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(54) Title: POLARITY REVERSAL ELECTROLYSIS

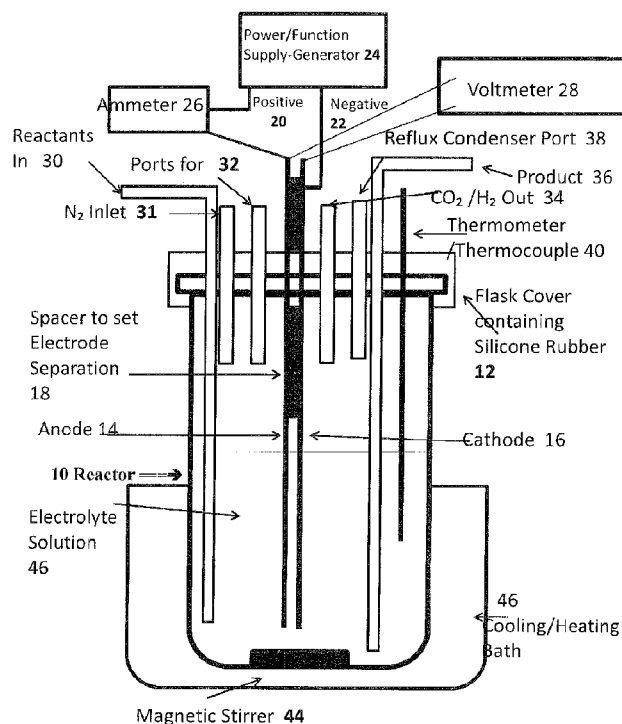


Figure 1

(57) Abstract: A process, apparatus and compositions for the preparation of decarboxylated derivatives of carboxylic acids which comprises performing polarity reversing electrolysis using an anode and a cathode on a solution of a carboxylic acid containing more than one carbon atom or salt of carboxylic acid or carboxylic acid ester or other derivative or precursor thereof, to decarboxylate said carboxylic acid or derivative and produce decarboxylated derivatives is described. More generally, the invention has utility in treating reactants that can undergo oxidation and reduction on changing polarity electrode surfaces to produce products different from direct electrolysis. The invention also has utility in the conversion of organic cations, radicals and anions such as carboxylic acids, fatty acids, alcohols, phenols, to renewable fuels, production of chemicals useful as chemicals and pharmaceuticals and producing alkanes, alkenes, hydrocarbon ethers, alkyl-aryl hydrocarbons, alcohols and hydrocarbon esters.

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POLARITY REVERSAL ELECTROLYSIS

FIELD

The invention relates to a process for producing decarboxylated derivatives from carboxylic acids by replacing the carboxylic group with hydrogen, an alkyl group, an alkene group, an alkoxy group, an aryloxy group, aryl group or hydroxyl group. The invention relates to novel compositions that can be obtained by the novel process. The inventions also relates to an apparatus for carrying out the process and producing the novel compositions. More specifically, the invention relates to a process for producing hydrocarbons and coupled products to be used as a chemical, pharmaceutical, lubricant, fuel or fuel additive from organic anions and carboxylic acids derived from the hydrolysis of triglycerides and esters. It also concerns production of an ether, an alkane, an alkene, an alkyl-aryl hydrocarbon, an alcohol and ester compounds as derivatives, and the use of the derivatives as pharmaceuticals, chemicals, fuels or fuel blends. The invention is particularly concerned with the field of renewable or biofuel alternatives to petroleum based fuels and chemicals, which are becoming increasingly scarce and costly. The fuels of the invention may be regarded as third generation renewables or biofuels and/or additives that have advantageous properties for storage and transportation, have lower cold flow and pour points, good performance and safety, utilize renewable and sustainable materials as feed stocks, burn more cleanly, preserve fossil fuels, are carbon neutral and, most importantly, can easily be adopted by most existing engines than the currently used methyl esters of fatty acids produced from triglycerides.

BACKGROUND

Biodiesel, methyl ester of fatty acids, and bioethanol are the main renewable biofuels that are currently available for commercial use. These biofuels can be easily manufactured from renewable feedstock (e.g. biomass, oils, fats) with existing technology. However, many applications that use standard fuels cannot easily be converted to use biodiesel or bioethanol. There are differences in the physical and chemical properties of biodiesel and bioethanol compared to standard fuels, such as differences in energy density, flammability, boiling point range (or lack thereof), shelf life, material compatibility and solvent properties. The specification of the fuel that may be used with many engines is very specific and may not permit the use of existing biofuel alternatives, such as biodiesel and bioethanol. There is therefore a need for new,

high density alternative biofuels and processes for producing renewable fuels economically on an industrial scale.

Electrolysis is known in the art as a method for performing chemical reactions on a laboratory scale and selected processes have reached industrial scales. Electrolysis of carboxylic and fatty acids and decarboxylation have been reported by Kolbe to form alkanes, called the Kolbe dimer. Laboratory experiments where a normal Kolbe reaction is prevented by drastically changed reaction conditions have been reported in the prior art, beginning with Moest et. al. (German patent 138442, issued 1903) who created alcohols, aldehydes and ketones from fatty acids using electrolysis.

Kronenthal et al focused on aliphatic ethers, and on methoxy-undecane in particular (U.S. Pat. No. 2,760,926, issued in 1956), but achieved yields of 40% or less while consuming large amounts of electricity (by at least a factor ten judging from the voltage applied (90+ Volts).

More recently, however, in US20060773279P and WO2007027669 the original Kolbe-reaction was quoted as a means, among numerous other techniques, to create useful hydrocarbons utilizing fatty acids of renewable origin. However due to the nature of the Kolbe-reaction, the chain length would almost double in the process, creating a mix of C30-C34 hydrocarbons that would need extensive conventional refining to yield useable, liquid transportation fuels. This may be contrasted with a one-step specialized Hofer-Moest process, where an alkene is produced, however at low current densities and at low productivity rates. However, even under these conditions considerable Kolbe dimer is formed. Furthermore, alkenes with terminal unsaturation are readily subject to oxidation, and decreases the oxidation stability of the fuels. Additional recent publications are PCT/US2008/010707, PCT Pub No. WO2009/035689, US Patent No. 8,444,846 B2, issued May 21, 2013 and JOSHI; CHANDRASHEKHAR H.; Horner; Michael Glenn; United States Patent Application, 20120197050, A1, Publication, August 2, 2012.

There have been references related to the use of alternating current for the electrolysis of aqueous solutions using sine waves compared to direct current. For example US Patent 2,385,410 issued September 25, 1945 to John Albert Gardner, describes a method of producing organic disulphides which consists in treating an aqueous solution of an alkali metal salt or alkaline earth metal salt of a mercapto thiazole or a dithiocarbamic acid by electrolysis with alternating current whereby the hydroxide of the alkali or alkaline earth metal is liberated and

the disulphide is formed by the union of the residues from two molecules. However, generally, those skilled in the art are aware that in direct current electrolysis, electrons flow in the same direction all the time, whereas in alternating current, the electrons flow one way (typically 1/60 of a sec in 60 Hz sine wave alternating current) and then they flow the other way. To get any electrolysis that is not immediately undone, direct current is required.

It would be possible to manufacture said liquid fuels by means of a regular, crossed Kolbe-electrolysis, e.g. using oleic acid and acetic acid as feedstock. This procedure would yield a C18-hydrocarbon and would maintain the configuration of the double bond of the fatty acid. However, it is believed that such a technique would be far less economical due to the consumption of acetic acid, the costly use of platinum anodes, and the low-value byproducts.(i.e. ethane and a doubly unsaturated C34 hydrocarbon in this case) generally unavoidable in a crossed or hetero Kolbe reaction.

It has been reported that many companies are cooperating with producers of animal fat and/or vegetable oils to create hydrocarbons from triglycerides, making straight C16/C18 alkanes and propane (from the glycerol contained in fats/oils). However, this process uses a catalyst and totally hydrogenates feedstock at high pressures and temperatures. It consumes large amounts of hydrogen, requires catalysts and destroys all special configurations of the fatty acid originated double bonds. The process described in this invention can preserve such double bonds and can utilize the hydrogen generated by the electrolysis. The need for an external source of hydrogen is avoided.

SUMMARY

The invention provides a process for decarboxylation of a carboxylic acid and anions such as an aliphatic, cyclic, heterocyclic or aromatic carboxylic acids to produce the corresponding decarboxylated and anion-free derivatives, such as hydrocarbons comprising alkanes, alkenes, alkyl-aryl hydrocarbons, hydrocarbon ethers or hydrocarbon esters in organic solvents, and the use of the derivatives as pharmaceuticals, chemicals, fuels or fuel blends. More generally, the invention can be used to produce organic radical cations, neutral radicals, cations and anions as reactive intermediates for further reaction with added solvents and other additives. More specifically, the invention is directed for producing a fuel additive or a fuel, which fuel may be, for example, a third-generation biofuel or that can be blended. The process may also be used to manufacture conventional hydrocarbon fuels from renewable feed stocks. In addition, the

invention also discloses decarboxylated compositions that can be used by the chemical, pharmaceutical and fuel industry and apparatus for carrying out the invention.

The invention also includes compositions that can be produced by the inventive process by decarboxylation including hydrocarbon compositions, alkanes, alkenes, alkyl-aryl hydrocarbons, hydrocarbon ethers, hydrocarbon alcohols and hydrocarbon esters. Product compositions can be selected by selecting the initial reagents, solvents and additives.

The invention also discloses an apparatus for carrying out the inventive process, in a batch process, semi-continuous process and a continuous process.

In particular the invention provides a process for producing a hydrocarbon composition and chemicals which comprises the step of performing polarity reversing electrolysis on a solvent solution of an anion such as a carboxylic acid or salt thereof or carboxylic acid ester or other derivative or precursor thereof to decarboxylate said carboxylic acid or derivative thereof, and produce a decarboxylated derivative product.

