A method of making hydrocarbons from polyalcohols, such as carbohydrates. The polyalcohols and carbohydrates may be provided from biomass, including paper, cardboard or urban generated paper product waste; wood and wood products, including forest slash and deadfall; agricultural waste; and the like. The polyalcohols and carbohydrates are combined with hydroiodic acid in aqueous solution to form the hydrocarbon and elemental iodine. Hydroiodic acid is then electrochemically regenerated by reducing the elemental iodine in a parallel reaction. A method of electrochemically generating hydroiodic acid from elemental iodine in aqueous solution is also described.
FIG. 1

100

Provide water-soluble polyalcohol to aqueous solution in electrochemical cell

120

Provide hydroiodic acid

130

Combine water-soluble polyalcohol with hydroiodic acid to form hydrocarbon and iodine

140

Electrochemically regenerate hydroiodic acid from iodine
FIG. 2

200
Provide electrochemical cell

220
Provide aqueous iodine solution to cathodic compartment of electrochemical cell

230
Provide potential across cathode and anode of cell

240
Electrolytically oxidize water in anodic compartment to produce O₂ gas and H⁺ ions

250
Diffuse H⁺ ions through cationic membrane from anodic compartment to cathodic compartment

260
Electrochemically dissociate iodine in cathodic compartment to produce I⁻ ions

270
React H⁺ ions with I⁻ ions in cathodic compartment to form HI
FIG. 3

300

2H₂O → 4H⁺ + O₂ + 4e⁻
2I₂ + 4e⁻ → 4I⁻
4H⁺ + 4I⁻ → 4HI
ELECTROCHEMICAL CONVERSION OF POLYALCOHOLS TO HYDROCARBONS

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/782,905, filed Mar. 15, 2006.

STATEMENT REGARDING FEDERAL RIGHTS

[0002] This invention was made with government support under Contract No. DE-AC51-06NA25396, awarded by the U.S. Department of Energy. The government has certain rights in the invention.

BACKGROUND OF INVENTION

[0003] The invention relates to the conversion of polyalcohols to hydrocarbons. More particularly, the invention relates to conversion of polyalcohols to hydrocarbons by reaction with hydroiodic acid (HI). Even more particularly, the invention relates to conversion of carbohydrates to hydrocarbons combined with the regeneration of HI.

[0004] A variety of applications use aliphatic hydrocarbons, including combustion fuels for heating, transportation, manufacturing, power generation, and the like. As world oil reserves dwindle, however, other means of maintaining hydrocarbon production rates at their current level must be sought.

[0005] Carbohydrates (i.e., biomass) are a potential alternative source of hydrocarbons for use as fuel oil. The conversion of carbohydrates to hydrocarbons can be accomplished using HI as a reducing agent. The reaction between HI and carbohydrates leads to the production of hydrocarbons and iodine (I₂) by first removing a hydroxyl radical from the carbohydrate which produces water and leaves the iodine ion attached to the carbon backbone of the carbohydrate molecule, and second exchanging the attached iodine for hydrogen which results in the corresponding hydrocarbon and one I₂ molecule.

[0006] The major expense incurred by the carbohydrate conversion process described above is the use of HI. To promote HI recycling, phosphorus acid (H₃PO₄) has been used. This method adds the cost of H₃PO₄, which is consumed as HI is recycled, to that of the overall process.

[0007] The current method for converting carbohydrates does not minimize the cost and effort required to regenerate HI. Therefore, what is needed is a method of converting carbohydrates that incorporates a HI regeneration cycle that is not based on chemical reduction of iodine. What is also needed is a method of regenerating HI that is not based upon chemical reduction of iodine.

SUMMARY OF INVENTION

[0008] The present invention meets these and other needs by providing a method of making hydrocarbons from polyalcohols, such as carbohydrates. The polyalcohols or carbohydrates may be provided from biomass, including paper, cardboard, or urban generated paper product waste; wood and wood products, including forest slash and deadfall; agricultural waste; and the like. The polyalcohols or carbohydrates are combined with HI in aqueous solution to form the hydrocarbon and elemental iodine. HI is then electrochemically regenerated by reducing the elemental iodine. A method of electrochemically generating HI from elemental iodine in aqueous solution is also described.

