CONVERSION OF CARBOXYLIC ACIDS TO ALPHA-OLEFINS

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ABSTRACT
An electrolytic method of producing olefins from alkali metal salts of carboxylic acids is disclosed. The carboxylic acid may be from a variety of sources including fermented biomass that is subsequently neutralized using an alkali metal base. The method enables the efficient production of olefins including alpha-olefins as well as useful olefin products such as synthetic oils.
FIG. 1
CONVERSION OF CARBOXYLIC ACIDS TO ALPHA-OLEFINS

CROSS-REFERENCE TO RELATED APPLICATION


U.S. GOVERNMENT INTEREST

[0002] This invention was made with government support under Contract No. 2012-10008-20263 awarded by the U.S. Department of Agriculture, National Institute of Food and Agriculture. The government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present application relates to methods of preparing olefins from carboxylic acids, particularly using electrolytic techniques.

BACKGROUND

[0004] For over a decade, government agencies like the U.S. Department of Energy have investigated biomass conversion into biofuels, bioproducts and biopower leading to advances in the research, development and deployment of different bioenergy technologies. The majority of this effort has focused on producing biofuels for the transportation markets, with successes in the renewable gasoline, biodiesel and bio-jet markets. Yet, the current large supply of natural gas and liquid petroleum from fracking technologies has made it difficult for biofuels to compete economically in these high-volume, low-margin markets.

[0005] The development of biofuels and other bioproducts has also resulted in the development of technologies for converting and upgrading those fuels and other bioproducts for specialty chemicals such as synthetic lubricants. High quality synthetic based oil is mainly composed of poly-alpha-olefins (PAOs), for which market demand outweighs available supply. The disparity between the supply and demand for PAOs arises because the necessary starting material is made using fractions of petroleum that are used in the production of kerosene and diesel. In most crude oil refineries, the later products take priority over the PAOs, and thus limited amounts of these fractions are diverted to make PAOs. To produce PAOs, not only is the volume of diesel and kerosene reduced, but the refinery must invest additional money and energy into converting the hydrocarbons from these fractions to alpha-olefins. This process produces a range of alpha-olefins, of which only a few have significant commercial value. One of the more valuable alpha-olefins, 1-decene (C12 alpha-olefin), is selectively used to make the PAOs for synthetic lubricants.

[0006] Another route currently used for the production of olefins requires steam cracking hydrocarbons to produce ultra-high-purity ethylene, followed by ethylene oligomerization that produces 1-decene (C10 alpha-olefin) and 1-dodecene. Because of the high production cost, the supply of C12 alpha-olefins available to make the PAOs synthetic oil is limited even though there is a large commercial market for this high performance oil. The higher market demand for PAO synthetic oil arises from their improved lubricating properties such as: higher viscosity index, lower temperature fluidity, lower volatility, better oxidative stability, greater thermal stability, and lower friction force.

[0007] Thus, there remains a need for alternative techniques for preparing alpha-olefins using hydrocarbon feedstock derived from biomass.

SUMMARY OF THE INVENTION

[0008] In one aspect, an electrochemical method of preparing olefins from an alkali metal salt of a carboxylic acid is disclosed. The method includes providing an electrochemical cell having an anolyte compartment, a catholyte compartment, and an alkali ion conductive membrane separating the anolyte compartment from the catholyte compartment. The method further includes providing an anolyte solution of an alkali metal salt of the carboxylic acid to the anolyte compartment. The anolyte solution may have a pH in the range from about 8 to 14. An electrical potential is applied to the anode and cathode to electrochemically decarboxylate the alkali metal salt of the carboxylic acid into one or more olefins.

[0009] The anolyte compartment comprises an electrochemically active anode selected to perform a two-electron decarboxylation reaction of the alkali metal salt of the carboxylic acid, wherein the anode comprises a carbonaceous surface. The catholyte compartment comprises an electrochemically active cathode where reduction reactions occur. The alkali ion conductive membrane permits selective transport of alkali ions between the anolyte compartment and the catholyte compartment under influence of the electric potential.

[0010] In some embodiments, the current has a voltage between 2 and 20 volts. In other embodiments, the voltage is between 4 and 12 volts. In some embodiments, the current has a current density of between 5 and 100 mA/cm². In other embodiments, the current density is between 5 and 50 mA/cm². In some embodiments, the carboxylic acid is neutralized to have a pH between about 8 and 14. In other embodiments, the pH is between 9 and 13. In still other embodiments, the pH is between 10 and 12.