In particular, the initial objective of the invention provides a process for producing a decarboxylated derivative, such as a saturated or unsaturated hydrocarbon, which comprises the step of performing polarity reversing electrolysis with an anode and a cathode on a solvent of an anion, a carboxylic acid or salt thereof or carboxylic acid ester or other derivative or precursor thereof to form a reactive radical intermediate or to decarboxylate said carboxylic acid or derivative, and produce the corresponding decarboxylated product or adduct with the radical intermediate. In addition, the process conditions can be adjusted to produce alkyl-aryl hydrocarbons, alkenes, ethers, alcohols and esters in addition to the preferred alkane in one step. Another inventive step is the composition of the solvent and carboxylic acid concentration such that the products of the electrolysis phase separates from the initial homogeneous reaction mixture and greatly simplifies the separation and purification of the products. This avoids or reduces substantially the need for separation by energy intensive distillation. In addition, the reaction medium containing solvents and salts can be reused to decarboxylate additional carboxylic acids without the need for additional reagents and solvents. Furthermore, the polarity reversal process overcomes the mass transfer limitations of direct current electrolysis and reduces electrode fouling by the products. Catalysts such as platinum, palladium nickel can be coated or impregnated onto the electrodes to further enhance the electrolysis.

By a precursor of a carboxylic acid (or of a salt or other derivative thereof) is referred to a

compound that will produce such a material under appropriate reaction conditions, in particular under the conditions under which electrolysis is to be carried out. An example of a suitable precursor is an ester that hydrolyses in situ. Other examples are carboxylic acid derivatives that allow for electrical conductivity and electrolysis, such as carboxylic acid salts, carboxylic acids and tertiary amines, both free and immobilized on solid supports that produce carboxylate anions. In addition, the tertiary amines can produce anions from the alcohol solvents to produce ethers during decarboxylation.

The invention also provides a product composition or compositions produced directly or indirectly by this process that can be used by the chemical, the pharmaceutical and the fuel industry.

The decarboxylated product compositions that is produced may be used to prepare other chemicals, pharmaceutical intermediates, fuels or fuel additives.

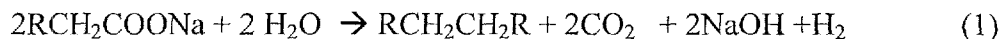
The process of the invention may further comprise the steps of purifying and separating the products from the reactive intermediates generated and decarboxylated product compositions from the reaction solvent. Additionally, the process of the invention may further comprise the step of adding the decarboxylated product alkane to a fuel to produce renewable fuel or as fuel additives to the fuel.

A further objective is to overcome the great limitation of mass transfer and ion-transport that limits the efficiency and productivity of direct current (DC) electrolysis. In DC electrolysis unidirectional ion transport is needed to complete the circuit. In AC electrolysis, this mass transfer limitation is avoided. Furthermore, the desired product is produced only at the anode or at the cathode, and undesired product is not used or wasted. Another objective of the invention is to improve the efficiency and productivity of electrolysis that is not possible with DC electrolysis, due to the fouling of the electrodes and decreased current density of the electrolysis. The above limitations can be overcome by disclosed invention as demonstrated in the examples. Furthermore, the use of different polarity reversing functions such as square wave function overcomes the limitations of sine wave AC electrolysis.

The decarboxylation of the anion or carboxylic acid group of the carboxylic or fatty acid by reverse polarity electrolysis generates a reactive intermediate such as a decarboxylated radical intermediate at both the anode and cathode during the anodic cycle of each electrode, and produces a hydrogen radical at the cathode during the cathodic cycle of each electrode. In

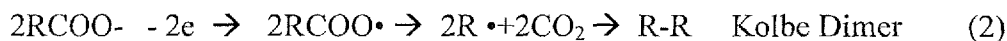
addition, carbocations (carbonium ions) can be produced at each electrode during the anodic cycle depending on the applied voltage and the ionization potential of the molecule. Without speculating on the mechanism of the invention, in order to understand the invention, it is possible, under some electrolysis reaction conditions, for the Kolbe reaction to occur, whereby the radical dimerises by reaction with another alkyl radical of the same type to produce a Kolbe dimer. If the frequency of the polarity reversal is low, there is sufficient time for the radical to react with another radical, dimerise and for the formation of the normal Kolbe dimer product. However, when the frequency of the polarity reversal is high, when the anode changes polarity, and the alkyl radical in the vicinity of the anode is now in the proximity of the polarity changed cathode. The cathode reduces hydrogen ions to hydrogen radicals that react with the alkyl radicals in the vicinity produced in the prior cycle to produce the alkane. This allows for the use of the hydrogen that is normally produced in the prior art Kolbe reaction to react directly with the alkyl radical and produce the alkane. This avoids the need to use a low molecular weight acid such as acetic, propionic or formic acid to produce a Kolbe low molecular weight dimer.

Kolbe Electrolysis



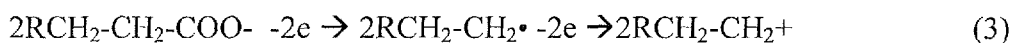
Anode

Cathode



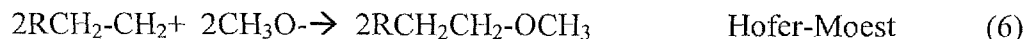
• Represents free radical

It is known in the art that to form the normal Kolbe dimer with two alkyl radicals, high current densities and high carboxylate concentrations are needed presumably to produce sufficiently high concentrations of radicals available on the electrode surface or in the vicinity for reaction. It is also known that at low current densities and higher electrode potentials, the alkyl radicals abstract hydrogen from the neighboring carbon atom and form an alkene, the Hofer-Moest reaction.



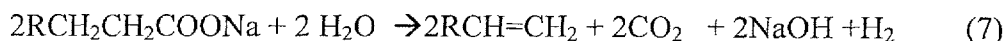
Carbocation



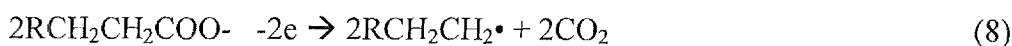


The conditions used for electrolysis in the Hofer-Moest process can be selected to generate a low concentration of free radicals, which minimizes the occurrence of free radical dimerization and thereby reduces the Kolbe reaction, but is not prevented. However, low current densities result in low reaction and production rates, and the hydrogen is released and lost with its energy. Furthermore, hydrogen is still generated and released at the cathode and requires schemes to capture and utilize the hydrogen.

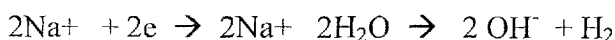
Electrolysis



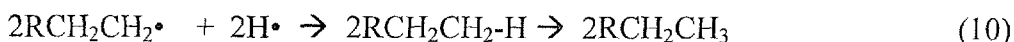
The anode cycle



The cathode cycle

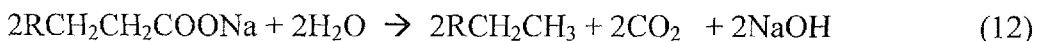
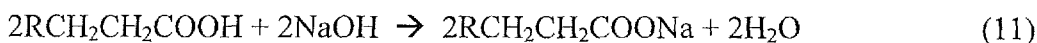


The reaction on and in the vicinity of the anode and cathode

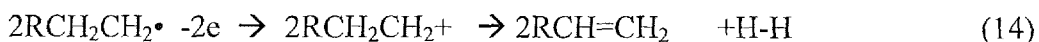
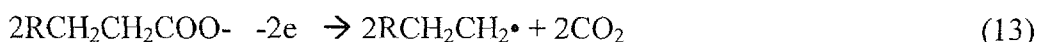


Non-Kolbe Alkane

Overall Reaction with polarity reversal electrolysis.



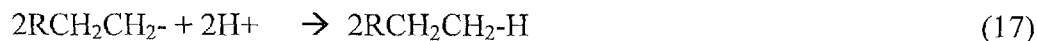
Anode -Cathode



Carbocation on further oxidation at Anode



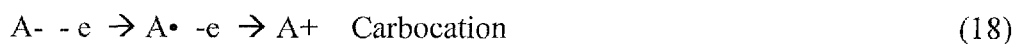
Carbanion on further reduction at cathode at cathode cycle



In general, besides the carboxylate anion and hydrogen ion, metal ion or amine cation, any anion or cation that that can interact with the anode and cathode can be used. Therefore, it is preferred that the anions and cations present in the electrolyte solution are restricted only to those that are desired to prevent the formation of unwanted side products.

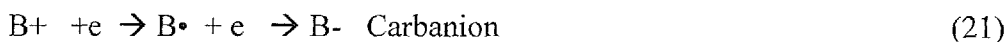
The invention can be described generally as given below.

Anode/Anode Cycle: A- is the anion



Nu⁻ is a Nucleophile

Cathode/Cathode Cycle: B+ is the cation



E⁺ is an Electrophile

Besides the radical reactions, A[•] and B[•], the carbocation and carbanion can then react with any nucleophile (Nu⁻) or electrophile (E⁺) present in its vicinity to produce the corresponding products.

In the process of the invention, the free radicals such as the alkyl free radicals generated by decarboxylation of the fatty acid react with a nearby hydrogen radical produced during the cathodic cycle to produce an alkane. If a reactive solvent molecule is present, such as an alcohol, the alkoxy free radical or an anion can react with the alkyl radical to produce an ether. The alkyl radical may eliminate a hydrogen atom to form an alkene and an alkane. In principle, the alkyl radicals could also be further oxidized (i.e. loose another electron) and become carbocations, which may undergo structural changes before either reacting with the hydrogen radical or

hydrogen ion to form an alkane, with the solvent to form an ether or eliminating a hydrogen atom to form an alkene before the polarity reversal. A mixture of ethers, a mixture of alkanes and alkenes and esters can sometimes be obtained from the process of the invention, and the formation of the Kolbe dimer is minimized. The number of carbon atoms in the alkanes and alkenes is one less than the number of carbon atoms in the carboxylic acid (the carboxyl group of the fatty acid splits off as CO_2).