[0009] Accordingly, one aspect of the invention is to provide a method of making at least one hydrocarbon. The method comprises the steps of: providing at least one water-soluble polyalcohol to an aqueous solution in an electrochemical cell; providing a predetermined concentration of HI; combining the HI with the at least one water-soluble polyalcohol in the aqueous solution to form the at least one hydrocarbon and elemental iodine; and electrochemically regenerating HI from the elemental iodine generated by the reaction of the water-soluble polyalcohol with HI within the electrochemical cell.

[0010] A second aspect of the invention is to provide a method of electrochemically generating HI from elemental iodine in aqueous solution. The method comprises the steps of: providing an electrochemical cell, the electrochemical cell comprising an anodic compartment having an anode disposed therein, a cathodic compartment having a cathode disposed therein, and a cationic membrane separating the anodic compartment and the cathodic compartment, wherein the cationic membrane is permeable with respect to protons (H⁺ ions) and impermeable with respect to HI, elemental iodine, water-soluble polyalcohols, and hydrocarbons; providing the aqueous solution containing elemental iodine to the cathodic compartment of the electrochemical cell; providing a predetermined potential across the cathode and anode; electrochemically oxidizing water to form oxygen gas and protons (H⁺ ions) in the anodic compartment; diffusing the protons from the anodic compartment through the cationic membrane into the cathodic compartment; electrochemically reducing the elemental iodine to form iodide ions in the cathodic compartment; and reacting the protons with the elemental iodide ions to regenerate the HI in the cathodic compartment.

[0011] A third aspect of the invention is to provide a method of making at least one of a hydrocarbon fuel and a hydrogenated fuel. The method comprises the steps of: providing an electrochemical cell, the electrochemical cell comprising an anodic compartment having an anode disposed therein, a cathodic compartment having a cathode disposed therein, and a cationic membrane separating the anodic compartment and the cathodic compartment, wherein the cationic membrane is hydrogen permeable and impermeable with respect to HI, elemental iodine, water-soluble polyalcohols, and hydrocarbons; providing at least one water-soluble carbohydrate to an aqueous solution in the cathodic compartment, wherein the at least one carbohydrate is derived from a biomass; providing a predetermined concentration of HI; combining the HI with the at least one water-soluble carbohydrate in the aqueous solution to form at least one of the hydrocarbon fuel and the hydrogenated fuel and elemental iodine; providing a predetermined potential across the cathode and anode; electrochemically oxidizing water to form oxygen gas and protons in the anodic compartment; diffusing the protons from the anodic compartment through the cationic membrane into the cathodic compartment; electrochemically reducing the elemental iodine in the cathodic compartment to form iodide ions; and reacting the protons with the elemental iodide ions to regenerate the HI in the cathodic compartment.

[0012] These and other aspects, advantages, and salient features of the present invention will become apparent from
the following detailed description, the accompanying drawings, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a flow chart for a method of making hydrocarbons from carbohydrates;

[0014] FIG. 2 is a flow chart for a method of electrochemically generating HI from elemental iodine in aqueous solution;

[0015] FIG. 3 is a schematic representation of a two-compartment electrochemical cell in which the conversion of carbohydrates to hydrocarbons is carried out.

DETAILED DESCRIPTION

[0016] In the following description, like reference characters designate like or corresponding parts throughout the several views shown in the figures. It is also understood that terms such as “top,” “bottom,” “outward,” “upward,” and the like are words of convenience and are not to be construed as limiting terms. In addition, whenever a group is described as either comprising or consisting of at least one of a group of elements and combinations thereof, it is understood that the group may comprise or consist of any number of those elements recited, either individually or in combination with each other.

[0017] Referring to the drawings in general and to FIG. 1 in particular, it will be understood that the illustrations are for the purpose of describing a particular embodiment of the invention and are not intended to limit the invention thereto.

