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ABSTRACT

INTEGRATED PROCESS TO SELECTIVELY CONVERT RENEWABLE ISOBUTANOL TO P-XYLENE

The present invention is directed to a method for preparing renewable and relatively high purity p-xylene from biomass. For example, biomass treated to provide a fermentation feedstock is fermented with a microorganism capable of producing a C_4 alcohol such as isobutanol, then sequentially dehydrating the isobutanol in the presence of a dehydration catalyst to provide a C_4 alkene such as isobutylene, dimerizing the C_4 alkene to a form one or more C_8 alkenes such as 2,4,4-trimethylpentenes or 2,5-dimethylhexene, then dehydrocyclizing the C_8 alkenes in the presence of a dehydrocyclization catalyst to selectively form renewable p-xylene in high overall yield. The p-xylene can then be oxidized to form terephthalic acid or terephthalate esters.

WE CLAIM:

1. A method for preparing renewable p-xylene comprising:

(a) treating biomass to form a fermentation feedstock;

(b) fermenting the fermentation feedstock with one or more species of microorganism to form a fermentation broth comprising aqueous isobutanol;

(c) removing aqueous isobutanol from the fermentation broth;

(d) dehydrating, in the presence of a dehydration catalyst, at least a portion of the aqueous isobutanol of step (c), thereby forming a dehydration product comprising one or more C_4 alkenes and water;

(e) dimerizing, in the presence of an oligomerization catalyst, a dimerization feedstock comprising at least a portion of the C_4 alkenes formed in step (d), thereby forming a dimerization product comprising one or more C_8 alkenes;

(f) dehydrocyclizing, in the presence of a dehydrocyclization catalyst, a dehydrocyclization feedstock comprising at least a portion of the C_8 alkenes of step (e), thereby forming a dehydrocyclization product comprising xylenes and hydrogen, wherein the xylenes comprise at least about 75% p-xylene.

2. The method of claim 1, wherein the dimerization product of step (e) further comprises one or more unreacted C_4 alkenes, and the dehydrocyclization product further comprises one or more unreacted C_8 alkenes, and the method further comprises:

(i) recycling at least a portion of the unreacted C_4 alkene(s) of the dimerization product and/or the unreacted C_8 alkene(s) of the dehydrocyclization product to the dimerization feedstock of step (e); and

(ii) recycling at least a portion of the unreacted C_8 alkene(s) of the dehydrocyclization product to the dehydrocyclization feedstock of step (f).

3. The method of claim 1, wherein at least about 95% of the one or more C_4 alkenes the dehydration product comprise isobutylene.

4. The method of claim 1, wherein said dehydrating of step (d) is carried out in the vapor phase, thereby producing isobutylene vapor and water.

5. The method of claim 1, wherein said dehydrating of step (d) is carried out in the liquid phase, thereby producing liquid isobutylene and water.

6. The method of claim 4, wherein after said dehydrating of step (d), at least a portion of the water produced thereby is removed from the isobutylene vapor using a gas-liquid separator.

7. The method of claim 5, wherein after said dehydrating step (d), a water rich phase is separated from an isobutylene rich phase using a liquid-liquid separator.

8. The method of claim 4, wherein the isobutylene vapor is condensed prior to said dimerizing of step (e).

9. The method of claim 4, wherein the isobutylene vapor and water are condensed after said dehydrating of step (d), prior to said dimerizing of step (e) a water rich phase is separated from an isobutylene rich phase using a liquid-liquid separator, and the dimerization feedstock comprises at least a portion of the isobutylene rich phase.

10. The method of claim 1, further comprising adding to the dimerization feedstock of step (e) at least one diluent selected from the group consisting of t-butanol, isobutanol, water, at least one hydrocarbon, and combinations thereof.

11. The method of claim 10, wherein the at least one diluent comprises at least one hydrocarbon, and the at least one hydrocarbon comprises at least one C_4 alkene recycled from the dimerization product of step (e) or the dehydrocyclization product of step (f), at least one C_4 alkane and/or C_8 alkane recycled from the dehydrocyclization product of step (f), or combinations thereof.

12. The method of claim 10, wherein the diluent comprises water and isobutanol.

13. The method of claim 2, further comprising adding to the dimerization feedstock of step (e) at least one diluent selected from the group consisting of t-butanol, isobutanol, water, at least one hydrocarbon, and combinations thereof.

