoride as a product.

4. The method as set forth in any one of claims 1 to 3 wherein the source of silicon is selected from the group consisting of sand, quartz, flint, diatomite, mineral silicates, metallurgical grade silicon, fumed silica, fluorosilicates and mixtures thereof.

5. The method as set forth in any one of claims 1 to 4 wherein the feed comprises at least about 50%, at least about 70%, at least about 80%, at least about 90%, from about 30% to about 95% or from about 70% to about 95% by weight fluoride salts of alkali metal or alkaline earth-metal and aluminum.

6. The method as set forth in any one of claims 1 to 5 wherein the acid is selected from hydrochloric acid, sulfuric acid and mixtures thereof.

7. The method as set forth in any one of claims 1 to 5 wherein the acid is hydrochloric acid.

8. The method as set forth in any one of claims 1 to 7 wherein the alkali or alkaline earth metal is selected from lithium, sodium, potassium, magnesium, barium, calcium and mixtures thereof.

9. The method as set forth in any one of claims 1 to 7 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum is selected from the group consisting of $NaAlF_4$, $Na_5Al_3F_{14}$, Na_3AlF_6 and mixtures thereof.

10. The method as set forth in any one of claims 1 to 7 wherein the feed comprises $NaAlF_4$, $Na_5Al_3F_{14}$ and Na_3AlF_6.

11. The method as set forth in claim 10 wherein the feed also includes aluminum fluoride and/or sodium fluoride.

12. The method as set forth in any one of claims 1 to 11 wherein hydrogen fluoride and a chloride or sulfate salt of alkali or alkaline earth-metal are produced as by-products.

13. The method as set forth in claim 12 wherein a chloride salt is produced as a by-product, the chloride salt being selected from the group consisting of LiCl, NaCl, KCl, $MgCl_2$, $BaCl_2$, $CaCl_2$ and mixtures thereof.

14. The method as set forth in claim 13 wherein the chloride salt is NaCl.

15. The method as set forth in claim 12 wherein the hydrogen fluoride is contacted with a source of silicon to produce silicon tetrafluoride.

16. The method as set forth in any one of claims 1 to 15 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with substantially anhydrous acid.

17. The method as set forth in claim 16 wherein the fluoride salt and the source of silicon are introduced to a fluidized bed reactor which contains acid as a fluidizing gas.

18. The method as set forth in claim 17 wherein a product gas and particulate chloride or sulfate salt of alkali or alkaline earth-metal is produced in the

fluidized bed reactor, the product gas comprising silicon tetrafluoride, hydrogen fluoride and unreacted acid.

19. The method as set forth in claim 18 comprising separating silicon tetrafluoride from at least one other gas in a distillation column.

20. The method as set forth in any one of claims 1 to 19 wherein the fluoride salt is particulate with an average nominal diameter of less than about 500 μm.

21. The method as set forth in any one of claims 1 to 19 wherein the fluoride salt is particulate with an average nominal diameter of less than about 300 μm.

22. The method as set forth in any one of claims 1 to 21 wherein the acid and fluoride salt are added to a reaction vessel in a molar ratio of at least about 1:1, at least about 2:1, at least about 3:1, at least about 10:1 or from about 1:1 to about 25:1.

23. The method as set forth in any one of claims 1 to 22 wherein the acid is added to a reaction vessel in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

24. The method as set forth in any one of claims 1 to 23 wherein the source of silicon and fluoride salt are added to a reaction vessel in a molar ratio based on the number of silicon atoms and fluorine atoms of about 1:4, at least about 1:3, at least about 1:2 or at least about 1:1.

25. The method as set forth in any one of claims 1 to 24 wherein a source of silicon is added to a reaction vessel such that silicon atoms are added in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

26. The method as set forth in any one of claims 1 to 25 wherein the conversion from the fluoride salt to silicon tetrafluoride is at least about 50%, at least

about 75%, at least about 90%, from about 50% to about 98%, from about 60% to about 98% or from about 75% to about 98%.

27. A method for producing silicon tetrafluoride, the method comprising:

contacting a fluoride salt of alkali metal or alkaline earth-metal and aluminum, hydrochloric acid and a source of silicon to produce silicon tetrafluoride and hydrogen fluoride; and

separating silicon tetrafluoride from hydrogen fluoride to recover silicon tetrafluoride as a product.

