Claims

We claim:

~~1. A method for the synthesis of 5-(chloromethyl)-2-furaldehyde (CMF) from monosaccharides, comprising contacting monosaccharides, hydrochloric acid, and an organic solvent in a continuous, biphasic-flow reactor assembly at a temperature from about 60 degree C to about 200 degree C and under pressure from about 1 atmospheres to about 20 atmospheres.~~

~~2. An apparatus for the synthesis of CMF from monosaccharides, comprising a biphasic –flow reactor assembly configured to accommodate contacting of monosaccharides, hydrochloric acid, and an organic solvent at a temperature from about 60 degree C to about 200 degree C and pressures from about 1 atmospheres to 10 atmospheres.~~

~~3. A method as in claim 1, wherein monosaccharides comprise any six-carbon containing, ketose and aldose isomers and diastereomers of glucose and fructose, including mannose, gulose, galactose, sorbose, psicose, tagatose, allose, altrose, idose, and talose, and any combination thereof.~~

~~4. A method as in claim 3, wherein the monosaccharides are in dry form or dissolved in a solvent.~~

~~5. A method as in claim 1, wherein hydrochloric acid comprises aqueous solutions of hydrogen chloride gas.~~

~~6. A method as in claim 5, wherein the concentration of hydrochloric acid is between 26% to 38% by weight.~~

~~7. A method as in claim 6, wherein the concentration of hydrochloric acid is between 30% to 33% by weight.~~

~~8. A method as in claim 7, wherein the hydrochloric acid contains one or more of: inorganic salts, lithium chloride, sodium chloride, mineral acids, sulfuric acid, and hydrobromic acid.~~

~~9. A method as in claim 1, wherein the organic solvent comprises dichloromethane, chloroform, carbon tetrachloride, diethyl ether, dipropyl ether, ethyl acetate, hexanes, dichloroethane and its isomers, trichloroethane and its isomers, toluene, benzene, and xylenes.~~

~~10. A method as in claim 9, wherein the organic solvent comprises a solvent with a density greater than the hydrochloric acid.~~

~~11. A method as in claim 10, wherein the organic solvent comprises one or more of: dichloromethane, chloroform, 1,2-dichloroethane, a halogenated organic solvent, and mixtures thereof.~~

~~12. A method as in claim 1, wherein temperatures are from 60 deg C to 200 deg C. preferably from 80 deg C to 120 deg C.~~

~~13. A method as in claim 12, wherein pressures range from 2 atmospheres to 10 atmospheres.~~

~~14. A method as in claim 1, wherein reaction times are from 1 second to 24 hours.~~

~~15. A method as in claim 14, wherein the reaction time is between 1 minute and 20 minutes.~~

16. A method as in claim 1, wherein the biphasic reaction mixture is contacted with a heat remover device and is cooled to between 30 deg C to 40 deg C.

17. A method as in claim 16, wherein the heat removal devices comprises one or more of: ice bath, heat sink, and glycol heat exchange pump.

18. A method as in claim 1, wherein the biphasic reaction mixture is subjected to solid/liquid phase separation through a semi-porous membrane, by the action of vacuum, gravity, or mechanical force.

19. A method as in claim 18, wherein the semi-porous membrane comprises one of more of: glass frit funnel, cellulose paper filter, silica gel, alumina, sand, plastic polymer sock-type filter, polypropylene sock-type filter and PTFE sock-type filter.

20. A method as in claim 1, in which insoluble HTC is removed and dried by way of solid/liquid phase separation.

21. A method as in claim 1, wherein the organic phase containing CMF is concentrated to reduce total volume by distillation or distillation.

22. A method as in claim 21, wherein the organic phase CMF is concentrated to a concentration in organic solvent of between about 5 milligrams per milliliter to about 1000 milligrams per milliliter.

23. A method as in claim 22, wherein the organic phase CMF is concentrated to a concentration in organic solvent of between about 30 milligrams per milliliter to about 500 milligrams per milliliter.

24. A method as in claim 1, wherein the organic phase is washed with an inorganic base dissolved in aqueous solution at or below the inorganic base's solubility limit in water to create a state of pH greater than or equal to seven.

25. A method as in claim 24, wherein the aqueous solution is used at a minimum of 5% by volume of the total volume of the organic phase solution to wash the total volume of organic phase.

26. A method as in claim 25, wherein the inorganic base comprises one or more of: (a) bicarbonate, (b) carbonate salts of alkali metals including one or more of lithium, sodium, potassium, and cesium; and (c) alkaline earth metals including one or more of calcium, barium, magnesium.

27. A method as in claim 26, wherein the concentration of inorganic bases in aqueous solution is from 0.1% to the respective solubility limit.

28. An apparatus as in claim 2, wherein the reactor is made of one or more of: Polypropylene, glass-filled polypropylene, Polytetrafluoroethylene (PTFE), Perfluoroalkoxy (PFA) resin, Fluorinated ethylene propylene (FEP), Polyethylene, Polyvinylidene fluoride (PVDF), Boro Silicate Glass or, Viton fluoroelastomer, Tantalum metal and Tantalum infused steel.

29. An apparatus as in claim 28, wherein every part of the apparatus that is in contact with the reaction is made of one of more of the materials set forth in claim 28.