[0011] In some non-limiting embodiments, the method also includes mixing the alkali metal salt of the carboxylic acid with an organic solvent. In some embodiments the organic solvent comprises one or more organic alcohols and mixtures thereof. In some embodiments, the one or more organic alcohols are selected from the group consisting of: methanol, ethanol, propanol, isopropanol, butanol, and mixtures thereof. In other embodiments, the organic solvent is selected from the group consisting of: acetonitrile, dimethylformamide, sulfolane, pyridine, 2,6-pyridine, and mixtures of the same.

[0012] In some non-limiting embodiments, the method also includes adjusting the pH of the alkali metal salt of the carboxylic acid with a base. In some embodiments, the base is an alkali metal hydroxide. In some embodiments, the base is sodium hydroxide.

[0013] In some non-limiting embodiments, the method also includes mixing the alkali metal salt of the carboxylic acid with an electrolyte selected from the group consisting of: a metal halide, a metal nitrate, a metal sulfate, a metal perchlorate, and a metal tetrafluoroborate.

[0014] In some non-limiting embodiments, the alkali ion conducting membrane is a NaSICON membrane.
In some non-limiting embodiments, the method also includes fermenting biomass to produce the carboxylic acid and neutralizing the carboxylic acid with an alkali metal hydroxide to form the alkali metal salt of the carboxylic acid. The carboxylic acid may have an even number of carbon atoms. In some embodiments, the carboxylic acid is selected from the group consisting of: octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, and octadecanoic acid. In some embodiments, the carboxylic acid is dodecanoic acid.

In some embodiments, the one or more olefins is an alpha-olefin. In some embodiments, the one or more olefins is 1-undecene. In another aspect, a method further comprises oligomerizing the one or more olefins to make a synthetic lubricant.

In another aspect, an electrochemical cell or reactor for producing olefins is disclosed. The reactor includes an anolyte compartment, a catholyte compartment, an alkali ion conductive membrane, and a source of electric potential to operate the electrochemical reactor.

The anolyte compartment includes a solution of an alkali metal salt of a carboxylic acid. The solution has a pH in the range from about 8 to 14, and preferably a pH in the range from 9 to 13, and more preferably a pH in the range from about 10 to 12. The anolyte compartment includes an electrochemically active anode selected to perform a two-electron decarboxylation reaction of the alkali metal salt of carboxylic acid. In one embodiment, the anode comprises a carbonaceous surface.

The catholyte compartment houses an electrochemically active cathode where reduction reactions occur.

The alkali ion conductive membrane separates the anolyte compartment from the catholyte compartment and permits selective transport of alkali ions between the anolyte compartment and the catholyte compartment.

The source of electric potential is electrically connected to the anode and to the cathode.

FIG. 3B is a chromatograph showing the resulting products from applying voltage and current densities for the decarboxylation process from FIG. 3A.

DETAILED DESCRIPTION

Reference throughout this specification to “one embodiment,” “an embodiment,” or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the innovation described herein. Thus, appearances of the phrases “in one embodiment,” “in an embodiment,” and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment. Additionally, while the following description refers to several embodiments and examples of the various components and aspects of the described innovation, all of the described embodiments and examples are to be considered, in all respects, as illustrative only and not as being limiting in any manner.

Furthermore, the described features, structures, or characteristics of the innovation may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are disclosed to provide a thorough understanding of embodiments of the innovation. One having ordinary skill in the relevant art will recognize, however, that the innovation may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the innovation.

To address the aforementioned need for alternative techniques to efficiently produce olefins, the present disclosure describes an economically viable and novel upgrading process to produce olefins from carboxylic acids, including biomass, without using hydrogen gas or expensive catalysis. In one embodiment, the present technique is used for the production of alpha-olefins. The olefins produced can be a direct replacement of the olefins synthesized from crude oil for a variety of applications, including but not limiting to co-monomers, PAO synthetic lubricants, drilling lubricants, and surfactants. Unlike the routes to producing olefins from petroleum, the method disclosed can selectively produce specific olefins with yields above 50% at moderate temperatures and pressures and without the use of a catalyst. Also, hydrogen gas can be concurrently produced in an electrochemical reactor such as with a two-compartment cell. This hydrogen can be recovered and used for other processes that require hydrogen input. Thus, the innovation can produce bio-derived olefins that are just an alternative to petroleum based olefins, but at an economical advantage.