A number of factors may influence the nature and concentration of the radicals, cations and anions that are produced during the polarity reversing electrolysis step. These factors include the size and shape of the electrodes, the material from which the electrodes are made, the surface characteristics of the electrodes, the distance separating the electrodes in solution, the electrolyte and solvents that are used, the concentration of the reactants such as carboxylic acid, the properties of the carboxylic acid salt, type of current, direct or with polarity reversal, the function and shape of the applied voltage and the polarity switch, the rise and fall times of the polarity reversal frequency, the symmetry of the polarity reversal function, the electrode potential voltage and the current density. In addition, the formation of organic radical cations, neutral radicals, cations and anions is specific to each molecule, and dependent on the ionization energy and the bond dissociation energy among other factors. Thus, the electrolysis step may be performed in a number of different ways in order to obtain the desired product or products and to produce the alkane, the alkene, ether or ester as described in the invention and to minimize the Kolbe dimer. The conditions also influence the amounts of alkane, ether and alkene that are produced. If an alkyl ether is not desired, a non-alcoholic solvent can be used. If an alkene is not desired, current density, voltage, frequency of the polarity switch, polarity switch function, and voltage function can be changed to obtain predominantly the desired products.

The general reactions given in equations (18) to (23) is further illustrated in Table I for the different molecules that may form reactive intermediates for further reaction to form products. For example, acetic acid, CH_3COOH acetic acid radical $\text{CH}_3\text{COO}^\bullet$ acetate anion CH_3COO^- from Table I can undergo decarboxylation similar to the experimental examples given for oleic acid.

Table I. Organic Radical Cations, Neutral Radicals, Cations, and Anions

Reactive Intermediates that may be generated and undergo reactions under polarity reversal Electrolysis Conditions that may undergo further reaction.

Hydrocarbons**C1**

methane, CH₄ methylene singlet, CH₂ methylene triplet, CH₂** methyl radical, CH₃• methyl cation, CH₃⁺ methyl anion, CH₃⁻

C2

ethane, CH₃CH₃ ethane radical cation, CH₃CH₃⁺• ethyl radical, CH₃CH₂• ethyl cation, CH₃CH₂⁺ ethyl anion, CH₃CH₂⁻

ethylene, CH₂=CH₂ ethylene radical cation, CH₂=CH₂⁺• vinyl radical, CH₂=CH• vinyl cation, CH₂=CH⁺

acetylene, HCCH deH-acetylene radical, HCC• acetylene anion, HCC⁻

C3

propane, CH₃CH₂CH₃ propane radical cation, CH₃CH₂CH₃⁺• propyl radical, CH₃CH₂CH₂• propyl cation, CH₃CH₂CH₂⁺

cyclopropane, CH₂(CH₂)CH₂ cyclopropane radical, CH₂(CH₂)CH₂•

isopropyl cation, (CH₃)₂CH⁺ isopropyl radical, (CH₃)₂CH•

propene, CH₂=CHCH₃ propene radical cation, CH₂=CHCH₃⁺• 1-deH-1-propene radical, CH₃CH=CH• 2-deH-propene cation, CH₂=C(+)CH₃ 1-deH-1-propene cation, CH₃CH=CH⁺

allyl cation, CH₂=CHCH₂⁺ allyl radical, CH₂=CHCH₂• allyl anion, CH₂=CHCH₂⁻

C4

butane, CH₃CH₂CH₂CH₃ butane radical cation, CH₃CH₂CH₂CH₃⁺• 1-deH-butane radical, CH₃CH₂CH₂CH₂•

2-deH-butane radical, CH₃CH₂CH(•)CH₃ 1-deH-butane cation, CH₃CH₂CH₂CH₂⁺ 2-deH-butane cation, CH₃CH₂CH(+)CH₃

2-methylpropane, (CH₃)₃CH 2-methylpropane radical cation, (CH₃)₃CH⁺•

isobutyl cation, (CH₃)₂CHCH₂⁺ isobutyl radical, (CH₃)₂CHCH₂•

2-methylpropene, (CH₃)₂C=CH₂ 2-methylpropene radical cation, (CH₃)₂C=CH₂⁺• 2-deH-1-

methylcyclopropane cation, CH₂(CH+)CHCH₃ 3-deH-butene cation,

CH₂=CHC(+)HCH₃ 2-deH-methylpropene cation, CH₂=CH(CH₃)CH₂⁺ 1-deH-1-

methylcyclopropane cation, CH₂(CH₂)C(+)CH₃

t-butyl radical, (CH₃)₃C• t-butyl cation, (CH₃)₃C⁺

C5

2-methylbutane, (CH₃)₂CHCH₂CH₃ 2-methylbutane radical cation,

(CH₃)₂CHCH₂CH₃⁺• isopentyl radical, (CH₃)₂C(•)CH₂CH₃

isopentyl cation, (CH₃)₂C(+)CH₂CH₃ 1-pentene, H₂C=CHCH₂CH₂CH₃ 1-pentene radical

cation, $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_3^+$

C6

2-methylpentane radical cation, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3^+$

2,2-dimethylbutane, $(\text{CH}_3)_3\text{CCH}_2\text{CH}_3$ 2,2-dimethylbutane radical cation, $(\text{CH}_3)_3\text{CCH}_2\text{CH}_3^+$

Aromatics

Benzene, C_6H_6 , Benzene Radical Cation, C_6H_6^+ Benzene Radical Anion, C_6H_6^- ,

Toluene, C_7H_8 , Toluene Radical Cation, C_7H_8^+ Toluene Radical Anion, C_7H_8^- ,

Phenyl Radical, $\text{C}_6\text{H}_5^\bullet$ Toly Radical, $\text{C}_6\text{H}_7^\bullet$,

Oxygen: Alcohols, Ethers, Aldehydes, Ketones, and Acids

C1

methanol, CH_3OH methanol radical cation, CH_3OH^+ methoxy radical,

$\text{CH}_3\text{O}^\bullet$ methylperoxyl radical, $\text{CH}_3\text{OO}^\bullet$

methoxy cation, CH_3O^+ methanol onium cation, CH_3OH_2^+ methoxy anion, CH_3O^- 1-deH-methanol radical, $\text{CH}_2\text{O}^\bullet$

formaldehyde, CH_2O formyloxonium cation, CH_2OH^+ deH-formaldehyde cation, HCO^+

deH-formaldehyde anion, HCO^- deH-formaldehyde radical, $\text{HCO}^\bullet$

formic acid, HCOOH 1-deH-formic acid radical, $\text{HOOC}^\bullet$ formate anion, HCOO^-

C2

ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ O-deH-ethanol radical, $\text{CH}_3\text{CH}_2\text{O}^\bullet$ ethoxy anion, $\text{CH}_3\text{CH}_2\text{O}^-$

methyl acylium cation, CH_3CO^+

ethyleneoxide, $\text{C}_2\text{H}_4\text{O}$ deH-ethyleneoxide cation, $\text{C}_2\text{H}_3\text{O}^+$

dimethylether radical, $\text{CH}_3\text{OCH}_2^\bullet$ dimethylether cation, $\text{CH}_3\text{OCH}_2^+$

vinyl alcohol, $\text{CH}_2=\text{CHOH}$ vinyl alcohol radical cation, $\text{CH}_2=\text{CHOH}^+$ vinyloxy radical,

$\text{CH}_2=\text{CHO}^\bullet$ vinyloxy anion, $\text{CH}_2=\text{CHO}^-$

1-deH-acetaldehyde cation, CH_3CO^+ 1-deH-acetaldehyde radical, $\text{CH}_3\text{CO}^\bullet$

2-deH-acetaldehyde cation, $\text{O}=\text{CHCH}_2^+$ 2-deH-acetaldehyde radical, $\text{O}=\text{CHCH}_2^\bullet$

acetic acid, CH_3COOH acetic acid radical, $\text{CH}_3\text{COO}^\bullet$ acetate anion, CH_3COO^-

deH-acetic acid radical, $\text{HOOCCH}_2^\bullet$ deH-acetic acid cation, HOOCCH_2^+ O-deH-acetic acid cation, CH_3COO^+

C3

propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ propanol radical cation, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^+$ 1-deH-propanol radical, $\text{CH}_3\text{CH}_2\text{CH}^\bullet\text{OH}$

1-deH-propanol cation, $\text{CH}_3\text{CH}_2\text{CH}(+)\text{OH}$ 2-deH-propanol radical, $\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{OH}$ 2-deH-propanol cation, $\text{CH}_3\text{CH}(+)\text{CH}_2\text{OH}$

3-deH-propanol cation, $\text{CH}_2(+)\text{CH}_2\text{CH}_2\text{OH}$ isopropanol, $(\text{CH}_3)_2\text{CHOH}$ isopropanol radical

cation, $(\text{CH}_3)_2\text{CHOH}^+\bullet$
 methylethylether, $\text{CH}_3\text{OCH}_2\text{CH}_3$ methylethylether radical cation, $\text{CH}_3\text{OCH}_2\text{CH}_3^+\bullet$
 deH-methylethylether radical, $\text{CH}_3\text{CH}_2\text{OCH}_2\bullet$ deH-methylethylether cation, $\text{CH}_3\text{CH}_2\text{OCH}_2^+$
 propanal radical cation, $\text{CH}_3\text{CH}_2\text{CO}^+\bullet$ 1-deH-propanal cation, $\text{CH}_3\text{CH}_2\text{CO}^+$ 1-deH-propanal radical, $\text{CH}_3\text{CH}_2\text{CO}\bullet$
 acetone, $\text{CH}_3\text{C}=\text{OCH}_3$ deH-propanone cation, $\text{CH}_3\text{C}=\text{OCH}_2^+$ deH-propanone radical, $\text{CH}_3\text{C}=\text{OCH}_2\bullet$
 propenol radical cation, $\text{H}_2\text{C}=\text{COHCH}_3^+\bullet$ allyl alcohol radical, $\text{HOCH}=\text{CHCH}_2\bullet$
 methylacetate, $\text{CH}_3\text{COOCH}_3$ methylacetate radical cation, $\text{CH}_3\text{COOCH}_3^+\bullet$
 methyl-deH-acetate radical, $\text{CH}_3\text{OOCCH}_2\bullet$ methyl-deH-acetate cation, $\text{CH}_3\text{OOCCH}_2^+$
 propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$ propanoic acid radical, $\text{CH}_3\text{CH}_2\text{COO}\bullet$
 2-deH-propanoic acid radical, $\text{CH}_3\text{CH}\bullet\text{COOH}$ 2-deH-propanoic acid cation, $\text{CH}_3\text{CH}(+)\text{COOH}$