[0018] For the purposes of understanding the invention, the term “hydrocarbon” is intended to mean compounds consisting of carbon and hydrogen. In some instances, such as where the invention is used to produce saturated hydrocarbon fuels, the polyalcohols may be unsaturated, saturated, linear aliphatic polyalcohols such as, for example, sorbitol. It has been demonstrated that conversion of polyalcohols (also known as “polys”) such as, for example, carbohydrates, to hydrocarbons can be chemically accomplished using HI as the reducing agent. The reaction leads to the production of hydrocarbons and iodine (I₂) in a two-step process. In the first step, one HI molecule removes a hydroxyl radical from the carbohydrate, producing water and leaving the iodine ion attached to the carbon backbone of the carbohydrate molecule. In the second step, a second HI molecule exchanges the attached iodine for hydrogen, which results in the corresponding hydrocarbon and one I₂ molecule. One example of carbohydrate conversion has been reported in which sorbitol, a water-soluble polyalcohol formed from cellulose, was converted into hexane, a hydrocarbon having the same number of carbon atoms.

[0019] The major expense incurred by the carbohydrate conversion process described above is the use of HI. In the original investigation, phosphorous acid (H₃PO₄) was used to promote recycling. Such a method adds the cost of H₃PO₄, which is consumed as HI is recycled, to that of the overall process. The production of carbohydrates and other polyols from biomass and their subsequent conversion to hydrocarbons are described in the article “The Use of Catalytic Hydrogenation to Interconvert Carbohydrates in a Dilute Acid Hydrolysis of Biomass to Effect a Clean Separation from Lignin,” by J. Michael Robinson et al., appearing in Biomass and Bioenergy, vol. 26 (2004), pp. 473-483, the contents of which are incorporated by reference herein in their entirety.

[0020] In the present invention, hydroiodic acid is recovered without the addition of phosphorous acid. Instead, HI is recovered by the electrochemical reduction of I₂, which is present in solution as a dissolved gas, as it is produced in the cathodic side of a two-compartment electrochemical cell. In this case, the carbohydrate conversion takes place in the cathodic compartment of the electrochemical cell. The cathodic compartment is separated from the anodic compartment by a cationic membrane that prevents oxidation of both polyalcohols and HI at the anode. Oxidation of these species at the anode would lead to I₂ production without reducing the carbohydrates to hydrocarbons. The final products of the conversion reactions will be oxygen gas at the anodic compartment and hydrocarbons in the cathodic compartment.

[0021] Turning to FIG. 1, a flow chart for a method 100 of making hydrocarbons from carbohydrates is shown. In step 110, at least one water-soluble polyalcohol is provided to an aqueous solution in an electrochemical cell. Such polyalcohols include, but are not limited to, carbohydrates. Although the following description refers to carbohydrates, it is understood that the methods described herein are equally applicable to other polyalcohols as well. An electrochemical cell that may be used to perform method 100 is schematically shown in FIG. 3.

[0022] Carbohydrates include sugars, starches, and fibers. Non-limiting examples of sugars include monosaccharides such as glucose, fructose, galactose, and the like; and disaccharides such as sucrose, lactose, maltose, and the like. Non-limiting examples of starches include polymers of alpha-D-glucose units, such as amylose (20-30% alpha-D-glucose) and amylopectin (70-80% alpha-D-glucose). Fibers include cellulose-based (cellulose is a polymer of beta-D-glucose units) polysaccharide fibers. Almost any source of cellulose or material composed of carbohydrates may be used as a source of the at least one carbohydrate. In one embodiment, the carbohydrate may be derived from biomass, such as paper, cardboard or urban generated paper product waste, wood and wood products, including forest slash and deadfall; agricultural waste; and the like. In another embodiment, the biomass is first digested, using methods known in the art, to convert at least a portion of the biomass into water-soluble carbohydrates. The water-soluble carbohydrates may include at least one sugar. The production of carbohydrates and other polyols from biomass is described in the reference by J. Michael Robinson et al., cited hereinabove.

[0023] In step 120, a predetermined concentration of HI is provided to the aqueous solution in the electrochemical cell. The HI concentration is in a range from about 5 M to about 10 M. The HI and the at least one water-soluble carbohydrate are then combined, thereby forming the hydrocarbon and elemental iodine (step 130).