Another benefit of the innovation is the resulting reduction in green-house gas (GHG) emissions relative to conventional production techniques of olefins. Such reductions arise from three aspects of the disclosed process: (1) the proposed electrochemical reactor produces olefins without the need for hydrogen gas for chemical reduction; (2) the source of feedstock of the olefins is renewable; and (3) and the reduced cost in producing poly-alpha-olefins will enable the greater availability and use of synthetic oil in the transportation market increasing fuel economy and reducing GHG emissions from combustion engines.

In one embodiment, the process uses an electrochemical reactor that converts an alkali metal salt of lauric
acid (a twelve-carbon (C12) carboxylic acid), optionally produced from the fermentation of lignocellulose sugar, into a corresponding alpha-olefin, for example undec-1-ene (also known as undec-1-ene).

[dodecanoic acid (lauroic acid)]

undec-1-ene

[0033] The oxidation is carried out in a simple electrochemical reactor that can be used on a distributed scale, following the two electron oxidation reaction represented as:

\[ \text{C}_11\text{H}_{22}\text{COO}^-\text{M}^- + \text{C}_11\text{H}_{22}\text{CO}_2\text{H} + 2\text{e}^- + \text{M}^+ + \text{OH}^- \]

and for example where the metal (M) is sodium as:

\[ \text{C}_11\text{H}_{22}\text{COO}^-\text{Na}^- + \text{C}_11\text{H}_{22}\text{CO}_2\text{H} + 2\text{e}^- + \text{Na}^+ + \text{H}^+ \]

[0034] The process described herein is a two electron decarboxylation. In contrast, a one electron decarboxylation process is known as Kolbe electrolysis that results in radical coupling products that are undesirable according to the presently disclosed invention. Thus, two electron decarboxylation to produce olefins is desired according to the present invention, whereas one electron decarboxylation to produce radical coupling products is not desired.

[0035] Upon diffusing through an optional membrane, the alkali metal ions, for example sodium ions, react with hydroxide anions produced by the corresponding reduction of water in the reaction shown below.

\[ 2\text{Na}^+ + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{NaOH} + \text{H}_2 \]

[0036] Thus, hydrogen and alkali hydroxide are produced at the cathode. The alkali hydroxide may optionally be used to saponify the feedstock carboxylic acid to form the alkali metal salt of the carboxylic acid as follows:

\[ \text{R}^-\text{COOH} + \text{NaOH} \rightarrow \text{R}^-\text{COONa} + \text{H}_2\text{O} \]

[0037] Advantageously, the alkali hydroxide may be regenerated in the catholyte compartment as described above.

[0038] FIG. 1 schematically shows one possible electrochemical cell or reactor 100 that may be used in the electrochemical process of producing olefins within the scope of the present invention. The electrolytic cell 100 includes an anolyte compartment 110, a catholyte compartment 112, and an alkali ion conductive membrane 114 separating the anolyte compartment 110 from the catholyte compartment 112.

[0039] The anolyte compartment 110 comprises an electrochemically active anode 116 selected to perform a two-electron decarboxylation reaction of an alkali metal salt of a carboxylic acid. The anode 116 preferably comprises a carbonaceous surface. The catholyte compartment 112 comprises an electrochemically active cathode 118 where reduction reactions occur. The alkali ion conductive membrane 114 permits selective transport of alkali ions (M⁺) 120 between the anolyte compartment 110 and the catholyte compartment 112 under influence of an electric potential 122 while preventing solvent or anion transfer between the anolyte and catholyte compartments. Alkali ions 120 include, but are not limited to, sodium ions, lithium ions, potassium ions and mixtures of the same.

[0040] The alkali ion conductive membrane 114 can be virtually any suitable alkali ion conductive membrane that selectively conducts alkali ions and prevents the passage of water, hydroxide ions, or other reaction products. The alkali ion conducting membrane 114 may include a ceramic, a polymer, or combinations thereof. In one embodiment, the alkali ion conducting membrane is an alkali ion super ion conducting (MSICON) membrane. Some non-limiting examples of such membranes include, but are not limited to, a NaSICON (sodium super ionic conductor membrane) and a NaSICON-type membrane. The alkali ion conductive membrane may be any of a number of sodium super ion conducting materials, including, without limitation, those disclosed in United States Patent Application Publications Nos. 2010/0331170 and 2008/0245671 and in U.S. Pat. No. 5,580,430. The foregoing applications and patent are hereby incorporated by reference. In some embodiments, a sodium selective ceramic membrane NaSelect® (Ceramatec, Salt Lake City, Utah USA) may be used.

[0041] Where other non-sodium alkali metals are used, it is to be understood that similar alkali ion conductive membranes such as a LiSICON, membrane, a LiSICON-type membrane, a KSiCON membrane, a KSiCON-type membrane may be used. In some embodiments, an alkali ion conducting ion-exchange polymeric membrane may be used. In some embodiments, the alkali ion conducting membrane may comprise an alkali ion conductive glass or beta alumina.