4. The method of claim 13, wherein the at least one diluent comprises at least one hydrocarbon, and the at least one hydrocarbon comprises at least one C_4 alkene recycled from step (e) or step (f), at least one C_4 alkane and/or C_8 alkane recycled from step (f), or combinations thereof.

15. The method of claim 1, wherein the at least one or more C_8 alkenes of the dimerization product comprises about 50-100% of 2,4,4-trimethylpentenes.

16. The method of claim 15, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 75% of 2,4,4-trimethylpentenes.

17. The method of claim 15, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 90% of 2,4,4-trimethylpentenes.

18. The method of claim 1, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 50-100% of 2,5-dimethylhexene.

19. The method of claim 18, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 75% of 2,5-dimethylhexene.

20. The method of claim 18, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 90% of 2,5-dimethylhexene.

21. The method of claim 1, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 50-100% of 2,5-dimethylhexadiene.

22. The method of claim 21, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 75% of 2,5-dimethylhexadiene.

23. The method of claim 21, wherein the at least one or more C_8 alkenes of the dimerization product comprises at least about 90% of 2,5-dimethylhexadiene.

24. The method of claim 1, further comprising adding to the dehydrocyclization feedstock of step (f) at least one diluent selected from the group consisting of nitrogen, argon, methane, isobutylene, isobutane, isooctane, light aromatics, and combinations thereof.

25. The method of claim 24, wherein the at least one diluent comprises isobutylene, which is unreacted isobutylene from steps (e) and/or (f), or a byproduct from step (f).

26. The method of claim 1, wherein:
said dehydrocyclization of step (f) is carried out at a conversion of less than about 100%; and
unreacted C_8 alkenes are recycled back to the dehydrocyclization feedstock of step (f).

27. The method of claim 1, wherein steps (e) and (f) are carried out simultaneously.

28. The method of claim 1, wherein steps (e) and (f) are carried out sequentially.

29. The method of claim 1, wherein the xylenes of the dehydrocyclization product comprise at least about 90% p-xylene.

30. The method of claim 1, wherein said dehydrating is carried out at temperature of at least about 100°C and a pressure of at least about 1 atm.

31. The method of claim 1, wherein the dehydration catalyst is an organic or inorganic acid, or a metal salt thereof.

32. The method of claim 26, wherein the dehydration catalyst is a heterogeneous acidic γ-alumina catalyst.

33. The method of claim 1, wherein the oligomerization catalyst is a heterogeneous acidic catalyst.

34. The method of claim 33, wherein the oligomerization catalyst is an acidic zeolite, solid phosphoric acid, or a sulfonic acid resin.

35. The method of claim 1, wherein the dehydrocyclization catalyst is a heterogeneous metal-containing dehydrogenation catalyst.

36. The method of claim 35, wherein the dehydrocyclization catalyst is a supported chromium-containing compound.

37. The method of claim 33, wherein the dehydrocyclization catalyst is selected from the group consisting of chromium-oxide treated alumina; platinum- and tin-containing zeolites; and alumina, cobalt- or molybdenum-containing alumina.

38. The method of claim 1, wherein the aqueous isobutanol removed in step (c) consists essentially of isobutanol and 0-15 % water.

39. The method of claim 1, further comprising hydrogenating an alkene in the presence of dehydrogenation catalyst with the hydrogen from step (f).

40. The method of claim 27, wherein said steps (e) and (f) are carried out simultaneously under oxidizing conditions.

41. The method of claim 40, wherein steps (e) and (f) are carried out in the presence of a single catalyst comprising bismuth oxide.

42. The method of claim 41, wherein the C_4 alkenes comprise isobutylene.

43. A method of preparing renewable terephthalic acid comprising:
preparing renewable p-xylene by the method of claim 1, then oxidizing the p-xylene in the presence of an oxidizing agent, thereby forming renewable terephthalic acid.

44. The method of claim 43, wherein the oxidizing agent comprises an oxidation catalyst and oxygen.

45. A method of preparing a renewable polyester comprising:

reacting renewable terephthalic acid prepared by the method of claim 40 with ethylene glycol or butylene glycol in the presence of an acidic polymerization catalyst.

46. The method of claim 45, wherein the acidic polymerization catalyst is antimony (III) oxide.

47. The method of claim 45, wherein the polyester is polyethylene terephthalate, and the ethylene glycol is renewable ethylene glycol.