28. The method as set forth in claim 27 wherein the silicon tetrafluoride is condensed for storage as a liquid product.

29. The method as set forth in claim 27 wherein the fluoride salt is a by-product of silane production.

30. The method as set forth in any one of claims 27 to 29 wherein the source of silicon is selected from the group consisting of sand, quartz, flint, diatomite, mineral silicates, metallurgical grade silicon, fumed silica, fluorosilicates and mixtures thereof.

31. The method as set forth in any one of claims 27 to 30 wherein the alkali or alkaline earth metal is selected from lithium, sodium, potassium, magnesium, barium, calcium and mixtures thereof.

32. The method as set forth in any one of claims 27 to 30 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum is selected from the group consisting of $NaAlF_4$, $Na_5Al_3F_{14}$, Na_3AlF_6 and mixtures thereof.

33. The method as set forth in any one of claims 27 to 30 wherein a mixture of $NaAlF_4$, $Na_5Al_3F_{14}$ and Na_3AlF_6 is contacted with hydrochloric acid.

34. The method as set forth in claim 33 wherein the mixture also includes aluminum fluoride and/or sodium fluoride.

35. The method as set forth in any one of claims 27 to 34 wherein hydrogen fluoride and a chloride salt of alkali or alkaline earth-metal are produced as by-products.

36. The method as set forth in claim 34 wherein the chloride salt is selected from the group consisting of LiCl, NaCl, KCl, $MgCl_2$, $BaCl_2$, $CaCl_2$ and mixtures thereof.

37. The method as set forth in claim 36 wherein the chloride salt is NaCl.

38. The method as set forth in claim 35 wherein the hydrogen fluoride is contacted with a source of silicon to produce silicon tetrafluoride.

39. The method as set forth in any one of claims 27 to 38 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with aqueous hydrochloric acid.

40. The method as set forth in claim 39 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are introduced to a reaction vessel to produce a product gas comprising silicon tetrafluoride and a slurry containing a chloride salt of alkali or alkaline earth-metal.

41. The method as set forth in claim 40 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are continuously fed to the reaction vessel and the slurry and product gas are continuously removed from the reaction vessel.

42. The method as set forth in claim 40 or claim 41 wherein the product gas comprises silicon tetrafluoride and hydrogen fluoride.

43. The method as set forth in claim 42 comprising separating hydrogen fluoride and silicon tetrafluoride in a distillation column.

44. The method as set forth in any one of claims 41 to 43 wherein the slurry is introduced into a solid-liquid separation unit to produce a solid fraction and a liquid fraction, the solid fraction containing a chloride salt of an alkali metal or alkaline earth-metal and the liquid fraction containing water, hydrogen fluoride, unreacted hydrochloric acid and a chloride salt of an alkali metal or alkaline earth-metal.

45. The method as set forth in claim 44 comprising separating at least one of water, hydrogen fluoride and unreacted hydrochloric acid in a distillation column.

46. The method as set forth in any one of claims 27 to 38 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with substantially anhydrous hydrochloric acid.

47. The method as set forth in claim 46 wherein the fluoride salt and the source of silicon are introduced to a fluidized bed reactor which contains hydrochloric acid as a fluidizing gas.

48. The method as set forth in claim 47 wherein a product gas and particulate chloride salt of alkali or alkaline earth-metal is produced in the fluidized bed reactor, the product gas comprising silicon tetrafluoride, hydrogen fluoride and unreacted hydrochloric acid.

49. The method as set forth in claim 48 comprising separating silicon tetrafluoride from at least one other gas in a distillation column.

50. The method as set forth in any one of claims 27 to 49 wherein the fluoride salt is particulate with an average nominal diameter of less than about 500 μm.

51. The method as set forth in any one of claims 27 to 49 wherein the fluoride salt is particulate with an average nominal diameter of less than about 300 μm.

52. The method as set forth in any one of claims 27 to 51 wherein the hydrochloric acid and fluoride salt are added to a reaction vessel in a molar ratio of at least about 1:1, at least about 2:1, at least about 3:1, at least about 10:1 or from about 1:1 to about 25:1.

53. The method as set forth in any one of claims 27 to 52 wherein the hydrochloric acid is added to a reaction vessel in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

54. The method as set forth in any one of claims 27 to 53 wherein the source of silicon and fluoride salt are added to a reaction vessel in a molar ratio based on the number of silicon atoms and fluorine atoms of about 1:4, at least about 1:3, at least about 1:2 or at least about 1:1.

