WHAT IS CLAIMED IS:

1. A method of reducing recalcitrance in cellulosic or lignocellulosic materials, the method comprising:

contacting, in a mixture, a first cellulosic or lignocellulosic material having a first level of recalcitrance with one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 7, 8, 9, 10 or 11 elements, to produce a second cellulosic or lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance.

2. The method of claim 1, wherein the one or more elements are in a 1+, 2+, 3+, 4+ or 5+ oxidation state.

3. The method of claim 1 or claim 2, wherein the one or more elements comprise Mn, Fe, Co, Ni, Cu or Zn.

4. The method of any one of the above claims, wherein the one or more elements comprise Fe in the 2+, 3+ or 4+ oxidation state.

5. The method of any one of the above claims, wherein the mixture further comprises one or more oxidants capable of increasing an oxidation state of at least some of said elements.

6. The method of any one of the above claims in which the oxidant comprises ozone and/or hydrogen peroxide.

7. The method of any one of the above claims further comprising maintaining pH at or below about 5.5 during contact, such as between 1 and 5, between 2 and 5, between 2.5 and 5 or between about 3 and 5.

8. The method of any one claims 5-7 further comprising dispersing the first cellulosic or lignocellulosic material in water or an aqueous medium, and then adding first the one or more compounds and then the one or more oxidants.

9. The method of any one of claims 5-7 further comprising dispersing the first cellulosic or lignocellulosic material in water or an aqueous medium, and then adding first the one or more oxidants and then the one or more compounds.

10. The method of any one of the above claims, wherein a total maximum concentration of the elements in the one or more compounds measured in the dispersion is from about 10 μM to about 500 mM, e.g., between about 25 μM and about 250 mM or between about 100 μM and about 100 mM.

11. The method of any one of claims 5-9, wherein a total maximum concentration of the one or more oxidants is from about 100 μM to about 1 M, e.g., between about 250 μM and about 500 mM, or between about 500 μm and 250 mM.

12. The method of any one of claims 5-9 in which the one or more oxidants are applied to the first cellulosic or lignocellulosic material and the one or more compounds as a gas, such as by generating ozone *in-situ* by irradiating the first cellulosic or lignocellulosic and the one or more compounds through air with a beam of particles, such as electrons or protons.

13. The method of any one of the above claims wherein the mixture includes one or more compounds and one or more oxidants, and wherein a mole ratio of the element(s) in the one or more compounds to the one or more oxidants is from about 1:1000 to about 1:25, such as from about 1:500 to about 1:25 or from about 1:100 to about 1:25.

14. The method of any one of the above claims, wherein the mixture further includes one or more hydroquinones, such as 2,5-dimethoxyhydroquinone and/or one or more benzoquinones, such as 2,5-dimethoxy-1,4-benzoquinone.

15. The method of any one of the above claims, wherein the one or more oxidants are electrochemically or electromagnetically generated *in-situ*.

16. A composition comprising 1) a cellulosic or lignocellulosic material, 2) one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 7, 8, 9, 10 or 11 elements, and, optionally, 3) one or more oxidants capable of increasing an oxidation state of at least some of said elements.

17. A method of reducing recalcitrance in cellulosic or lignocellulosic materials, the method comprising:

contacting a first lignocellulosic material having a first level of recalcitrance with one or more ligninases and/or one or more biomass-destroying, e.g., lignin-destroying organisms, to produce a second lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance and

contacting the second lignocellulosic material with an enzyme and/or microorganism.

18. The method of claim 17, wherein the ligninases are selected from the group consisting of manganese peroxidases, lignin peroxidases, laccases and mixtures thereof.

19. The method of claim 17, wherein the biomass-destroying organisms are selected from the group consisting of white rot, brown rot, soft rot and mixtures thereof.

20. The method of claim 1, wherein the method further comprises contacting the second cellulosic or lignocellulosic material with an enzyme and/or microorganism.

21. The method of claim 1, wherein the method further comprises saccharifying the reduced recalcitrance material and then fermenting the saccharified material.

22. A method of reducing recalcitrance in cellulosic or lignocellulosic materials, the method comprising:

contacting, in a mixture, a first cellulosic or lignocellulosic material having a first level of recalcitrance with one or more compounds comprising one or more naturally-occurring, non-radioactive metallic elements, to produce a second cellulosic or lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance.

CLAIMS

1. A method of reducing recalcitrance in cellulosic or lignocellulosic materials, the method comprising:

adding to a first cellulosic or lignocellulosic material that has been irradiated with about 10 to about 50 Mrad of radiation one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 8, 9, 10 or 11 elements, the first cellulosic or lignocellulosic material being dispersed in water or an aqueous medium and having a first level of recalcitrance, to produce a second cellulosic or lignocellulosic material having a second level of recalcitrance lower than the first level of recalcitrance.