C4-C5 Alcohols, Ethers

C4 2-methylpropanol, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ 2-methylpropanol radical cation, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}^+\bullet$
 2-deH-2-methylpropanol radical, $(\text{CH}_3)_2\text{C}\bullet\text{CH}_2\text{OH}$ 2-methylpropoxy radical, $(\text{CH}_3)_2\text{CHCH}_2\text{O}\bullet$
 t-butanol, $(\text{CH}_3)_3\text{COH}$ t-butanol radical cation, $(\text{CH}_3)_3\text{COH}^+\bullet$
 t-butyloxy cation, $(\text{CH}_3)_3\text{CO}^+$ 2-deH-isopropylmethylether cation, $(\text{CH}_3)_2\text{C}(+)\text{OCH}_3$ t-butyloxy radical, $(\text{CH}_3)_3\text{CO}\bullet$
 diethylether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ diethylether radical cation, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3^+\bullet$
 ethylvinylether, $\text{CH}_3\text{CH}_2\text{OCH}=\text{CH}_2$ ethylvinylether radical cation, $\text{CH}_3\text{CH}_2\text{OCH}=\text{CH}_2^+\bullet$

C5

methyl-t-butylether, $(\text{CH}_3)_3\text{COCH}_3$ methyl-t-butylether radical cation, $(\text{CH}_3)_3\text{COCH}_3^+\bullet$

C4-C5 Aldehydes, Ketones, Carboxylic Acids

C4 butyraldehyde, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ butyraldehyde radical cation, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}^+\bullet$
 1-deH-butyraldehyde radical, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}\bullet$ 1-deH-butyraldehyde cation, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$
 2-butanone, $\text{CH}_3\text{CH}_2\text{COCH}_3$ 2-butanone radical cation, $\text{CH}_3\text{CH}_2\text{COCH}_3^+\bullet$
 methylpropionate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$ methylpropionate radical cation, $\text{CH}_3\text{CH}_2\text{COOCH}_3^+\bullet$

C5

2-pentanone, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ 2-pentanone radical cation, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3^+\bullet$
 pentenol radical cation, $\text{CH}_3\text{COH}=\text{CH}_2\text{CH}_2\text{CH}_2^+\bullet$

Nitrogen

methylamine, CH_3NH_2 N-deH-methylamine radical, $\text{CH}_3\text{NH}\cdot$ methaniminonium ion, CH_2NH_2^+ methylamide anion, CH_3NH^- methylammonium radical, $\text{CH}_3\text{NH}_3\cdot$
2-aminobutane, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$ 2-aminopropyl radical, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\cdot$ imine, $\text{CH}_2=\text{NH}$
N-deH-ethanimine radical, $\text{CH}_3\text{CH}=\text{N}\cdot$ acetonitrile, CH_3CN 1-deH-acetonitrile radical, $\text{NCCH}_2\cdot$ 1-deH-acetonitrile anion, NCCH_2^-
propylimmonium cation, $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$ 2-aminopropyl cation, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2^+$
dimethylamine, CH_3NHCH_3 dimethylamine radical cation, $\text{CH}_3\text{NHCH}_3^+\cdot$ dimethylamine radical, $\text{CH}_3\text{N}\cdot\text{CH}_3$
N-methylmethaniminonium cation, $\text{CH}_3\text{NH}=\text{CH}_2^+$
formamide, HCONH_2 formamidate anion, HCONH^- N-methylacetamide, $\text{CH}_3\text{C}=\text{ONHCH}_3$
N-methylacetamide radical cation, $\text{CH}_3\text{C}=\text{ONHCH}_3^+\cdot$ N-methylacetamide radical, $\text{CH}_3\text{C}=\text{ON}\cdot\text{CH}_3$
N-methylacetamide cation, $\text{CH}_3\text{C}=\text{ON}(+)\text{CH}_3$
N,N-dimethylacetamide, $\text{CH}_3\text{C}=\text{ON}(\text{CH}_3)_2$ N,N-dimethylacetamide radical cation, $\text{CH}_3\text{C}=\text{ON}(\text{CH}_3)_2^+\cdot$

Halogens

difluorocarbene singlet, CF_2 methylfluoride cation, CH_2F^+ methylchloride cation, CH_2Cl^+ methylchloride anion, CH_2Cl^-
ethylfluoride, $\text{CH}_3\text{CH}_2\text{F}$ 1,1-difluoroethane, CH_3CHF_2 ethylfluoride radical cation, $\text{CH}_3\text{CH}_2\text{F}^+\cdot$
fluoroethylene, CH_2CHF 1-deH-1-fluoroethylene anion, CH_2CF^-
chloroethane, $\text{CH}_3\text{CH}_2\text{Cl}$ 1-deH-1-chloroethane radical, $\text{CH}_3\text{CH}(\cdot)\text{Cl}$ chloroethylene, CH_2CHCl
bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$ 1-deH-1-bromoethane radical, $\text{CH}_3\text{CH}(\cdot)\text{Br}$
anti-dichloroethane radical cation, anti- $\text{C}_2\text{H}_4\text{Cl}_2^+\cdot$
allylchloride radical, $\text{ClCH}=\text{CHCH}_2\cdot$ 1-chloropropane radical, $\text{ClCH}_2\text{CH}\cdot\text{CH}_3$
chloroacetic acid, ClCH_2COOH chloroacetate anion, $\text{ClCH}_2\text{COO}^-$

Allylic

allyl cation, $\text{CH}_2=\text{CHCH}_2^+$ allyl radical, $\text{CH}_2=\text{CHCH}_2\cdot$ allyl⁻ allyl alcohol radical allylchloride radical 1-chloropropane radical

Small Radicals and Ions

OH radical HOO radical HCO_3 radical CO_3^- radical

Stable Neutral Molecules

Hydrides: H_2O HCN HNCO HOCN HNCS HSCN HF HCl

Footnote: The above list of organic reactive intermediates (Table I) are representative of the cations, radicals and anions that can be formed by the disclosure and that can react. Table data is referenced from <http://www.colby.edu/chemistry/webmo/radcat.html>.

In this embodiment, the radical, the carbocation can act as an electrophile and subsequently involved in the electrophoretic substitution reaction. In such a reaction,, the electrophile substitutes one of the substituents on an aromatic group, for example, hydrogen, instead of the hydrogen generated by the electro-reversal, as shown below as a non-limiting example with benzene.



The H^+ or the $\text{H}^\bullet$ may then be consumed, further reacted, etc., in the reactor in the vicinity of the electrodes or in the bulk solution. In the embodiment shown above, benzene is shown as the aromatic solvent or additive, instead of water or n-hexane given in the examples. Those skilled in the art will appreciate that other aromatics such as toluene or non-aromatic organic solvents or additives may also be used, that will react with the radical or the carbocation.

Electrolysis may be performed using a relatively low current density, medium current density or a high current density. If the current density is low, the frequency of the electrode polarity switch can be low. If the current density is high, the frequency of the reverse polarity switch may need to be sufficiently high to produce hydrogen radicals that will react with the alkyl radicals and minimize Kolbe dimer formation. Furthermore, the profile of the function generator of the polarity switch, sine wave, square wave or triangular wave or other function will determine the concentration of the reaction intermediates and the reaction products on and around the electrode at a particular instant. Typically, the electrolysis is performed using a current density of 0.002 to 4 A cm⁻². It is preferred that the current density be 0.01 to 1 A cm⁻², particularly 0.02 to 1.0 A cm⁻². The voltage can be high, as high as 250 V for high productivity, especially in the industrial scale. Usually it is preferred to employ a low voltage because of efficiency, equipment availability, heat transfer and safety reasons, for example less than 48V,

particularly 3 to 15 V. The voltage may be chosen to achieve a balance between economy (at low voltage) and avoidance of by-products (at high voltages) and electrical efficiency and the symmetry of the polarity reversing function. As the voltage source, solar panels producing direct current can be used and avoid the use of inverters to convert alternating current to direct current and avoid the conversion losses, and allow the invention to be practiced in remote locations to produce fuels and chemicals.

A relatively low or high current density may be achieved in any suitable way, for example by selecting appropriate electrode distance, electrolyte concentration and or cell voltage.

The anode and cathode of the apparatus used to perform electrolysis may be composed of materials that are the same as or different from one another, and each may be independently selected from carbon, natural graphite, synthetic graphite, conductive polymers, platinum, palladium, steel, copper, silver, gold, nickel, Ti/RuO₂ or any transition metal or transition metal compound, or other materials mentioned herein. In addition, catalysts can be deposited on the electrodes in order to enhance the electrolysis efficiency and product selection, such as the deposition of platinum, palladium and other transition metal catalysts on carbon electrodes. If the anode and/or cathode comprises carbon, then it is preferred that it comprise graphite or boron doped diamond.

In one embodiment of the invention, the anode is composed of a material other than graphite. In another embodiment of the invention both the anode and cathode are composed of the same material. In this embodiment it is preferred that they both comprise graphite.

In another embodiment of the invention the anode and cathode are composed of different materials. In this embodiment it is preferred that one of the materials comprise graphite.

The material of the electrodes is often critical, and the surface characteristics, the frequency of the switch and the type of function in the frequency switch will in general be important and critical. It is preferred that the electrodes have a rough surface, such as that provided by graphite rather than the smooth or glassy surface usually provided by, say, platinum. Porous electrodes with high internal surface areas are specifically preferred. This gives reaction intermediates the location and time to react at the surface or vicinity of the electrodes. A composite electrode could be provided having a highly conductive core of one material and a coating of a material of a suitable roughness and surface area. Also, a usually smooth material could be treated to produce the desired roughness and electro-catalytic activity to produce the

desired product.

The anode and cathode of the apparatus in which electrolysis is to be performed may be arranged in such a manner that when they are placed in the solvent, the closest spacing between the anode and cathode in the solvent is from 0.1 to 10 mm. It is preferred that the closest spacing between the anode and cathode in solution is from 1 to 3 mm, in order to obtain high current densities and have sufficient space for the release of the products from the electrodes or for reactant flow in a flow through reactor. Multiple electrodes can be arranged so that the total surface area of the electrode can be increased to increase productivity.