[0042] The electrochemical cell 100 may be a parallel plate configuration where flat plate electrodes and membranes are used. The anode 116 can be any suitable anode material that allows two-electron oxidation (decarboxylation) reaction in the anolyte compartment 110 when electrical potential 122 passes between the anode 116 and the cathode 118. Some non-limiting examples of suitable anode materials include carbonaceous electrodes or electrodes with carbonaceous surfaces such as natural or artificial graphite, graphite nanopowder, acetylene black, Super P® (available from Westlake Chemical, Westlake, Ohio), MesoCarbon, high surface active carbon, glassy carbon, carbon nanotubes, and graphene.

[0043] The cathode 118 may be any suitable cathode that allows the cell to reduce water, methanol, or other suitable electrolyte containing-solvent in the catholyte compartment 112 to produce hydroxide ions, methoxide ions, or other corresponding organic oxide ions and hydrogen gas. Some non-limiting examples of suitable cathode materials include, without limitation, nickel, stainless steel, graphite, and any other suitable cathode material that is known or novel.

[0044] In one embodiment, the electrochemical cell 100 is operated by feeding or otherwise providing an anolyte solution 124 into the anolyte compartment 110. The anolyte solution 124 includes a solvent and a carboxylic acid or an alkali metal salt of carboxylic acid. The alkali metal salt of the carboxylic acid can be obtained by reacting the carboxylic acid with alkali metal hydroxide, for example sodium hydroxide (NaOH), lithium hydroxide (LiOH), and potassium hydroxide (KOH).

[0045] The carboxylic acid can be obtained from a variety of sources, including biomass. Some non-limiting examples of suitable carboxylic acids are fatty acids listed in Table 1. In some embodiments, the carboxylic acid has from 6-20 carbon
atoms. In some embodiments, the carboxylic acid has from 6-12 carbon atoms. In some embodiments, the carboxylic acid has from 16-18 carbon atoms. In some embodiments, the carboxylic acid has from 12-18 carbon atoms.

<table>
<thead>
<tr>
<th>Number of carbon atoms</th>
<th>Common name</th>
<th>IUPAC name</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Caproic acid</td>
<td>Hexanoic acid</td>
</tr>
<tr>
<td>7</td>
<td>Caprylic acid</td>
<td>Heptanoic acid</td>
</tr>
<tr>
<td>8</td>
<td>Pelargonic acid</td>
<td>Nonanoic acid</td>
</tr>
<tr>
<td>9</td>
<td>Capric acid</td>
<td>Decanoic acid</td>
</tr>
<tr>
<td>10</td>
<td>Undecylic acid</td>
<td>Undecanoic acid</td>
</tr>
<tr>
<td>11</td>
<td>Lauric acid</td>
<td>Dodecanoic acid</td>
</tr>
<tr>
<td>12</td>
<td>Tridecylic acid</td>
<td>Tridecanoic acid</td>
</tr>
<tr>
<td>13</td>
<td>Myristic acid</td>
<td>Tetradecanoic acid</td>
</tr>
<tr>
<td>14</td>
<td>Pentadecylic acid</td>
<td>Pentadecanoic acid</td>
</tr>
<tr>
<td>15</td>
<td>Palmitic acid</td>
<td>Hexadecanoic acid</td>
</tr>
<tr>
<td>16</td>
<td>Margaric acid</td>
<td>Heptadecanoic acid</td>
</tr>
<tr>
<td>17</td>
<td>Stearic acid</td>
<td>Octadecanoic acid</td>
</tr>
<tr>
<td>18</td>
<td>Arachidic acid</td>
<td>Nonadecanoic acid</td>
</tr>
<tr>
<td>19</td>
<td>Hydroxymyristic acid</td>
<td>No acid</td>
</tr>
<tr>
<td>20</td>
<td>Arachidic acid</td>
<td>Icosanoic acid</td>
</tr>
</tbody>
</table>

As can be appreciated by one of skill in the art, a decarboxylation using the techniques disclosed herein would result in the loss of one carbon atom from any of the fatty acids identified in Table 1. Thus, in some embodiments, the resulting olefins have from 5-19 carbon atoms. In some embodiments, the olefins have from 5-11 carbon atoms. In some embodiments, the olefins have from 15-17 carbon atoms. In some embodiments, the olefins have from 11-17 carbon atoms.