55. The method as set forth in any one of claims 27 to 54 wherein a source of silicon is added to a reaction vessel such that silicon atoms are added in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

56. The method as set forth in any one of claims 27 to 55 wherein the conversion from the fluoride salt to silicon tetrafluoride is at least about 50%, at least about 75%, at least about 90%, from about 50% to about 98%, from about 60% to about 98% or from about 75% to about 98%.

57. A method for producing silane and silicon tetrafluoride, the method comprising:

contacting silicon tetrafluoride and an alkali or alkaline earth-metal salt of aluminum tetrahydride to produce silane and an effluent comprising a fluoride salt of alkali metal or alkaline earth-metal and aluminum;

contacting the effluent, hydrochloric acid and a source of silicon to produce silicon tetrafluoride and hydrogen fluoride; and

separating the silicon tetrafluoride from the hydrogen fluoride.

58. The method as set forth in claim 57 wherein the silicon tetrafluoride is bubbled through a reaction solution that contains the aluminum tetrahydride.

59. The method as set forth in claim 57 or claim 58 wherein the silicon tetrafluoride and aluminum tetrahydride are contacted in a reaction medium that is maintained from about 30°C to about 80°C.

60. The method as set forth in claim 59 wherein the fluoride salt is separated from the reaction medium in a solid-liquid separation unit.

61. The method as set forth in any one of claims 57 to 60 wherein the silicon tetrafluoride separated from hydrogen fluoride is used to produce additional silane by reacting the silicon tetrafluoride with an alkali or alkaline earth-metal salt of aluminum tetrahydride.

62. The method as set forth in any one of claims 57 to 61 wherein the silicon tetrafluoride is condensed for storage as a liquid product.

63. The method as set forth in any one of claims 57 to 62 wherein the source of silicon is selected from the group consisting of sand, quartz, flint, diatomite, mineral silicates, metallurgical grade silicon, fumed silica, fluorosilicates and mixtures thereof.

64. The method as set forth in any one of claims 57 to 63 wherein the effluent comprises from about 30% to about 95% by weight fluoride salts of alkali metal or alkaline earth-metal and aluminum.

65. The method as set forth in any one of claims 57 to 63 wherein the effluent comprises from about 70% to about 95% by weight fluoride salts of alkali metal or alkaline earth-metal and aluminum.

66. The method as set forth in any one of claims 57 to 65 wherein the alkali or alkaline earth metal is selected from lithium, sodium, potassium, magnesium, barium, calcium and mixtures thereof.

67. The method as set forth in any one of claims 57 to 65 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum is selected from the group consisting of $NaAlF_4$, $Na_5Al_3F_{14}$, Na_3AlF_6 and mixtures thereof.

68. The method as set forth in any one of claims 57 to 65 wherein the effluent comprises $NaAlF_4$, $Na_5Al_3F_{14}$ and Na_3AlF_6.

69. The method as set forth in claim 68 wherein the effluent also includes aluminum fluoride and/or sodium fluoride.

70. The method as set forth in any one of claims 57 to 69 wherein hydrogen fluoride and a chloride salt of alkali or alkaline earth-metal are produced as by-products.

71. The method as set forth in claim 70 wherein the chloride salt is selected from the group consisting of LiCl, NaCl, KCl, $MgCl_2$, $BaCl_2$, $CaCl_2$ and mixtures thereof.

72. The method as set forth in claim 71 wherein the chloride salt is NaCl.

73. The method as set forth in claim 70 wherein the hydrogen fluoride is contacted with a source of silicon to produce silicon tetrafluoride.

74. The method as set forth in any one of claims 57 to 73 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with aqueous hydrochloric acid.

75. The method as set forth in claim 74 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are

introduced to a reaction vessel to produce a product gas comprising silicon tetrafluoride and a slurry containing a chloride salt of alkali or alkaline earth-metal.

76. The method as set forth in claim 75 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are continuously fed to the reaction vessel and the slurry and product gas are continuously removed from the reaction vessel.

77. The method as set forth in claim 75 or claim 76 wherein the product gas comprises silicon tetrafluoride and hydrogen fluoride.

78. The method as set forth in claim 77 comprising separating hydrogen fluoride and silicon tetrafluoride in a distillation column.