The electrolysis step in the process of the invention is typically carried out on a solvent solution of a carboxylic acid, or salt or other derivative thereof, wherein the total concentration of the carboxylic acid and/or derivative in the solvent solution is usually around 2 molar, more usually at least 1 molar, for example about 1 molar. The precise value will often depend on the ability of a solvent to keep the material in solution. In the case where the reactants phase separates, the electrolysis reaction can be carried out under sonication or an externally generated emulsion by mechanical mixing such as by using a mechanical homogenizer or a fluidizer that generate emulsions by cavitation.

In principle any solvent or alcohol may be used as the solvent for the electrolysis process, provided that it is a liquid at the temperature at which the reaction is to be performed. It is preferred that the solvent dissolves the carboxylic acid, and the product alkane is insoluble or sparingly soluble so that the product hydrocarbons phase separate from the reaction solution. This phase separation greatly facilitates the separation of the alkane or products from the reaction vessel by simple decantation from the solvent or by removal from the bottom, and makes the process an economically competitive separation process compared to separation by distillation. If the decarboxylated product is soluble in the solvent or solvent mixture, the product can still be separated by conventional distillation to recover the solvent and product.

Any solvent or solvent mixtures can be used for the process. Alkyl alcohols are more preferred, especially saturated, linear or branched C₁–C₅ alkyl alcohols. Alcohols that are particularly suitable include methanol, ethanol, n-propanol, i-propanol, n-butanol, s-butanol or t-butanol, ethylene glycol, especially methanol, ethanol and n-propanol.

It is not essential for the solvent or alcoholic solution to be anhydrous. Up to 10% or more by volume of the solution may be water, more typically up to 8% by volume, and more

preferably up to 4% by volume. In another embodiment, the solvent solution is anhydrous. In another embodiment the solvent is water or primarily water.

The solution of the fatty acid, or salt thereof, may comprise an alkali metal or alkaline earth metal hydroxide salt (especially LiOH, NaOH, KOH or in some situations $\text{Ca}(\text{OH})_2$ although the latter material may have insufficient solubility in some solvents), or an amine salt from a tertiary, secondary, primary amine or an ammonium salt. A concentration of at least 0.5 M, preferably at least 1 M, particularly about 2 M will usually be suitable to achieve the desired current density, the metal ions and anions being the principle charge carriers during electrolysis. If a carboxylic acid is initially added to the solvent solution, then the alkali metal or alkaline earth metal hydroxide salt may be added to deprotonate the fatty acid in-situ. In one embodiment of the process, electrically conductive inorganic salts, particularly alkali metal (especially sodium and potassium) chlorides, sulfates, persulfates, perchlorates, carbonates and acetates are excluded from the solvent solution.

The electrolysis step generates heat and with heat the solvent solution may cause reflux of the solvent. It is preferred that electrolysis be performed at the reflux temperature of the solvent or the reactor immersed in a cold liquid bath or a jacketed reactor to remove the heat. It will usually be satisfactory to carry out the polarity reversing electrolysis at atmospheric pressure. In some situations, however, a high pressure might be desirable in order to allow a higher temperature to be used without excessive bubbling and for product selection and to increase the rate of reaction.

The process of the invention converts a carboxylic acid or salt thereof, into an alkane or alkene or a mixture of an alkane, and alkene or alkyl-aryl compound depending on the initial reactants used.. An ether can be produced depending on the polarity reversal electrolysis conditions and solvent used. In addition some esters may also be produced. The term carboxylic acid refers to any organic compound, aliphatic, cyclic, heterocyclic, or aromatic, that contains a carboxylic acid that can be decarboxylated by this invention to produce the decarboxylated product. The term fatty acid as used herein refers to an organic compound having a single carboxylic acid attached to an aliphatic chain, which may be branched or unbranched and may be saturated or unsaturated. Typically, the fatty acid has at least 8 carbon atoms. The aliphatic chain of the fatty acid may be branched or unbranched, and typically the fatty acids are derived from triglycerides and lipids from oils and fats from plant and animal sources by hydrolysis using

acids, bases or at high temperatures and pressures with water and steam and is known in the art.

Suitable unbranched saturated carboxylic acids include one or more of butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid, tricosanoic acid.

Suitable monounsaturated fatty acids include one or more of cis-5-dodecenoic acid, myristoleic acid, palmitoleic acid, oleic acid, eicosenoic acid, erucic acid, and nervonic acid. Suitable polyunsaturated fatty acids include linoleic acid, alpha.-linoleic acid, linolenic acid, arachidonic acid, eicosapentaenoic acid, and docosahexaenoic acid.

The term salt of a fatty acid refers to the carboxylate salts of the fatty acid (e.g. sodium oleate). The counter cation to the carboxylate anion is typically an alkali metal cation, an alkaline earth metal cation, ammonium or alkylated ammonium (NR_4 where each R is independently a C1-4 alkyl group). In particular, the counter cation is preferably selected from one or more of lithium, sodium, potassium, rubidium, and ammonium. More preferably, the counter cation is sodium or potassium.

In one embodiment of the invention, the use of alkali metal salts of propionic acid (particularly sodium propionate), caprylic acid (particularly potassium caprylate), lauric acid (particularly sodium laurate), myristic acid (particularly sodium myristate), oleic acid (particularly potassium oleate), stearic acid (particularly potassium stearate), tridecanoic acid (particularly potassium tridecanoate), pentadecanoic acid (particularly potassium pentadecanoate), heptadecanoic acid (particularly potassium heptadecanoate) can also be used depending on the desired physical properties.

In one embodiment, the fatty acid, or salt thereof, is unsaturated, more preferably is monounsaturated or polyunsaturated. Preferably, the fatty acid, or salt etc. thereof, is monounsaturated and has a double bond. More preferably, the fatty acid is derived from vegetable oils, animal fats, and waste oils containing high free acid content by hydrolysis that is generally known in the art of triglyceride and ester hydrolysis.

Analysis of experimental results reveals that alkanes, ethers, alkenes and cyclo- alkenes are formed during the reaction based on the reaction conditions used in a ratio based on the frequency, voltage and current density with straight chain fatty acids. This ratio varies

significantly, however, depending on the fatty acids involved, as well as on the reaction conditions of the inventive steps and departs from the prior art expected Kolbe dimer product and Hofer-Moest process and product compositions.

If the product compounds of the electrolysis constitute a fuel, rather than act solely or mainly as a fuel additive or chemical, it is preferred that the alkanes, ethers, the alkenes, aryl-alkanes, or the ethers, alkanes and alkenes together constitute at least 15% particularly at least 40%, preferably at least 75%, and more preferably at least 90% by weight of the total fuel composition.

Thus, the invention provides a fuel composition comprising an ether and an alkane compound represented by formula AB, ANu or BE as defined in Equation, (19), (20) and (23) above.

In particular, the amount of the alkane, the ether, or the amount of alkene, or the amount of ether plus the amount of alkene, present may be for example at least 20% by weight of the composition, preferably at least 30, 40, 50, 60, 70, 80, 90 or 95%.

In the use or in the composition of the invention, the fuel composition may include one or more of a lubricity additive, combustion improver, detergent, dispersant, cold flow improver, dehazer, demulsifier, cetane improver, antioxidant, scavenger or a pollution suppressant typically used in the industry.

The hydrocarbon or hydrocarbon chain can be derived from any suitable feed stocks, and in particular from any biomass feedstock or in any way from biomass. For example, the hydrocarbon or hydrocarbon chain can be derived from a saturated fatty acid, or salt or other derivative from plant and animal origin triglycerides.

The composition can be formed by a process including electrolysis. Moreover, it can be formed by a process further including catalysis to further change the properties to meet the specification of a particular use by further transformation or reformation.

The polarity switching electrolysis can be performed in a batch, semi-continuous, or continuous mode of operation.

The product may be a hydrocarbon, alkyl-aryl hydrocarbon, hydrocarbon-ether mix which may be subjected to one or more further processing steps including but not limited to distillation, catalysis and crystallization. Thus, the ether and the hydrocarbon may be further separated or purified and/or reacted. The result may be a pure hydrocarbon and/or pure ether useful as

synthetic fuel components.

The core manufacturing process is preferably therefore a non-Kolbe electrolysis of fatty acid salts (for instance sodium, potassium), performed in solution in a solvent or a lower alcohol (methanol, ethanol, isopropanol etc.) using a simple electrolysis cell with, for example, two or more graphite electrodes with relatively small nominal spacing in between (about 2 mm) and medium to high current density (less than approximately $0.05\text{--}0.2\text{ Acm}^{-2}$) under near reflux conditions, where evaporation heat can be used to discharge excess heat created by the current involved. The current density may be increased from 0.01 to 2 Acm^{-2} provided the heat can be removed by reflux or by cooling of the reactor, with minimal production of the Kolbe dimer at a high production rate.

It is believed that polarity reversing electrolysis has not previously been used directly to produce the alkane from the decarboxylation of a carboxylic acid. Acetic acid and formic acids have been used to produce alkanes by cross Kolbe electrolysis to create alkanes with fewer carbon atoms beyond the fatty acid. In fact, such a process is not used today to create any hydrocarbons or fuels at any significant scale, let alone biofuels due to the cost of acetic acid and formic acid. The formation of an alkane by cross Kolbe reaction with formic acid is uncertain. Also, very few hydrocarbons today are being created commercially at any scale from biomass feed stocks, except using gasification and Fischer-Tropsch processes, which work very differently from electrolysis and by high temperature catalytic decarboxylation using hydrogen gas.