The anolyte solution 124 may include one or more solvents. In some embodiments, the solvent may be an organic lower alkane such as methanol, ethanol, propanol, isopropanol, butanol, or mixtures of the same. In some embodiments, the solvent may be acetonitrile, dimethylformamide, sulfolane, pyridine, 2,6-pyridine, and mixtures of the same. In some embodiments the solvent may be comprised of an ionic liquid. In other embodiments that solvent may be comprised of a molten salt. It should be clear to those familiar with the art that the choice of solvent for the anolyte will be determined in part by the carboxylic acid or alkali carboxylate solubility, the electrochemical stability of the solvent, the lack of nucleophilic nature, and other properties that improve the electron oxidation and subsequent E1 elimination reaction.

The anolyte solution 124 may optionally contain a supporting electrolyte that is soluble in the solvent and which provides high electrolyte conductivity in the anolyte solution. One non-limiting example of a supporting electrolyte includes an alkali metal tetrafluoroborate. Another example may include tetramethylammonium hexafluorophosphate. Other ionic solids may also be used such as metal halides, nitrates, sulfates, perchlorates, and mixtures of the same. In one embodiment, supporting electrolytes that act as a Bronsted base are used. In such a case, the supporting electrolyte not only increases the conductivity of the anolyte solution, it also increases the rate of the olefin formation by promoting an E1 elimination reaction.

An electrical potential 122 is applied to the anode 116 and cathode 118 to electrochemically decarboxylate the alkali metal salt of the carboxylic acid into one or more olefins 126 and carbon dioxide (CO₂) 128. The olefins produced include alpha olefins and internal linear olefins. The carbon number of the olefin produced depends on the carboxylic acid or alkali carboxylate salts used in the decarboxylation. In one embodiment the decarboxylation of laureate (C12) produces the C11 alpha-olefin, 1-undecene, and also the internal linear olefins such as 2-undecene, 3-undecene, 4-undecene, and 5-undecene, and mixtures of the same.

The electric potential 122 may be applied at a voltage of between 2 and 50 V. In some embodiments, the voltage applied is between 4 and 18 V. In some embodiments, the voltage applied is between 4 and 12 V. The electric potential may be applied with a current density of between 5 and 100 mA/cm². In some embodiments, the current density is between 5 and 500 mA/cm². In some embodiments, the anolyte solution 110 has a pH in the range from about 8 to 14. In other embodiments, the anolyte solution 110 has a pH in the range from about 9 to 13. In still other embodiments, the anolyte solution 110 has a pH in the range from about 10 to 12. It should be understood by those of ordinary skill that the electrical potential, current density, and pH can be controlled to modify the ratio of olefins produced by the electrochemical decarboxylation.

In some non-limiting embodiments, the anolyte compartment may have an operating temperature in the range from 20° C. to 150° C. In other embodiments, the anolyte compartment may have an operating temperature in the range from 50° C. to 150° C. It is believed that a temperature greater than ambient temperature (>20° C.) may facilitate the decarboxylation reaction to produce olefins.

In some embodiments, a catholyte solution 130 is provided into the catholyte compartment 112. The catholyte solution 130 may comprise a solvent that is the same or different than the anolyte solvent. The anolyte and catholyte solvents may be different because the alkali conductive membrane 114 isolates the compartments and from each other. The catholyte solution may comprise a mixture of solvents with or without water. In the embodiment shown in FIG. 1, the catholyte solution comprises water. At least initially, the catholyte solution includes alkali ions, which may be in the form of an unsaturated alkali hydroxide solution. The concentration of alkali hydroxide can be between about 0.1% by weight and about 50% by weight of the solution. In one embodiment, the catholyte solution includes a dilute solution of alkali hydroxide. During operation, the source of alkali ions may be provided by alkali ions transporting across the alkali ion conductive membrane from the anolyte compartment to the catholyte compartment. While alkali hydroxide is used in the following discussion and shown in FIG. 4, persons skilled in the art will appreciate that methanol may substitute alkali hydroxide in the apparatus for preparing alkali methylene instead. Thus, the catholyte solution may include methanol.

At the cathode 118, reduction of water to form hydrogen gas 132 and hydroxide ions takes place (Reaction 1). The hydroxide ions react with available alkali ions (M⁺) 120 transported from anode compartment 110 via the alkali conductive membrane 114 to form alkali hydroxide as shown in Reaction 2. The alkali hydroxide 134 may be recovered from the catholyte compartment 112.