79. The method as set forth in any one of claims 75 to 78 wherein the slurry is introduced into a solid-liquid separation unit to produce a solid fraction and a liquid fraction, the solid fraction containing a chloride salt of an alkali metal or alkaline earth-metal and the liquid fraction containing water, hydrogen fluoride, unreacted hydrochloric acid and a chloride salt of an alkali metal or alkaline earth-metal.

80. The method as set forth in claim 79 comprising separating at least one of water, hydrogen fluoride and unreacted hydrochloric acid in a distillation column.

81. The method as set forth in any one of claims 57 to 73 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with substantially anhydrous hydrochloric acid.

82. The method as set forth in claim 81 wherein the fluoride salt and the source of silicon are introduced to a fluidized bed reactor which contains hydrochloric acid as a fluidizing gas.

83. The method as set forth in claim 82 wherein a product gas and particulate chloride salt of alkali or alkaline earth-metal salt is produced in the fluidized

bed reactor, the product gas comprising silicon tetrafluoride, hydrogen fluoride and unreacted hydrochloric acid.

84. The method as set forth in claim 83 comprising separating silicon tetrafluoride from at least one other gas in a distillation column.

85. The method as set forth in any one of claims 57 to 84 wherein the fluoride salt is a particulate with an average nominal diameter of less than about 500 μm.

86. The method as set forth in any one of claims 57 to 84 wherein the fluoride salt is a particulate with an average nominal diameter of less than about 300 μm.

87. The method as set forth in any one of claims 57 to 86 wherein the hydrochloric acid and fluoride salt are added to a reaction vessel in a molar ratio of at least about 1:1, at least about 2:1, at least about 3:1, at least about 10:1 or from about 1:1 to about 25:1.

88. The method as set forth in any one of claims 57 to 87 wherein the hydrochloric acid is added to a reaction vessel in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

89. The method as set forth in any one of claims 57 to 88 wherein the source of silicon and fluoride salt are added to a reaction vessel in a molar ratio based on the number of silicon atoms and fluorine atoms of about 1:4, at least about 1:3, at least about 1:2 or at least about 1:1.

90. The method as set forth in any one of claims 57 to 89 wherein a source of silicon is added to a reaction vessel such that silicon atoms are added in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

91. The method as set forth in any one of claims 57 to 90 wherein the conversion from the fluoride salt to silicon tetrafluoride is at least about 50%, at least about 75%, at least about 90%, from about 50% to about 98%, from about 60% to about 98% or from about 75% to about 98%.

92. A method for producing silane and silicon tetrafluoride, the method comprising:

contacting a fluoroaluminate feed comprising a fluoride salt of alkali metal or alkaline earth-metal and aluminum, an acid and a source of silicon to produce silicon tetrafluoride and at least one by-product;

separating the silicon tetrafluoride from the by-product; and

reacting the silicon tetrafluoride with alkali or alkaline earth-metal salt of aluminum tetrahydride to produce silane.

93. The method as set forth in claim 92 wherein the silicon tetrafluoride is bubbled through a reaction solution that contains the aluminum tetrahydride.

94. The method as set forth in claim 92 or claim 93 wherein the silicon tetrafluoride and aluminum tetrahydride are reacted in a reaction medium that is maintained from about 30°C to about 80°C.

95. The method as set forth in claim 94 wherein the fluoride salt is separated from the reaction medium in a solid-liquid separation unit.

96. The method as set forth in any one of claims 92 to 95 wherein the source of silicon is selected from the group consisting of sand, quartz, flint, diatomite, mineral silicates, metallurgical grade silicon, fumed silica, fluorosilicates and mixtures thereof.

97. The method as set forth in any one of claims 92 to 96 wherein the fluoroaluminate feed comprises from about 30% to about 95% by weight fluoride salts of alkali metal or alkaline earth-metal and aluminum.

98. The method as set forth in any one of claims 92 to 96 wherein the fluoroaluminate feed comprises from about 70% to about 95% by weight fluoride salts of alkali metal or alkaline earth-metal and aluminum.

99. The method as set forth in any one of claims 92 to 98 wherein the acid is selected from hydrochloric acid, sulfuric acid and mixtures thereof.

100. The method as set forth in any one of claims 92 to 98 wherein the acid is hydrochloric acid.

101. The method as set forth in any one of claims 92 to 100 wherein the alkali or alkaline earth metal is selected from lithium, sodium, potassium, magnesium, barium, calcium and mixtures thereof.