2. The method of claim 1, wherein the one or more elements are in a (I), (II), (III), (IV), or (V) oxidation state.

3. The method of claim 1, wherein the one or more elements comprise Fe, Co, Ni, Cu or Zn.

4. The method of claim 1, wherein the one or more elements comprise Fe in the (II), (III) or (IV) oxidation state.

5. The method of claim 1, wherein the mixture further comprises one or more oxidants capable of increasing an oxidation state of at least some of said elements.

6. The method of claim 5 in which the oxidant comprises ozone and/or hydrogen peroxide.

7. The method of claim 1 further comprising maintaining pH at or below about 5.5.

8. The method of claim 5 further wherein the one or more compounds are added first and then the one or more oxidants are added.

9. The method of claim 5 wherein the one or more oxidants are added first and then the one or more compounds are added.

10. The method of claim 1, wherein a total maximum concentration of the elements in the one or more compounds measured in the dispersion is from about 10 μM to about 500 mM.

11. The method of claim 5, wherein a total maximum concentration of the one or more oxidants is from about 100 μM to about 1 M.

12. The method of claim 5 in which the one or more oxidants comprises ozone and the ozone is applied to the first cellulosic or lignocellulosic material and the one or more compounds in-situ by irradiating the first cellulosic or lignocellulosic material and the one or more compounds through air with a beam of particles.

13. The method of claim 12 wherein the particles are selected from the group consisting of electrons and protons.

14. The method of claim 1 wherein the mixture includes one or more compounds and one or more oxidants, and wherein a mole ratio of the element(s) in the one or more compounds to the one or more oxidants is from about 1:1000 to about 1:25.

15. The method of claim 1, wherein the mixture further includes one or more hydroquinones and/or one or more benzoquinones.

16. The method of claim 5, wherein the one or more oxidants are electrochemically or electromagnetically generated in-situ.

17. A composition comprising 1) an irradiated cellulosic or lignocellulosic material, 2) one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 8, 9, 10 or 11 elements, and 3) water or an aqueous medium, in which (1) is first irradiated and then (2) is subsequently dispersed.

18. The method of claim 1, wherein the method further comprises contacting the second cellulosic or lignocellulosic material with an enzyme and/or microorganism.

19. The method of claim 1, wherein the method further comprises saccharifying the reduced recalcitrance material and then fermenting the saccharified material.

20. The method of claim 1, wherein the one or more compounds are added to the water or aqueous medium after the dispersing step.

21. The method of claim 1, wherein the one or more compounds are added to the water or aqueous medium prior to the dispersing step.

22. The method of claim 1, wherein the one or more compounds are added to the first cellulosic or lignocellulosic material before the dispersing step.

23. The method of claim 3, wherein the one or more elements are in the form of a sulfate.

24. The method of claim 23, wherein the one or more elements are in the form of iron(II) sulfate or iron(III) sulfate.

25. The method of claim 15, wherein the hydroquinone is 2,5-dimethoxyhydroquinone.

26. The method of claim 15, wherein the benzoquinone is 2,5-dimethoxy-1,4-benzoquinone.

27. The method of claim 1, wherein the first cellulosic or lignocellulosic material is a sheared fibrous material.

28. The method of claim 27, wherein the fibrous material is Kraft paper.

29. The method of claim 27, wherein the sheared fibrous material has an average length-to-diameter ratio of greater than 5 to 1.

30. The method of claim 27, wherein the sheared fibrous material has a BET surface area of greater than 0.25 square meters per gram.

31. The method of claim 27, wherein the sheared fibrous material has a porosity of greater than 25 percent.

32. The method of claim 1, wherein the cellulosic or lignocellulosic material is selected from the group consisting of: paper, paper products, paper waste, wood, wood wastes and residues, particle board, sawdust, agricultural waste and crop residues, sewage, silage, grasses, rice hulls, bagasse, cotton, jute, hemp, flax, bamboo, sisal, abaca, straw, corn cobs, corn stover, switchgrass, alfalfa, hay, rice

hulls, coconut hair, cotton, synthetic celluloses, seaweed, algae, municipal waste, and mixtures thereof.

33. The method of claim 1, wherein the cellulosic or lignocellulosic material has been irradiated with an electron beam.

34. The method of claim 1, wherein the irradiated cellulosic or lignocellulosic material has received a dose of more than 10 Mrad.