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)
\]
\[
M^+ + 2H_2O + 2e^- \rightarrow 2MOH + H_2 \quad (2)
\]

In the case of catholyte solution 130 having methanol, methoxide ions will react with available alkali ions to
form alkali methoxide as shown in Reaction 3. The alkali methoxide may be recovered from the catholyte compartment 112.

\[ 2\text{M}^+ + 2\text{CH}_3\text{OH} + 2e^- \rightarrow \text{MOCH}_3\text{H} + \text{H}_2 \]  

(3)

[0055] It will be appreciated that the catholyte solution comprises a base which may be used to neutralize the carboxylic acid to produce the alkali metal salt of the carboxylic acid. Thus, the base consumed in the acid neutralization step may be produced in the catholyte compartment, recovered, and re-used in acid neutralization reactions or other chemical processes.

[0056] In one embodiment, the electrolytic cell may be operated in a continuous mode. In a continuous mode, the cell is initially filled with anolyte solution and catholyte solution and then, during operation, additional solutions are fed into the cell and products, by-products, and/or diluted solutions are removed from the cell without ceasing operation of the cell. The feeding of the anolyte solution and catholyte solution may be done continuously or it may be done intermittently, meaning that the flow of a given solution is initiated or stopped according to the need for the solution and or to maintain desired concentrations of solutions in the cell compartments, without emptying any one individual compartment or any combination of the two compartments. Similarly, the removal of solutions from the anolyte compartment and the catholyte compartment may also be continuous or intermittent. Control of the addition and removal of solutions from the cell may be done by any suitable means. Such means include manual operation, such as by one or more human operators, and automated operation, such as by using sensors, electronic valves, laboratory robots, etc. operating under computer or analog control. In automated operation, a valve or stopcock may be opened or closed according to a signal received from a computer or electronic controller on the basis of a timer, the output of a sensor, or other means. Examples of automated systems are well known in the art. Some combination of manual and automated operation may also be used. Alternatively, the amount of each solution that is to be added or removed per unit time to maintain a steady state may be experimentally determined for a given cell, and the flow of solutions into and out of the system set accordingly to achieve the steady state flow conditions.

[0057] In another embodiment, the electrolytic cell is operated in batch mode. In batch mode, the anolyte solution and catholyte solution are fed initially into the cell and then the cell is operated until the desired concentration of product is produced in the anolyte and catholyte. The cell is then emptied, the products collected, and the cell refilled to start the process again. Alternatively, combinations of continuous mode and batch mode production may be used. Also, in either mode, the feeding of solutions may be done using a pre-prepared solution or using components that form the solution in situ.

[0058] It should be noted that both continuous and batch mode have dynamic flow of solutions. In one embodiment of continuous mode operation, the anolyte solution is added to the anolyte compartment so that the sodium concentration is maintained at a certain concentration or concentration range during operation of the electrolytic cell. In one embodiment of batch mode operation, a certain quantity of alkali ions are transferred through the catholyte compartment conductive membrane to the anolyte compartment and are not replenished, with the cell operation stopped when the alkali ion concentration in the anolyte compartment reduces to a certain amount or when the appropriate product concentration is reached in the catholyte compartment.

[0059] In some embodiments, the resulting alpha-olefins may be oligomerized to poly-alpha-olefins (PAOs) by conventional techniques to synthetic oils. In one embodiment, the C11 olefins are oligomerized to produce poly-internal-olefins (PIOs) by conventional techniques and thereby produce synthetic oil.

[0060] In some embodiments, the entire process is hydrogen-independent. In some embodiments, the process requires small amounts of electricity. In some embodiments, the electrochemical reactor can be commercialized for distributed manufacturing of the olefins. In some embodiments, the sodium salt of lactic acid obtained from fermentation from biomass can be directly fed into the membrane reactor, thereby obviating the need for any separation or purification. In some embodiments, the electrochemical reactor uses inexpensive electrode materials with low power consumption. In some embodiments, the resulting alpha-olefins are oligomerized to produce a synthetic bio-lubricant.

EXAMPLES

[0061] Several examples will be given to demonstrate the technical feasibility of producing olefins via the decarboxylation of carboxylic acids or alkali carboxylates. The examples demonstrate the decarboxylation of sodium salts of carboxylic acids using electrolytic cells equipped with a NaSelect® NaSICON membrane manufactured by Ceramatec, Inc., Salt Lake City, Utah.