Further technical details relating to preferred embodiments of the invention follow. An intermediate bio-fuel, lubricant or renewable chemical composition according to the present invention can have the following structures:

Ether, $\text{RCH}_2\text{CH}_2\text{OR}'$ (I)

Alkane, $\text{RCH}_2\text{CH}_2\text{-H}$ (II)

Alkene, $\text{RCH}_2\text{=CH}_2$ (III)

Alcohol, $\text{RCH}_2\text{CH}_2\text{-OH}$ (IV)

Alkyl-Aromatic, $\text{RCH}_2\text{CH}_2\text{Ar}$ (V)

The residues R, R', Ar can represent one or more selected from the group consisting of a single H as well as any branched or unbranched, saturated or unsaturated alkyl group including, but not limited to methyl, ethyl, n-propyl, iso-propyl, allyl, all 4 butyls, E- or Z-crotonyl, neo-

pentyl, all possible isoprenyls, octyls, nonyls, decyls, undecyls, dodecyls, tridecyls, tetradecyls, pentadecyls, pentadecenyls, hexadecyls, heptadecyls, heptadecenyls and heptadecadienyls and aromatic groups.

The alkyl chain R' can be an alkoxyalkane or aryloxy, such as the phenoxy group, and can comprise one or more selected from a group consisting of H, methyl, ethyl, propyl/iso-propyl, allyl, and all isomers of butyl, butenyl, pentyl, pentenyl and hexyl or aromatic group.

Hydrocarbon compositions, aliphatic as well as aliphatic-aromatic are a main product of the core process. Ethers and alcohols are the other products of the core process. Both are formed in varying amounts. These ethers can be used together with those hydrocarbons as a novel fuel mixture, with properties similar to B20/50/80 (i.e. a 20/50/80% biodiesel/petroleum fuel mixture or sequence) while performing better (higher energy content, lower cold filter plugging point (CFPP), less aggressive solvent properties, etc.). In this case the core process need be the only process employed. When water is used as an additional reagent, alcohols are produced, represented by formula (IV), and can be used as specialty chemicals as well as fuel additives. When aromatic solvents or additives are used as an additional reagent, alkyl-aryl products are produced, represented by formula (V), and can be used as specialty chemicals as well as fuel additives and fuels.

Alternatively, these ethers can be seen as intermediates that can be refined further, for instance into hydrocarbons using a catalytic process. The resulting products may be "pure" hydrocarbons (i.e. having no more than traces of other compounds). This is possible for applications where fuels containing ethers are unappealing for whatever reason. If catalytic processing is not desirable for any reason, the hydrocarbon/ether mixture can also be separated by means of conventional distillation or other suitable means.

Currently, ethers are not commonly used in diesel type of formulations. The processes used to prepare ethers based on gasification are very different from the invented process in that, for example, gasification and associated processes used to form ethers cannot easily produce other, for example longer-chain, ethers. The mixed alkyl-aryls are expected to contain favorable fuel properties such as low freezing points and therefore can be used advantageously as fuels, especially jet fuels.

In addition, the invention produces hydroxyl compounds if water is used along with the other solvents that can be used as oxygenated fuels or chemicals such as fatty alcohols.

In contrast to prior art biodiesel formulations (the main renewable fuel for diesel engines) having two oxygen atoms per molecule, the present ethers preferably have only one oxygen atom per molecule, and thus have greater energy content. In other words, the energy density of prior art biodiesel fuel formulations is lower than that of the present biofuel formulations. Moreover, prior art biodiesel formulations have some undesirable properties, e.g. they act as solvents that attack rubber and other materials in engines, and they have a fairly high melting range (e.g. palm oil biodiesel without additives melts between 5 and 10.degree. C.). In contrast, the present biofuel having ethers as their only non-hydrocarbon component in general act as very mild solvents at best, and they generally have a much lower melting range than biodiesel made from the same feedstock. This results in the present biofuel melting at or below well below--instead of above--the freezing point of water.

Furthermore, the low oxygen content in the present biofuel helps making internal combustion burn more completely and thereby results in less toxic emissions due to a cleaner combustion. In addition, the low oxygen content fuels produced fuels with high octane numbers without undesirable material interaction properties.

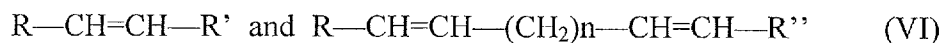
The present fuel composition consisting mainly of hydrocarbons is also much closer to petroleum-based diesel fuel in terms of engine and fuel distribution network material compatibility as well as shelf life.

Alkenes

The invention also relates to a hydrocarbon composition comprising any unsaturated hydrocarbon, derived from any fatty acid or from any renewable source, utilizing any of the above or below described processes with or without variations with at least one double bond with cis- or "Z-" configuration.

The invention also concerns a hydrocarbon composition comprising any hydrocarbon manufactured using any one of the above or below described processes from any fatty acid or fatty acid derivative sourced from any non-fossil feedstock, characterized by three to twenty-two carbon atoms with any number of double bonds.

A particularly useful group of hydrocarbons forms another part of the present invention: short, medium or long chain alkenes, having one or more double bonds, with either of the general formulae (VI):



where the double bond has a "cis" or "Z-" configuration, n and the length of the R groups preferably being such that the total number of carbon atoms is from 10 to 21, and R and R' may themselves contain further unsaturation. In the examples, Oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ was used.

Those proficient in the art will, after reading this specification, appreciate the significance of this group of compounds specifically emphasized here, i.e. unsaturated hydrocarbons having 10 to 21 carbon atoms and double bond(s) with cis- or "Z-" configuration. For example, mention may be made of heptadecenes of the general formula $C_{17}H_{34}$ or similar compounds with more than one double bond--at least one of which has cis-configuration--with similar properties. The above groups are found in oils and fats feed stocks. Furthermore, these compounds can have multiple uses as specialty chemicals.

These compounds differentiate themselves by the distinguished stereo chemistry of that particular middle double bond(s), which is always "cis" or "Z-" (same-sided), while the stereo chemistry of double bonds in refined petroleum feedstock is arbitrary in almost all cases. The hydrocarbons described immediately above, as well as those more generally described by formula (VI) can be directly derived by the manufacturing process that forms part of the invention. For instance, some members of the family of hydrocarbons in formula (VI) are unsaturated hydrocarbons with 17 carbon atoms, and can be derived from one particular unsaturated fatty acid, namely oleic acid, which is abundant in nature in both vegetable as well as animal fats and oils. The stereo chemistry of its double bond has a very well-defined configuration, practically 100% Z/cis, and the invented manufacturing process preserves this configuration after cleavage of the carboxyl group, reflected in the retained cis-, or "Z-" configuration of the hydrocarbons created. This is of tremendous advantage, as explained below.

This distinguished stereo chemistry leads to a certain preferred spatial molecular "bent" geometry of these compounds, which ultimately lowers their melting point (MP) significantly. This can also be observed in nature in many vegetable oils, which, despite having a fatty acid spectrum that is dominated by C_{18} fatty acids, are liquid at room temperature. Conversely, animal fats with less oleic acid or other unsaturated fatty acids with cis- or "Z-" configuration are solid at room temperature. Furthermore, by using Alkyl-Aryl hydrocarbons as in formula V, the

melting point can be further reduced, and would allow for the resulting alkyl-aryl hydrocarbons to be used as jet fuels as well as non-freezing renewable biofuels. In addition, this would allow for the use of unsaturated trans fatty acids such as elaidic acid, vaccenic acid and linoelaidic acid as well. Furthermore saturated fatty acids such as , palmitic acid, $C_{15}H_{31}COOH$ that generally have high melting points and is the most common saturated fatty acid found in animals, plants and microorganisms, is widely available and can be used for producing low-melting biofuels.

Hence hydrocarbons created from natural unsaturated fatty acids using the present process and having 17 or 15 carbon atoms melt far below zero or lower. At the same time, they are characterized by extremely low volatility and, hence, flammability (i.e. there is far less chance of igniting them accidentally during handling). This may be compared with straight heptadecane ($C_{17}H_{36}$), which has a melting point of 22.degree. C. (72.degree. F.), and would, on its own and without further refining, be practically unusable for diesel and, especially, jet fuel and aviation fuel.

Thus, the present C17 alkenes can provide an excellent blend stock for use with conventional diesel and jet fuel, and can even stand on their own and replace conventional diesel and jet fuel. Those of skill in the art will be aware that jet fuels require lower melting points than previously has been achievable with biofuels. Low melting points are required due to the extended stratospheric flights of jets, and accordingly, extended crossing through regions with very low temperatures.

Alkyl-Aryl Coupling

In addition, the invention can be used for alkyl-aryl coupling by using the radicals carbocations produced by decarboxylation. In addition to using methanol, added water as a reactant, or using hexane as a solvent, aryl compounds and solvents can be used that are reactive to the generated radicals and carbocations during the reverse polarity electrolysis to produce alkylated aromatics.

The present embodiments in addition, teach a method to produce alkylated aromatics (AR) products which may, for example, be used as components in lubricants or as surface active agents. The properties of the formed AR products depend on the structure of both the alkyl and aryl components as well as the number of alkyl components that are coupled to a single aryl component. Common methods of preparing AR compounds are based on the Friedel-Crafts alkylation which uses a catalyst to alkylate aromatic compounds. Such a process can lead to the

formation of monoalkylaromatics (MAR), dialkylaromatics (DAR) and polyalkaromatics (PAR). Because the properties of the MAR, DAR, and PAR may differ significantly from each other, a material with the desired properties is obtained by separating the different compounds through distillation and/or blending. One advantage of the present alkyl-aryl coupling of the aromatic component, or other component, is that by controlling the conditions and parameters of the electrolysis, one can control the degree of alkylation that occurs on the aromatic group, and thus control whether MAR products, DAR products, or PAR products are obtained and thus provides control over the properties of the synthesized compounds

In this embodiment the radical, the carbocation can act as an electrophile and subsequently involved in the electrophoretic substitution reaction. In such a reaction,, the electrophile substitutes one of the substituents on an aromatic group, for example, hydrogen, instead of the hydrogen generated by the electro-reversal, as shown below as a non-limiting example with toluene.



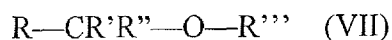
The H^+ or the $H\bullet$ may then be consumed, further reacted, etc., in the reactor in the vicinity of the electrodes or in the bulk solution. In the embodiment shown above, benzene is shown as the aromatic solvent or additive, instead of water or n-hexane. Those skilled in the art will appreciate that other aromatic or non-aromatic organic solvent or additives may also be used, that will react with the radical or the carbocation.