[0024] In one embodiment, the electrochemical cell has an anodic compartment in which the anode is disposed, and a cathodic compartment, in which the cathode is disposed. A cationic membrane separates the anodic compartment and cathodic compartment. The cationic membrane is permeable with respect to protons (e.g., H⁺ ions) and impermeable with respect to HI, elemental iodine, water-soluble polyalcohols, and hydrocarbons. In this embodiment, the HI and the at
least one water-soluble carbohydrate are combined in the cathodic compartment of the electrochemical cell.

[0025] HI is then electrochemically regenerated in step 140 by reducing the I₂—which is present as a gas dissolved in solution—generated by the formation of the hydrocarbon. A potential V is provided across the cathode and anode of the electrochemical cell, causing water to be oxidized at the anode of the electrochemical cell, producing oxygen gas and protons (H⁺). Iodine is electrochemically reduced to iodide (I⁻) ions at the cathode. The potential is in the range from about 0.7 volts to about 2.5 volts. In one embodiment, the potential is about 0.7 volts. The actual potential needed depends on the conductivity of the cationic membrane and the concentration of electrolyte in the electrochemical cell. With the potential applied, protons migrate through the cationic membrane to the cathode region of the electrochemical cell, where they combine with the iodide ions formed by the reduction of I₂ to regeneratively form HI. The regenerated HI may then be used in the continued conversion of carbohydrate. Where the electrochemical cell has anodic and cathodic compartments separated by a cationic membrane, protons migrate from the anodic compartment through the cationic membrane to the cathodic compartment, where they combine with the iodide ions generated by the reduction of I₂ to form HI. Because iodine is continually recycled to regenerate HI, the cell is not limited by HI consumption, and can be run continuously (i.e., as long as water-soluble polyalcohol is provided).

[0026] In one embodiment, formation of the at least one hydrocarbon by the method 100 described above is carried out in a two-compartment electrochemical cell, shown in FIG. 3. Electrochemical cell 300 includes an anode 320, disposed in an anodic compartment 322, and a cathode 310 disposed in a cathodic compartment 312. Potential V is applied across cathode 310 and anode 320 to drive the oxidation of water and I₂. A cationic membrane 330 separates anodic compartment 322 and cathodic compartment 312. In one embodiment, cationic membrane is a proton exchange membrane such as those known in the art, including, for example, poly(perfluoro sulfonic) or the like. One non-limiting example of a poly(perfluoro sulfonic) acid proton exchange membrane is NafionR.

[0027] Cationic membrane 330 is needed to separate anionic and cathodic processes while ionic contact between anionic compartment 322 and cathodic compartment 312 is maintained. The ionic contact is based on protons (H⁺ in FIG. 3) flowing through cationic membrane 330 from anodic compartment 322 to cathodic compartment 312.

[0028] The electrical energy needed to convert carbohydrate from biomass into the analogous hydrocarbon is only 20% of the energy that could be harvested through combustion. Where the energy required to electrochemically recycle the twelve HI molecules that drive the hexane conversion process of the present invention (assuming sorbitol to be the water soluble analog for the cellulose raw material) is 810 kJ/mol (194 kcal/mol) at perfect yield, the total energy released by the combustion of a representative hydrocarbon, hexane, is 4163 kJ/mol (995 kcal/mol).

[0029] The carbohydrate to hydrocarbon electrochemical conversion process described herein can take advantage of the solar energy already stored by photosynthesis in the original production of the carbohydrate. Thus, the conversion process may potentially yield eight times the combustion energy (per unit of electrical energy stored) that is available through electrolysis. The voltage V (FIG. 3) required to promote the electrochemical conversion is at least about 0.7 volts, which is considerably less than the voltage needed to electrolyze water, which is 2.06 volts. The electrical energy required to electrolyze water is 397 kJ/mol (94.8 kcal/mol). However, the energy that can be retrieved by the combustion of hydrogen is only 236 kJ/mol (56.4 kcal/mol), or 59% of the electrical energy invested in the separation.