[0062] The examples disclosed herein, used an experimental setup which consisted of a micro flow cell, allowing both the anolyte and catholyte to be pumped through the cell while minimizing the distance between the electrodes and the membrane. The membranes used in the examples consisted of 2.54 cm diameter NaSICON disks of about 1 mm thickness that were housed on scaffolds in the center of the cells. As the scaffold and membrane physically separate the anode and cathode compartments, there was a separate reservoir and temperature controlled hotplate for the anolyte and catholyte. This allowed the chemistry and conditions of each electrolyte to be optimized for the respective electrode reactions. A multiple-head peristaltic pump was used to pump both electrolyte solutions into the electrolysis cell. The tubing between the cell, pump, and reservoir was insulated for temperature sensitive electrolytes.

[0063] The anolyte solution that contains the sodium salt of the carboxylic acid, was made by dissolving at least 10% of the salt into a solvent system consisting of different mixtures that contain water, methanol, ethanol, and butanol. The sodium salts were prepared in separate solutions following conventional saponification reactions followed by dissolution of the prepared salt into an electrolyte solution. For this method, a general saponification product was used during which the sodium carboxylate forms as the carboxylic acid is neutralized. The details of the electrolyte preparation will be given in the different examples. The catholyte was made from aqueous sodium hydroxide solutions. To obtain low solution resistance the temperature of the electrolyte were increased to 50° C. to improve both the solubility and conductivity.

[0064] Once the reservoirs reached the desired temperature, a power supply was connected and a current density between 10 and 100 mA/cm² was applied. During electrolysis, the voltage and current were monitored using a Data
Acquisition Unit (Agilent 3490A) controlled by LabVIEW software. The applied current density caused oxidation to occur at the anode (smooth platinum or graphite) and reduction to occur at the cathode (nickel), with each electrode having a surface area of 11 cm². As the power supply transport electrons from the anode to the cathode, a charge balance must be maintained across the cell by the diffusion or positively charge ions. Given the high selectivity of the NaSICON membrane for Na-s ions, sodium ions are the only species that can provide this balance. Thus, a high concentration of the sodium salts was desired and used.

To separate the olefins from the electrolyte, hexane was used to perform liquid-liquid extraction. After the extraction, the olefins were analyzed in the hexane using IR (Bruker, Tensor 37), GC (Bruker, SICON 465), and GC-MS (Bruker, SCION465 GC-MS). The olefins could be isolated and purified by removing the hexane using a slight vacuum and low heat affording the recovered olefins at a 98% purity level.

Comparative Example 1

To show the conventional product selectivity of the one electron Kolbe electrolysis, a reaction was performed using 10% sodium octanoate dissolved in a water methanol solution as the anolyte having a pH of 8. 10% aqueous sodium hydroxide was used as the catholyte. The catholyte was heated to 50°C, and the anolyte was maintained at room temperature. The electrolysis was conducted in batch mode, during which the anolyte and catholyte were cycled through the corresponding anode and cathode compartments of the cell. The cell was operated until enough charge passed to theoretically convert 80% of the sodium octanoate. As shown in FIG. 2A the electrolysis was conducted at a constant current density of 65 mA/cm², which produced a cell potential of 8 V.

The reactions that occurred during the electrolysis in the anode and cathode compartment are shown below.

C₁₅H₃₁CO₃Na⁺→C₁₅H₃₃CO₂⁺Na⁺+e⁻

H₂O+e⁻→H₂+OH⁻

The conditions used in this example promoted the radical-radical coupling and produced tetradecane according to the reaction below.

2C₁₅H₃₁→C₁₅H₃₃

After the electrolysis was complete the product was extracted/removed from the electrolyte using liquid-liquid extraction with hexane. The product of the electrolysis was then analyzed using GC-MS, producing the GC shown in FIG. 2B. From this it was determined that the product distribution was 80% tetradecane, 5% heptanol, 10% esters, and 5% heptanes.

EXAMPLE 2

The electrolysis conditions from Example 1 were changed to show the selective production of olefins instead of paraffins using the techniques disclosed herein. One difference between the two examples that caused the change in product selectivity was the use of a graphite electrode in this example while a platinum electrode was used in Example 1. For this example, 10% sodium laurate was dissolved in an electrolyte containing a mixture of methanol, butanol, and water having a pH of 10.5. The catholyte consisted of 10% aqueous sodium hydroxide. The catholyte and anolyte were heated to 50°C. Electrolysis was conducted in batch mode during which the anolyte and catholyte were cycled through the corresponding anode and cathode compartments of the cell. The cell was operated until enough charge passed to theoretically convert 80% of the sodium laurate. As shown in FIG. 3A, electrolysis was conducted at a constant cell potential of 4 V and a current density of 20 mA/cm².

The reactions that occurred during the electrolysis in the anode and cathode compartment are shown below.