There are a large number of inexpensive carboxylic acid substrates that are available to use as the alkyl component of the alkyl-aryl coupling product. These carboxylic acid substrates can be coupled to a large number of possible aromatic compounds. The abundance of inexpensive substrates enhances the ability to control and fine-tune the properties of the synthesized AR compound to match the specific needs of the lubricant application (or any other desired application). The length of the alkyl group may affect the physical properties of the material, such as pour point, viscosity index, and flash point. The substitution on the aromatic system may increase the pour point, the viscosity index, and the flash point. The aryl component of the alkyl-aryl compound may affect the thermo-oxidative stability of the formed compound (because the electron-rich aromatic portion of the molecule can scavenge radicals and disrupt oxidation

processes).

Manufacturing

A preferred manufacturing process will now be explained, by which, in accordance with the invention, renewable or non-fossil (i.e. not derived from fossilization) feed stocks may be converted into useful hydrocarbons, ethers, or a mix of the two.



The carbon chain in formula (VII) is determined by the type of renewable feedstock being used, and it typically has a chain length between three and twenty-two, depending on the kind of fatty acids that is decarboxylated in the process. Furthermore, Aromatic groups such as toluene or benzene may also be used as desired to obtain the desired properties for R', R'' or R'''. Moreover, those of skill in the art will appreciate that general melting and boiling ranges correspond to molecular mass. In other words, the choice of chain length is determined in practice by final product requirements (e.g. broad liquid temperature range, low flammability, etc.). The fatty acid feed stocks can be obtained by the hydrolysis of fats and oils as is known in the art.

Fuels

The present invention relates to a composition that can be particularly used as a biofuel, the composition comprising one or more of an ether, alkyl-aryl hydrocarbon compound and a hydrocarbon or a hydrocarbon chain. The ether and the hydrocarbon are preferably in a useful ratio and mixed in liquid form at room temperature. Such a composition and also the compositions described below are particularly suitable as biofuel.

The ether and the hydrocarbon can be mixed in any suitable ratio, preferably from about 1:99 to about 99:1, preferably from about 10:90 to about 90:10, more preferably from about 20:80 to about 80:20, more preferably from about 30:70 to about 70:30, more preferably from about 40:60 to about 60:40 and more preferably about 50:50.

The described hydrocarbon-ether compositions can be used directly as fuel, lubricant, or they can be processed in a catalytic or other process using, for example, modified alumina (Al_2O_3) or similar catalysts at about 350-400.degree. for a specified time, to split the long alkyl off as alkene and to recycle the short-chain alcohol. This can, at the same time, be used to rearrange the long alkyl chain into something more branched using more sophisticated catalysts/conditions, such as those that the person skilled in the art will be aware of.

It is highly desirable to increase the branching of the long alkyl chain and hence lower the melting point of any resulting hydrocarbons longer than thirteen carbons (which have a melting point higher than desirable in a commercial product, especially for jet fuel and aviation fuel).

Those skilled in the art will appreciate that, by substituting ubiquitous fatty acids as starting material for a high-performance biofuel, use of the invention directly impacts the alternative use of dwindling supplies of fossil fuels. It will also be appreciated that, by producing carbon-neutral biofuels, use of the invention can directly impact the environment in a positive way by reducing or eliminating carbon emissions. Thus, the invention can preserve fossil fuels while also protecting the environment.

In short, the invented hydrocarbon-ether and hydrocarbon compositions are more similar to conventional petroleum products than existing biodiesel, whilst being advantageously derived from similar natural and renewable sources, and whilst minimizing emissions of fossil CO₂, i.e. whilst maintaining carbon neutrality.

Moreover, the ethers that are produced can, in accordance with one embodiment of the invention, be drawn off using suitable separation techniques, e.g. by fractionation techniques well known to those versed in the arts or any by other suitable process. These materials can stand on their own as biodiesel fuels or can be used as diesel fuel additives (e.g. to improve pour-point or cetane number, or to act as oxygenaters diminishing toxins in engine exhaust, etc.).

Uses for the present compositions include their applications as fuel and chemicals in any application where petroleum or products are used today. Thus, the present compositions may be similar to those in conventional use, but are made in a different way, from different sources, and have improved properties, e.g. the invented compositions may exhibit naturally ultra-low sulfur, estimated 90+% carbon-neutrality, etc.

Lubricants and Chemicals

By the choice of the solvent or additives, lubricants and other chemical intermediates may be made by the above process. The choice is only limited by the selection of the reactants and the conditions of the polarity-reversal electrolysis.

The embodiments of the above recited patent application and invention are summarized further below.

The Process

A process for the preparation of decarboxylated derivatives which comprises performing polarity reversing electrolysis using an anode and a cathode on a solvent of a carboxylic acid containing more than one carbon atom or salt of carboxylic acid or carboxylic acid ester or other derivative or precursor thereof, to decarboxylate said carboxylic acid or derivative, and produce the corresponding adduct hydrocarbons, alkanes, alkenes, alkyl ethers, alcohols and alkyl-aryl hydrocarbons. The polarity reversal electrolyses may be performed using a frequency range from 0.001Hz to 3 MHz at a current density of 0.001 to 4.0 Acm^{-2} . The polarity reversal electrolyses may be performed using a polarity reversal voltage function selected from a sine wave, square wave or triangular wave at a frequency range from 0.001Hz to 3 MHz at a current density of 0.001 to 4.0 Acm^{-2} with a voltage range from 2 volt to 240 volts. The polarity reversal electrolyses may be performed using a polarity reversal voltage function that is symmetrical or unsymmetrical. The polarity reversal electrolyses may be performed using an anode and a cathode using materials comprising the same or different from one another selected from the group consisting of platinum, nickel, palladium, steel, copper, silver, gold, carbon, natural graphite, synthetic graphite or boron doped diamond.

The acid or carboxylic acid derivative may be selected from the group consisting of saturated or unsaturated aliphatic, aromatic, cyclic, heterocyclic acid or mixtures thereof. The carboxylic acid salt may be selected from the group consisting of an alkali metal, an alkaline earth metal salt, a salt formed by the alkali metal or alkaline earth hydroxide, a tertiary amine, a secondary amine, a primary amine or ammonia salt. The solvent may be selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, pentanol, water, dimethyl sulfoxide, acetonitrile, dimethyl formamide, formamide and N-methyl pyrrolidone, aromatics, hexane or mixtures thereof.

The total concentration of the carboxylic acid or salt thereof in the alcoholic solution may be maintained to be between 0.1 and 4 molar. The solvent solution of the carboxylic acid or derivative thereof may be treated with and in contact with a tertiary amine, secondary amine, primary amine or ammonia. The solvent solution of the carboxylic acid or derivative thereof may be treated and in contact with an amine immobilized on a polymeric or silica support. The solvent solution of the carboxylic acid or derivative thereof may be treated and in contact with an alkali metal immobilized on a polymeric or silica support. The tertiary amine may be selected

from the group consisting of triethyl amine, diethyl cyclohexylamine, dimethyl cyclohexyl amine, piperidine, imidazole, benzoimidazole, and morpholine, or mixtures thereof.

The polarity reversal electrolysis may be performed between 0 degrees and 100 degrees Celsius. The polarity reversal electrolysis may be performed at substantially the reflux temperature of the solvent and solvent mixtures. The polarity reversal electrolysis may be performed between 1 bar and 100 bar pressure. The polarity reversal electrolysis may be performed in an apparatus having an anode and cathode wherein the closest spacing between the anode and cathode in the solvent is from 0.1 to 10 mm.

The carboxylic acid may be selected from the group consisting of saturated fatty acid, monounsaturated fatty acid, polyunsaturated fatty acid, aliphatic carboxylic acid, aromatic carboxylic acid, a derivative or precursor thereof, or mixtures thereof.

The process may comprise the step of separating the hydrocarbon from the solvent by phase separation. The process may comprise the step of separating the hydrocarbon from the solvent by distillation of the solvent. The process may comprise the step of separating the hydrocarbon from the solvent by freezing of the reaction mixture.

The carboxylic acid or derivative may be prepared by the hydrolysis of the triglyceride ester or the ester of the carboxylic acid. The triglyceride ester or ester may be derived from vegetable oils, animal fats, waste vegetable oils or waste animal fats. The hydrocarbon may be mixed with other hydrocarbons, alkyl-aryl hydrocarbons, hydrocarbon ethers or fatty acid esters or mixtures thereof to produce fuels, lubricants and chemicals. The hydrocarbon may be a saturated or an unsaturated alkane, an alkene, an alkyl-aryl hydrocarbon, an ether or an ester derivative.

The polarity reversing electrolysis may be carried out under vigorous mechanical mixing of the solution or under sonication in order to remove products away from the electrodes. The polarity reversing electrolysis may be carried out while the anode and cathode are subjected to mechanical vibration at 0.01 Hz to 100 kHz in order to remove reaction products and expose fresh electrode surfaces.

Product by Process

Also featured is a product by process composition. The product may be of decarboxylated derivatives prepared by performing polarity reversing electrolysis using an anode and a cathode on a solution of a carboxylic acid containing more than one carbon atom or salt of

carboxylic acid or carboxylic acid ester or other derivative or precursor thereof, to decarboxylate said carboxylic acid or derivative to produce the corresponding decarboxylated derivative. In addition, the solution may comprise solvents and additives that can react by radical coupling or by carbocation coupling with the solvent molecule or additives such as aryl additives, to form decarboxylated aryl compounds.

The carboxylic acid may be selected from the group consisting of a saturated or an unsaturated aliphatic, aromatic, cyclic, heterocyclic, fatty acid or mixtures thereof.