102. The method as set forth in any one of claims 92 to 100 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum is selected from the group consisting of $NaAlF_4$, $Na_5Al_3F_{14}$, Na_3AlF_6 and mixtures thereof.

103. The method as set forth in any one of claims 92 to 100 wherein the fluoroaluminate feed comprises $NaAlF_4$, $Na_5Al_3F_{14}$ and Na_3AlF_6.

104. The method as set forth in claim 103 wherein the fluoroaluminate feed also includes aluminum fluoride and/or sodium fluoride.

105. The method as set forth in any one of claims 92 to 104 wherein hydrogen fluoride and a chloride or sulfate salt of alkali or alkaline earth-metal are produced as by-products.

106. The method as set forth in claim 105 wherein a chloride salt is produced as a by-product, the chloride salt being selected from the group consisting of LiCl, NaCl, KCl, $MgCl_2$, $BaCl_2$, $CaCl_2$ and mixtures thereof.

107. The method as set forth in claim 106 wherein the chloride salt is NaCl.

108. The method as set forth in claim 105 wherein the hydrogen fluoride is contacted with a source of silicon to produce silicon tetrafluoride.

109. The method as set forth in any one of claims 92 to 108 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with aqueous acid.

110. The method as set forth in claim 109 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are introduced to a reaction vessel to produce a product gas comprising silicon tetrafluoride and a slurry containing a by-product.

111. The method as set forth in claim 110 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are continuously fed to the reaction vessel and the slurry and product gas are continuously removed from the reaction vessel.

112. The method as set forth in claim 110 or claim 111 wherein the product gas comprises silicon tetrafluoride and hydrogen fluoride.

113. The method as set forth in claim 112 comprising separating hydrogen fluoride and silicon tetrafluoride in a distillation column.

114. The method as set forth in any one of claims 110 to 113 wherein the slurry is introduced into a solid-liquid separation unit to produce a solid fraction and a liquid fraction, the solid fraction containing a chloride or sulfate salt of an alkali metal or alkaline earth-metal and the liquid fraction containing water, hydrogen fluoride, unreacted acid and a chloride or sulfate salt of an alkali metal or alkaline earth-metal.

115. The method as set forth in claim 114 comprising separating at least one of water, hydrogen fluoride and unreacted acid in a distillation column.

116. The method as set forth in any one of claims 92 to 108 wherein the fluoride salt of alkali metal or alkaline earth-metal and aluminum and the source of silicon are contacted with substantially anhydrous acid.

117. The method as set forth in claim 116 wherein the fluoride salt and the source of silicon are introduced to a fluidized bed reactor which contains acid as a fluidizing gas.

118. The method as set forth in claim 117 wherein a product gas and particulate chloride or sulfate salt of alkali or alkaline earth-metal salt is produced in the fluidized bed reactor, the product gas comprising silicon tetrafluoride, hydrogen fluoride and unreacted acid.

119. The method as set forth in claim 118 comprising separating silicon tetrafluoride from at least one other gas in a distillation column.

120. The method as set forth in any one of claims 92 to 119 wherein fluoride salt contacted with the acid is particulate with an average nominal diameter of less than about 500 μm.

121. The method as set forth in any one of claims 92 to 119 wherein fluoride salt contacted with the acid is particulate with an average nominal diameter of less than about 300 μm.

122. The method as set forth in any one of claims 92 to 121 wherein the acid and fluoride salt are added to a reaction vessel in a molar ratio of at least about 1:1, at least about 2:1, at least about 3:1, at least about 10:1 or from about 1:1 to about 25:1.

123. The method as set forth in any one of claims 92 to 122 wherein the acid is added to a reaction vessel in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

124. The method as set forth in any one of claims 92 to 123 wherein the source of silicon and fluoride salt are added to a reaction vessel in a molar ratio based on the number of silicon atoms and fluorine atoms of about 1:4, at least about 1:3, at least about 1:2 or at least about 1:1.

125. The method as set forth in any one of claims 92 to 124 wherein a source of silicon is added to a reaction vessel such that silicon atoms are added in at least about a 5%, at least about a 25%, at least about a 50%, at least about a 100%, at least about a 250% or at least about a 500% molar excess relative to the fluoride salt added to the reaction vessel.

126. The method as set forth in any one of claims 92 to 125 wherein the conversion from the fluoride salt to silicon tetrafluoride is at least about 50%, at least about 75%, at least about 90%, from about 50% to about 98%, from about 60% to about 98% or from about 75% to about 98%.