CLAIMS

1. A method of enhancing oxidative recalcitrance reduction ~~reducing recalcitrance~~ in cellulosic or lignocellulosic materials, the method comprising: providing~~adding to~~ a first cellulosic or lignocellulosic material that has been exposed to an ion beam to impart ~~irradiated with~~ about 10 to about 50 Mrad of ionizing radiation the first cellulosic or lignocellulosic material having a first level of recalcitrance, and one or more functional groups formed by the ion beam exposure; and oxidizing the first cellulosic or lignocellulosic material in water or an aqueous medium together with one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 8, 9, 10 or 11 elements, the one or more elements substantially dissociating as cations ~~first cellulosic or lignocellulosic material being dispersed~~ in the water or ~~an~~ aqueous medium, and the cations participating in a Fenton-type reaction while oxidizing ~~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, wherein the functional groups enhance the effectiveness of the oxidizing reaction.

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~~ the ion beam ~~of particles~~.

13. The method of claim 12 wherein the ~~particles are~~ ion beam comprises ions selected from the group consisting of ~~electrons and~~ protons, helium nuclei, argon ions, silicon ions, neon ions, carbon ions, phosphorus ions, oxygen ions, and nitrogen ions.

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 a pretreated cellulosic or lignocellulosic material having a modified level of recalcitrance, the composition having been formed by: providing a first ~~1) an irradiated~~ cellulosic or lignocellulosic material that has been exposed to an ion beam, the cellulosic or lignocellulosic material having a first level of recalcitrance that is greater than the modified level of recalcitrance, and one or more functional groups formed by the ion beam exposure; and

oxidizing the first cellulosic or lignocellulosic material in water or an aqueous medium together with, ~~2)~~ one or more compounds comprising one or more naturally-occurring, non-radioactive group 5, 6, 8, 9, 10 or 11 elements, the one or more elements substantially dissociating as cations in the ~~and 3)~~ water or ~~an~~ aqueous medium, ~~in which (1) is first irradiated and then (2) is subsequently dispersed~~and the cations participating in a Fenton-type reaction while oxidizing, wherein the functional groups enhance the effectiveness of the oxidizing reaction, thereby enhancing oxidative recalcitrance modification of the first cellulosic or lignocellulosic material.

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 second cellulosic or lignocellulosic ~~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 first cellulosic or lignocellulosic material has been addeddispersing step.

21. The method of claim 1, wherein the one or more compounds are added to the water or aqueous medium prior to the first cellulosic or lignocellulosic material having been addeddispersing step.

22. The method of claim 1, wherein the one or more compounds are added to the first cellulosic or lignocellulosic material before the water or aqueous medium has been introduceddispersing 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.~~

3433. The method of claim 1, wherein the first ~~irradiated~~ cellulosic or lignocellulosic material has received ~~a~~ an irradiation dose of more than 10 Mrad from the ion beam.