~~30. A method as in claim 1, wherein the flow of organic and aqueous phase liquids is without substantial interruption from exiting the pump until reaching the receiving vessel.~~

~~31. An apparatus as in claim 2, comprising a metered chemical delivery apparatus configured to pressurize the organic phase and hydrochloric acid.~~

~~32. A method as in claim 1, wherein HCl gas is communicated through the aqueous phase liquid so that the concentration is returned to at least 26% by weight hydrochloric acid.~~

1. A method for the synthesis of 5-(chloromethyl)-2-furaldehyde (CMF) from saccharides, comprising (a) contacting saccharides in a pure or crude form, hydrochloric acid, and an organic solvent in a continuous, biphasic-flow reactor assembly at a temperature from about 60 degrees C to about 200 degrees C and under pressure from about 1 atmospheres to about 20 atmospheres producing a biphasic liquid mixture containing (x) an organic phase that contains CMF and (y) an aqueous acid phase; (b) separating the organic phase from the aqueous acid phase; (c) cooling the organic phase; and (d) after separating the organic phase from the aqueous acid phase, washing the organic phase with an inorganic base dissolved in aqueous solution at or below the inorganic base's solubility limit in water to create a state of pH not less than seven to remove Hydrothermal Carbon (HTC) dissolved or suspended in the organic phase, wherein the aqueous solution of an inorganic base is used at a minimum of 5% by volume of the total volume of the organic phase solution.

2. A method as in claim 1, comprising continuously supplying saccharides in a pure or crude form, hydrochloric acid and an organic solvent into a biphasic-flow reactor assembly, and wherein the residence time of the reaction is less than 60 minutes.

3. A method as in claim 1, further comprising continuously contacting the biphasic reaction output with a heat removal device after reaction is completed such that the output is cooled to 50 degrees C or below in 5 minutes or less.

4. A method as in claim 2, further comprising continuously contacting the biphasic reaction output with a heat removal device after reaction is completed such that the output is cooled to 50 degrees C or below in 5 minutes or less.

5. A method as in claim 1, wherein the concentration of hydrochloric acid is from 1% to 38% by weight, and wherein the hydrochloric acid contains one or more constituents selected from the group consisting of: inorganic salts, and mineral acids.

6. A method as in claim 1, wherein the organic solvent comprises dichloromethane, chloroform, carbon tetrachloride, diethyl ether, dipropyl ether, ethyl acetate, hexanes, dichloroethane and its structural isomers, trichloroethane and its structural isomers, toluene, benzene, xylenes, and 7. A method as in claim 3, wherein the heat removal devices comprises one or more of: ice bath, heat sink, and heat exchange pump with coolant fluid.

8. A method as in claim 1, wherein the biphasic reaction mixture is subjected to solid/liquid phase separation through a semi-porous membrane, by the action of vacuum, gravity, or mechanical force, wherein the semi-porous membrane comprises one of more of: glass frit funnel, cellulose paper filter, silica gel, alumina, sand, plastic polymer sock-type filter, polypropylene sock-type filter and PTFE sock-type filter.

9. A method as in claim 1, in which insoluble HTC and HTC dissolved or suspended in the organic phase is removed and dried by way of solid/liquid phase separation, and wherein the organic phase containing CMF is concentrated to reduce total volume by distillation to a concentration in organic solvent of between about 5 milligrams per milliliter to about 1000 milligrams per milliliter.

10. A method for the synthesis of 5-(chloromethyl)-2-furaldehyde (CMF) from saccharides, comprising contacting saccharides in a pure or crude form, hydrochloric acid, and an organic solvent in a continuous, biphasic-flow reactor assembly at a temperature from about 60 degrees C to about 200 degrees C and under pressure from about 1 atmospheres to about 20 atmospheres, producing a biphasic mixture containing an organic phase and an aqueous acid phase, wherein the organic phase is washed with an aqueous solution of an inorganic base dissolved in aqueous solution at or below the inorganic base's solubility limit in water to create a state of pH not less than seven, and wherein the aqueous solution of an inorganic base is used at a minimum of 5% by volume of the total volume of the organic phase solution.

11. A method as in claim 10, wherein the inorganic base comprises one or more constituents selected from the group consisting of: (a) bicarbonate, (b) a carbonate salt of an alkali metal, (c) an alkaline earth metal, and wherein the concentration of inorganic bases in aqueous solution is from 0.1% to the respective solubility limit.

12. A method as in claim 5, wherein the inorganic salt contains one or more constituents selected from the group consisting of: lithium chloride, and sodium chloride.

13. A method as in claim 5, wherein the mineral acid contains one or more constituents selected from the group consisting of: sulfuric acid, and hydrobromic acid.

14. A method as in claim 11, wherein the carbonate salt of an alkali metal comprises one or more constituents selected from the group consisting of: (b1) a carbonate salt of lithium, (b2) a carbonate salt of sodium, (b3) a carbonate salt of potassium, (b4) a carbonate salt of cesium.

15. A method as in claim 11, wherein the alkaline earth metal comprises one or more constituents selected from the group consisting of: (c1) calcium, (c2) barium, and (c3) magnesium.