[0030] The invention also provides a method of electrochemically generating HI from elemental iodine in aqueous solution. A flow chart for the method is shown in FIG. 2. An electrochemical cell 300, shown in FIG. 3 and described hereinabove, is provided in step 210. In step 220, an aqueous solution containing elemental iodine is provided to cathodic compartment 312 of electrochemical cell 300, and a potential V is applied across cathode 310 and anode 320 (step 230). The potential is in the range from about 0.7 volts to about 2.5 volts. In one embodiment, the potential is at least about 0.7 volts. The actual potential needed depends on the conductivity of the cationic membrane 330 and the concentration of electrolyte in the electrochemical cell. In one embodiment, the potential is about 0.7 volts. Water is oxidized at anode 320 in anodic compartment 322 (step 240), producing oxygen gas and protons (H⁺ ions). In step 260, elemental iodine (I₂), which is present in aqueous solution as a dissolved gas, is reduced at cathode 310 to form iodide (I⁻) ions. Protons diffuse from anodic compartment 322 through cationic membrane 330 to cathodic compartment 312 (step 250) where they react with iodide ions to form HI (step 260).

[0031] Given that hydrocarbons generated by method 100 are generally either gases or oils that float on the surface of aqueous chemical solution 305, the hydrocarbons may be physically separated from chemical solution 305 once conversion of polyalcohols to hydrocarbons has taken place. Hydrocarbons generated by method 100 may be used in various applications such as, but not limited to, combustion fuels for heating, transportation, manufacturing, power generation, and the like. In addition to hydrocarbons, method 100 may be used to generate oxygenated fuels such as, but not limited to, ethanol. Such oxygenated fuels may be made by halting step 130 prior to removal of all the hydroxyl groups from the saturated polyalcohol. Step 130 may be stopped or controlled by limiting the amount of HI added in step 120, or by stopping the electrochemical regeneration of HI (step 150).

[0032] Although typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present invention.

1. A method of making at least one hydrocarbon, the method comprising the steps of:
   a. providing at least one water-soluble polyalcohol to an aqueous solution in an electrochemical cell;
   b. providing a predetermined concentration of hydroiodic acid;
   c. combining the hydroiodic acid with the at least one water-soluble polyalcohol in the aqueous solution to form elemental iodine and the at least one hydrocarbon; and
d. electrochemically regenerating hydroiodic acid from the elemental iodine generated by the reaction of the at least one water-soluble polyalcohol with hydroiodic acid within the electrochemical cell.

2. The method according to claim 1, wherein the at least one water-soluble polyalcohol includes at least one water-soluble carbohydrate.

3. The method according to claim 2, wherein the at least one water-soluble carbohydrate comprises at least one of a sugar, a starch, and a fiber.

4. The method according to claim 3, wherein the at least one water-soluble carbohydrate comprises at least one sugar selected from the group consisting of glucose, fructose, galactose, sucrose, lactose, and maltose.

5. The method according to claim 3, wherein the fiber is a biomass derived from at least one of paper, paper product waste, wood, wood products, agricultural waste, and combinations thereof.

6. The method according to claim 5, wherein the step of providing at least one water-soluble polyalcohol to an aqueous solution in an electrochemical cell comprises digesting the biomass to convert at least a portion of the biomass into the at least one water-soluble carbohydrate.

7. The method according to claim 2, wherein the at least one water-soluble carbohydrate comprises sorbitol, and wherein the at least one hydrocarbon comprises hexane.

8. The method according to claim 1, wherein the electrochemical cell comprises an anodic compartment having an anode disposed therein, a cathodic compartment having a cathode disposed therein, and a cationic membrane separating the anodic compartment and a cathodic compartment, wherein the cationic membrane is permeable with respect to protons and impermeable with respect to hydroiodic acid, elemental iodine, water-soluble polyalcohols, and hydrocarbons.

9. The method according to claim 8, wherein the step of combining the hydroiodic acid with the at least one water-soluble polyalcohol in the aqueous solution to form the at least one hydrocarbon and elemental iodine comprises combining the hydroiodic acid with the at least one water-soluble polyalcohol in the aqueous solution in the cathodic compartment to form the at least one hydrocarbon and elemental iodine.