C₁₇H₃₇CO₂Na⁺→C₁₇H₃₅CO₂⁺Na⁺+2e⁻+H⁺

H₂O+e⁻→H₂+OH⁻

After the electrolysis was complete the product was extracted/removed from the electrolyte using liquid-liquid extraction with hexane. The product of the electrolysis was then analyzed using GC-MS, producing the GC chromatogram shown in FIG. 3B. From this it was determined that the product distribution was <5% decosane, 40% undecanol, <5% esters, and over 50% undecenes. Of the undecenes, 50% corresponded to the alpha-olefin, 1-undecene.

It will be appreciated that the disclosed invention provides an electrochemical method of preparing olefins from alkali metal salts of carboxylic acids. Low-cost, renewable biomass may provide a source of alkali metal salts of carboxylic acids.

1. A electrochemical method of preparing olefins from an alkali metal salt of a carboxylic acid, comprising:
   providing an electrochemical cell comprising:
   an anolyte compartment comprising an electrochemically active anode selected to perform a two-electron decarboxylation reaction of an alkali metal salt of a carboxylic acid, wherein the anode comprises a carbonaceous surface;
   a catholyte compartment comprising an electrochemically active cathode where reduction reactions occur; an alkali ion conductive membrane separating the anolyte compartment from the catholyte compartment that permits selective transport of alkali ions between the anolyte compartment and the catholyte compartment;
   providing a solution of an alkali metal salt of the carboxylic acid to the anolyte compartment, wherein the solution has a pH in the range from about 8 to 14; and
   applying an electrical potential to the anode and cathode to electrochemically decarboxylate the carboxylic acid salt into one or more olefins.

2. The method of claim 1, wherein the cell has a voltage between 2 and 20 volts.

3. The method of claim 1, wherein a current density of between 5 and 100 mA/cm² is applied to the anode.

4. The method of claim 1, wherein the solution has a pH in the range of about 10 to 12.
5. The method of claim 1, further comprising mixing the alkali metal salt of the carboxylic acid with an organic solvent.

6. The method of claims 5, wherein the organic solvent comprises one or more organic alcohols and mixtures thereof.

7. The method of claim 6, wherein the one or more organic alcohols are selected from the group consisting of: methanol, ethanol, propanol, isopropanol, butanol, and mixtures of the same.

8. The method of claim 5, wherein the organic solvent is selected from the group consisting of: acetonitrile, dimethylformamide, sulfolane, pyridine, 2,6-pyridine, and mixtures thereof.

9. The method of claim 1, further comprising adjusting the pH of the alkali metal salt of the carboxylic acid with a base.

10. The method of claim 9, wherein the base is an alkali metal hydroxide.

11. The method of claim 1, further comprising mixing the alkali metal salt of the carboxylic acid with an electrolyte selected from the group consisting of: a metal halide, a metal nitrate, a metal sulfate, a metal perchlorate, and a metal tetrafluoroborate.

12. The method of claim 1, wherein the alkali ion conducting membrane is a NaSICON membrane.

13. The method of claim 1, further comprising fermenting biomass to produce the carboxylic acid and neutralizing the carboxylic acid with an alkali metal hydroxide to form the alkali metal salt of the carboxylic acid.

14. The method of claim 1, wherein the alkali metal salt of the carboxylic acid has an even number of carbon atoms.

15. The method of claim 1, wherein the alkali metal salt of the carboxylic acid is derived from a carboxylic acid selected from the group consisting of: octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, and octadecanoic acid.

16. The method of claim 1, wherein the one or more olefins comprises an alpha-olefin.

17. The method of claim 1, wherein the olefin comprises 1-undecene.

18. The method of claim 1, further comprising oligomerizing the one or more olefins to make a synthetic lubricant.

19. An electrochemical reactor comprising:
   an anolyte compartment comprising:
   an alkali metal salt of a carboxylic acid having a pH in the range from about 9 to 12; and
   an electrochemically active anode selected to perform a two-electron decarboxylation reaction of the alkali metal salt of carboxylic acid, wherein the anode comprises a carbonaceous surface;
   a catholyte compartment housing an electrochemically active cathode where reduction reactions occur;
   an alkali ion conductive membrane separating the anolyte compartment from the catholyte compartment that permits selective transport of alkali ions between the anolyte compartment and the catholyte compartment; and
   a source of electric potential connected to the anode and to the cathode.

20. The electrochemical reactor of claim 19, wherein the alkali metal ion is sodium and the alkali ion conducting membrane is a NaSICON membrane.

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