48. The method of claim 45, wherein the polyester is polypropylene terephthalate, and the propylene glycol is renewable propylene glycol.

49. The method of claim 1, further comprising hydrogenating a portion of the dimerization product with at least a portion of the hydrogen of the dehydrocyclization product.

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Figure 1: Process for Preparing p-Xylene from Isobutanol

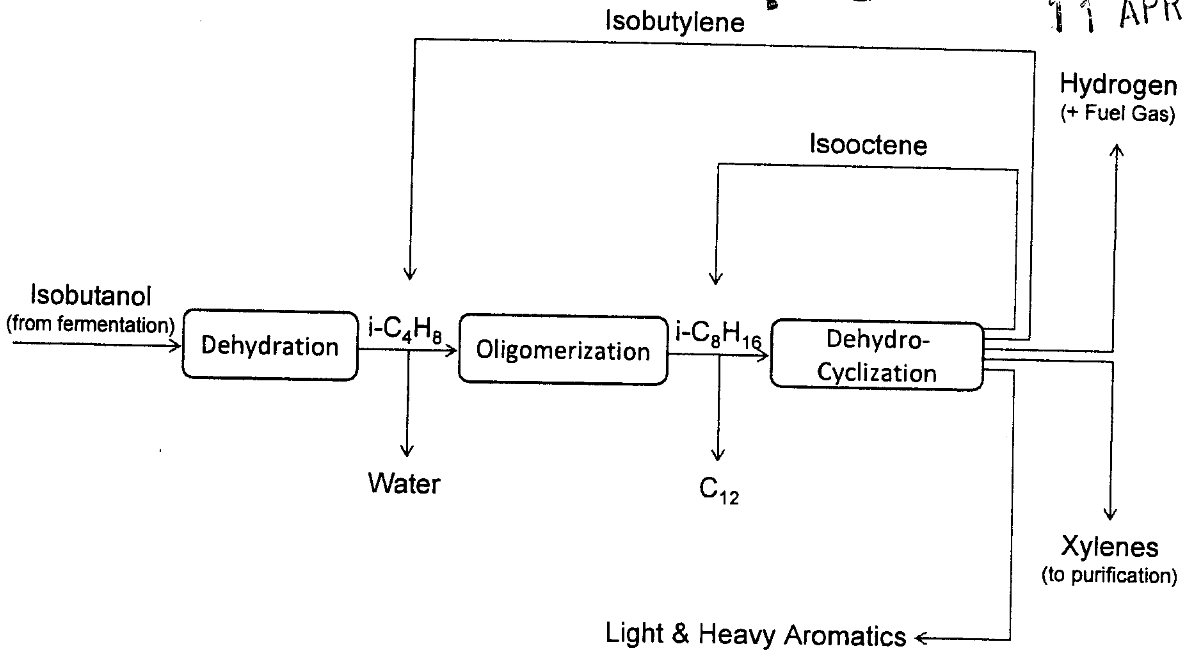

Figure 2: Single Pass Process for Preparing p-Xylene from Isobutanol

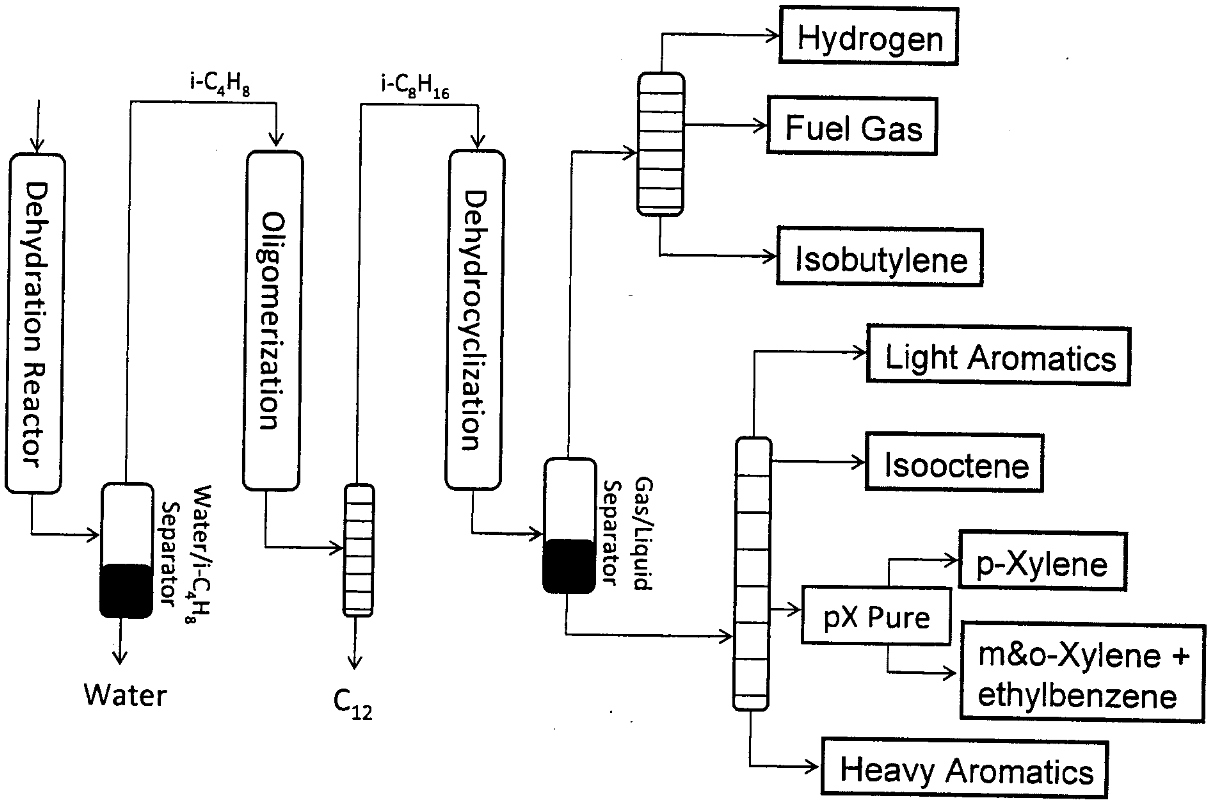

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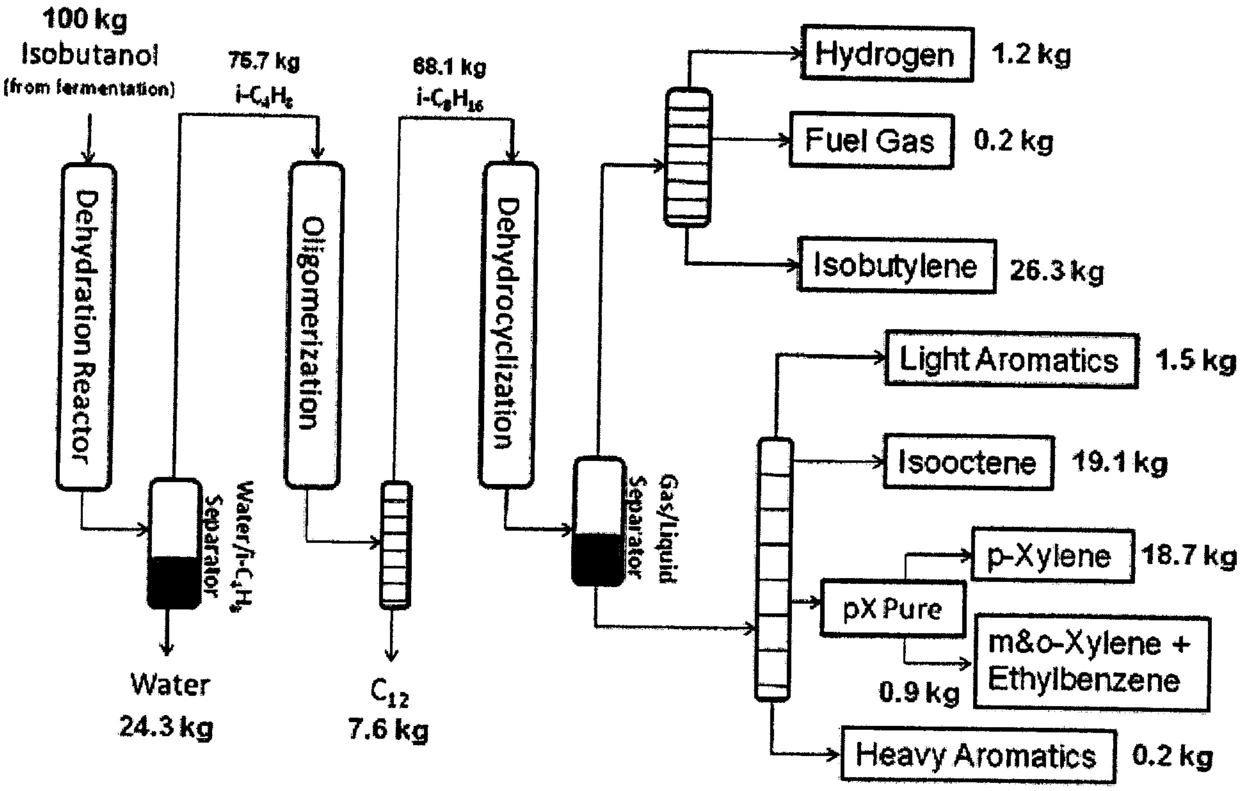
Figure 3: Single Pass Process for Preparing p-Xylene from Isobutanol (Including Yields)