10. The method according to claim 8, wherein the step of regenerating hydroiodic acid from the elemental iodine comprises:
   a. providing a predetermined potential across the cathode and anode;
   b. electrochemically oxidizing water to form oxygen gas and protons in the anodic compartment;
   c. diffusing the protons through the cationic membrane from the anodic compartment through the cationic membrane into the cathodic compartment;
   d. electrochemically reducing the elemental iodine to form iodide ions in the cathodic compartment;
   e. reacting the protons with the elemental iodide ions to regenerate the hydroiodic acid in the cathodic compartment.

11. The method according to claim 10, wherein the predetermined potential is less than the voltage needed to electrolyze water.

12. The method according to claim 1, wherein the predetermined concentration of hydroiodic acid is in a range from about 5 M to about 10 M.

13. A method of electrochemically generating hydroiodic acid from elemental iodine in aqueous solution, the method comprising the steps of:
   a. providing an electrochemical cell, the electrochemical cell comprising an anodic compartment having an anode disposed therein, a cathodic compartment having a cathode disposed therein, and a cationic membrane separating the anodic compartment and the cathodic compartment, wherein the cationic membrane is permeable with respect to protons and impermeable with respect to hydroiodic acid, elemental iodine, water-soluble polyalcohols, and hydrocarbons;
   b. providing the aqueous solution containing elemental iodine to the cathodic compartment of the electrochemical cell;
   c. providing a predetermined potential across the cathode and anode;
   d. electrochemically oxidizing water to form oxygen gas and protons in the anodic compartment;
   e. diffusing the protons from the anodic compartment through the cationic membrane into the cathodic compartment;
   f. electrochemically reducing the elemental iodine to form iodide ions in the cathodic compartment; and
   g. reacting the protons with the elemental iodide ions to regenerate the hydroiodic acid in the cathodic compartment.

14. The method according to claim 13, wherein the predetermined potential is less than the voltage needed to electrolyze water.

15. A method of making at least one of a hydrocarbon fuel and an oxygenated fuel, the method comprising the steps of:
   a. providing an electrochemical cell, the electrochemical cell comprising an anodic compartment having an anode disposed therein, a cathodic compartment having a cathode disposed therein, and a cationic membrane separating the anodic compartment and the cathodic compartment, wherein the cationic membrane is permeable with respect to protons and impermeable with respect to hydroiodic acid, elemental iodine, water-soluble polyalcohols, and hydrocarbons;
   b. providing at least one water-soluble carbohydrate to an aqueous solution in the cathodic compartment, wherein the at least one water-soluble carbohydrate is derived from a biomass;
   c. providing a predetermined concentration of hydroiodic acid;
   d. combining the hydroiodic acid with the at least one water-soluble carbohydrate in the aqueous solution to form at least one of the hydrocarbon fuel and the oxygenated fuel and elemental iodine;
   e. providing a predetermined potential across the cathode and anode;
   f. electrochemically oxidizing water to form oxygen gas and protons in the anodic compartment;
   g. diffusing the protons through the cationic membrane from the anodic compartment through the cationic membrane into the cathodic compartment;
   h. electrochemically reducing the elemental iodine to form iodide ions in the cathodic compartment; and
   i. reacting the protons with the elemental iodide ions to regenerate the hydroiodic acid in the cathodic compartment.
16. The method according to claim 15, wherein the at least one water-soluble carbohydrate comprises at least one of a sugar, a starch, and a fiber.

17. The method according to claim 16, wherein the at least one water-soluble carbohydrate comprises at least one sugar selected from the group consisting of glucose, fructose, galactose, sucrose, lactose, and maltose.

18. The method according to claim 15, wherein the biomass is derived from at least one of paper, paper product waste, wood, wood products, agricultural waste, and combinations thereof.

19. The method according to claim 15, wherein step of providing at least one water-soluble carbohydrate to an aqueous solution in an electrochemical cell comprises digesting the biomass to convert at least a portion of the biomass into the at least one water-soluble carbohydrate.

20. The method according to claim 15, wherein the at least one carbohydrate comprises sorbitol, and wherein the hydrocarbon comprises hexane.

21. The method according to claim 15, wherein the predetermined potential is less than the voltage needed to electrolyze water.

22. The method according to claim 15, wherein the predetermined concentration of hydroiodic acid is in a range from about 5 M to about 10 M.

23. The method according to claim 15, wherein the oxygenated fuel comprises ethanol.