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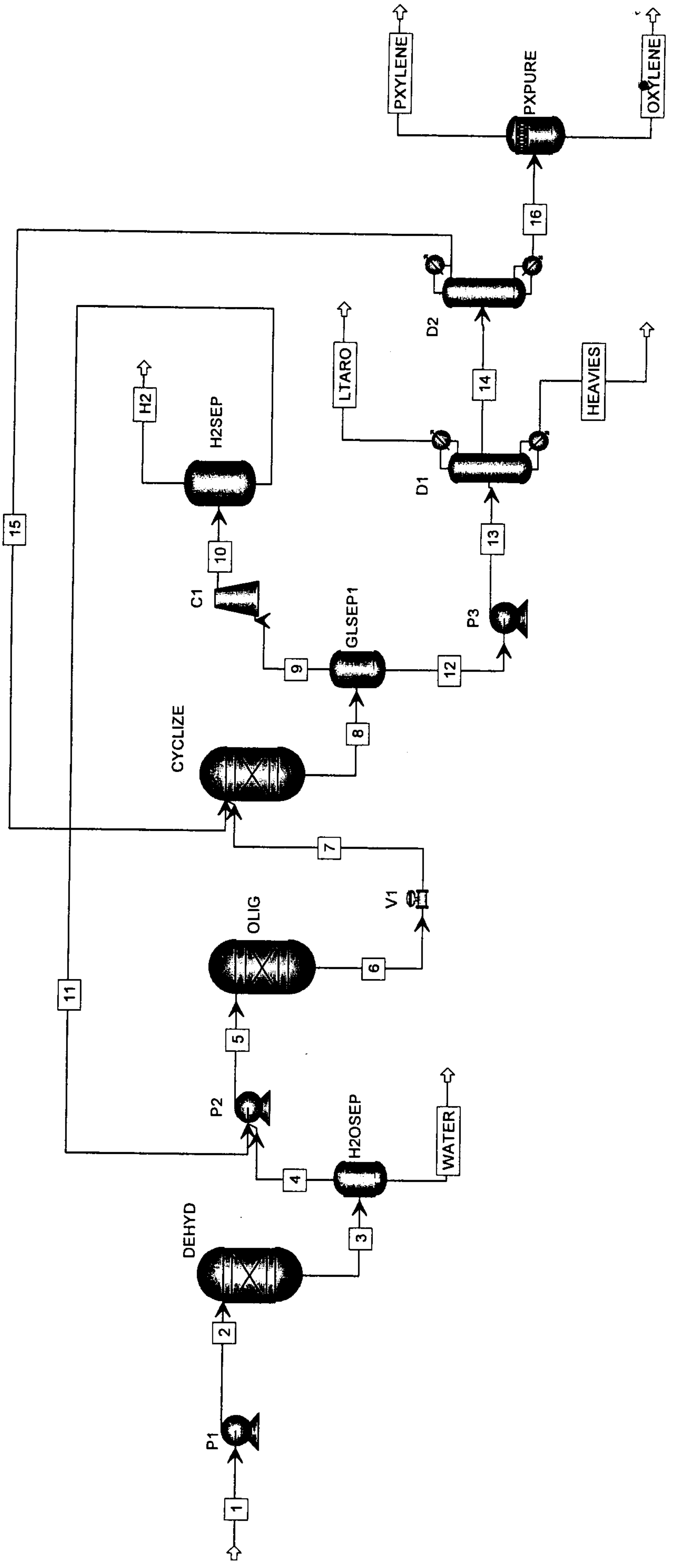

Figure 4: Integrated Process of Example 16

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