The product by process composition of the polarity reversal electrolysis may be generated using a polarity reversal voltage function selected from a sine wave, a square wave or a triangular wave at a frequency range from 0.001Hz to 3 MHz at a current density of 0.001 to 4.0 Acm^{-2} with a voltage range from 2 volt to 240 volts. The product by process composition of the polarity reversal electrolysis may be performed using a polarity reversal voltage function that is symmetrical or unsymmetrical. The product by process composition using a polarity reversal electrolysis process may be performed using an anode and a cathode comprising materials that are the same or different from one another, selected from the group consisting of platinum, nickel, palladium, steel, copper, silver, gold, carbon, natural graphite, synthetic graphite or boron doped diamond. Furthermore, the electrode surfaces may be coated with particles of platinum, nickel, palladium, copper, silver, gold and/or boron doped diamond, to catalyze the reaction. The above particles can be nanoparticles or micron-sized particles, or even a coating of the metals on internal surfaces of the electrodes. The coating of the metals can be performed by using electrolytic deposition of the metal ions or metal salts.

The product by process decarboxylated derivative may be further selected from the group consisting of saturated or unsaturated aliphatic, aromatic, cyclic, heterocyclic, or mixtures thereof. The carboxylic acid salt of the product by process invention may be selected from the group consisting of an alkali metal, an alkaline earth metal salt, a salt formed by the alkali metal or alkaline earth hydroxide, a tertiary amine, a secondary amine, a primary amine or ammonia salt. The solvent and solution for carrying out the product by process may be selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, pentanol, water, dimethyl sulfoxide, acetonitrile, dimethyl formamide, formamide and N-methyl pyrrolidone, aryloxy, alkoxy, hexane or mixtures thereof. In addition, additional reactants that can react with the decarboxylated radicals and carbocations, such as aromatic hydrocarbons and other compounds

containing reactive groups, can be used to make novel adducts. The total concentration of the above carboxylic acid or salt thereof in the alcoholic solution or solvent is preferably maintained to be between 0.1 to 4 molar.

The solvent solution of the carboxylic acid or derivative thereof may be treated with and in contact with a tertiary amine, secondary amine, primary amine or ammonia during electrolysis. Furthermore, the amine can be immobilized on a polymeric or silica support for easy separation of the amine and the products. The tertiary amine may be selected from the group consisting of triethyl amine, diethyl cyclohexylamine, dimethyl cyclohexyl amine, piperidine, imidazole, benzoimidazole, and morpholine or mixtures thereof. The solvent solution of the carboxylic acid or derivatives can be treated and be in contact with an alkali metal immobilized on a polymeric or silica support.

The polarity reversal electrolysis may be performed between 0 degrees and 100 degrees Celsius, or performed at substantially the reflux temperature of the solvent. The polarity reversal electrolysis may be performed between 1 bar and 100 bar pressure. The polarity reversal electrolysis may be performed in an apparatus having an anode and cathode, and wherein the closest spacing between the anode and cathode in the solvent is from 0.1 to 10 mm.

Furthermore, the separation of the hydrocarbon and reaction products from the solvent may be performed by phase separation or by distillation of solvent. Furthermore, the hydrocarbon and reaction products may be separated from the solvent by freezing.

The carboxylic acid or derivative may be prepared by the hydrolysis of the triglyceride ester or ester of the carboxylic acid or other esters. The triglyceride ester or ester may be derived from vegetable oils, animal fats, waste vegetable oils or waste animal fats. The hydrocarbons produced by the product by process may be mixed with other hydrocarbons, alkyl-aryl hydrocarbons, hydrocarbon ethers or fatty acid esters or mixtures thereof to produce fuels, lubricants and chemicals. The hydrocarbon may comprise a saturated or an unsaturated alkane, alkyl-aryl, an alkene, an ether or an ester.

The polarity reversing electrolysis may be carried out under vigorous mechanical mixing of the solution or under sonication. The polarity reversing electrolysis may be carried out while the anode and cathode are subjected to mechanical vibration at 0.01 Hz to 100 kHz.

Apparatus

Further disclosed is an apparatus for the preparation of decarboxylated derivatives which comprises performing polarity reversing electrolysis using an anode and a cathode using a polarity reversing device on a solution of a carboxylic acid containing more than one carbon atom or salt of carboxylic acid or carboxylic acid ester or other derivative or precursor thereof, to decarboxylate said carboxylic acid or derivative, by applying a voltage and current function sufficient to produce the corresponding decarboxylated hydrocarbon derivative. The polarity reversal electrolysis may be performed using a frequency range from 0.001Hz to 3 MHz at a current density of 0.001 to 4.0 Acm⁻². The polarity reversal electrolysis may be performed using a polarity reversal voltage function selected from a sine wave, square wave or triangular wave at a frequency range from 0.001Hz to 3 MHz at a current density of 0.001 to 4.0 Acm⁻² with a voltage range from 2 volt to 240 volts. The polarity reversal electrolysis may be performed in an apparatus using a polarity reversal voltage function that is symmetrical or unsymmetrical.

The polarity reversal electrolysis may be performed in an apparatus using an anode and a cathode using materials comprising the same or different from one another selected from the group consisting of platinum, nickel, palladium, steel, copper, silver, gold, carbon, natural graphite, synthetic graphite or boron doped diamond, or particles thereof.

The polarity reversal electrolysis may be performed in an apparatus containing a carboxylic acid or carboxylic acid derivative selected from the group consisting of saturated or unsaturated aliphatic, aromatic, cyclic, heterocyclic acid or mixtures thereof. The carboxylic acid salt in the polarity reversal electrolysis apparatus may be selected from the group consisting of an alkali metal, an alkaline earth metal salt, or a salt formed by the alkali metal or alkaline earth hydroxide, a tertiary amine, a secondary amine, a primary amine or ammonia salt. The solvent may be selected from the group consisting of methanol, ethanol, propanol, isopropanol, butanol, pentanol, water, dimethyl sulfoxide, aromatic hydrocarbon, aryl-compounds, phenols, acetonitrile, dimethyl formamide, formamide and N-methyl pyrrolidone, hexane or mixtures thereof. The total concentration of the carboxylic acid or salt thereof in the solution may be between 0.1 to 4 molar.

The solvent solution of the carboxylic acid or derivative thereof may be treated with and in contact with a tertiary amine, secondary amine, primary amine or ammonia. The solvent solution of the carboxylic acid or derivative thereof may be treated and in contact with an amine

immobilized on a polymeric or silica support. The solvent solution of the carboxylic acid or derivative thereof may be treated and in contact with an alkali metal immobilized on a polymeric or silica support. The tertiary amine may be selected from the group consisting of triethyl amine, diethyl cyclohexylamine, dimethyl cyclohexyl amine, piperidine, imidazole, benzoimidazole, and morpholine or mixtures thereof.

The polarity reversal electrolysis may be performed at between 0 degrees and 100 degrees Celsius. The polarity reversal electrolysis may be performed at substantially the reflux temperature of the solvent. The polarity reversal electrolysis may be performed at between 1 bar and 100 bar pressure. The apparatus may have a closest spacing between the anode and cathode in the solvent that is from 0.1 to 10 mm.

The carboxylic acid may be selected from the group consisting of saturated fatty acid, monounsaturated fatty acid, polyunsaturated fatty acid, aliphatic carboxylic acid, aromatic carboxylic acid, a derivative or precursor thereof, or mixtures thereof.

The hydrocarbon may be separated from the solvent by phase separation, by distillation of the solvent, phase separation, or freezing.

The carboxylic acid or derivative may be prepared by the hydrolysis of the triglyceride ester or the ester of the carboxylic acid. The triglyceride ester or ester may be derived from vegetable oils, animal fats, waste vegetable oils or waste animal fats. The hydrocarbon may be mixed with other hydrocarbons, alkyl-aryl hydrocarbons, hydrocarbon ethers or fatty acid esters or mixtures thereof to produce fuels. The hydrocarbon may comprise a saturated or an unsaturated alkane, an alkene, an ether or an ester derivative.

The apparatus may further comprise a mechanical mixer or a sonicator wherein the polarity reversing electrolysis is carried out under vigorous mechanical mixing of the solution or under sonication. The apparatus may further comprise a mechanical vibrator, wherein the polarity reversing electrolysis is carried out while the anode and cathode are subjected to mechanical vibration at 0.01 Hz to 100 kHz.

This disclosure features a polarity-reversal electrolysis process, comprising providing a reactor that comprises at least one pair of spaced electrodes, providing a controlled polarity-reversing power supply that is constructed and arranged to provide polarity-reversed power to the electrodes, providing to the reactor an electrically-conductive liquid reaction medium that comprises reactants, wherein the electrodes are at least partially immersed in the reaction

medium, and operating the power supply such that the polarity of the electrodes of the pair of electrodes reverses at a frequency rate. Also featured are products produced by the disclosed processes.

The reactor may comprise multiple separate pairs of spaced electrodes, each such pair supplied with polarity-reversed power by the power supply. The reactants may comprise a species that has an anion, and wherein the process produces a reactive radical intermediate at each electrode during the anodic cycle of each electrode. The reactants may comprise a species that has a carboxylic acid group, and wherein the process produces a decarboxylated radical intermediate at each electrode during the anodic cycle of each electrode.

The reactants may comprise a species that has a cation, and wherein the process produces a reactive radical intermediate at each electrode during the cathodic cycle of each electrode. The cation may comprise a hydrogen ion, and wherein the process produces a hydrogen radical intermediate at each electrode during the cathodic cycle of each electrode. The cation may comprise a species that has an alkali cation, or an alkali earth cation, and wherein the process produces an alkali metal radical intermediate at each electrode during the cathodic cycle of each electrode. Reactive radical intermediates may be produced at each electrode during the anodic cycle of each electrode or the cathodic cycle of each electrode, and the intermediates may react with the reactants selected from a group of reactants consisting of compounds that contain an alkyl group, an alkene group, an alkoxy group, an aryloxy group, an aryl group, a hydroxyl group, a ketone group, an aldehyde group, a carboxyl group, a nitrogen group, a halogen group, an allylic group, or a nitrile group.

The process may produce a hydrogen radical at the cathode electrode during the cathodic cycle of each electrode. The process may produce carbonium ions at each electrode during the anodic cycle of each electrode. The process may produce carbanion ions at each electrode during the cathodic cycle of each electrode.

The spaced electrodes may comprise one or more materials selected from the group consisting of platinum, nickel, palladium, steel, copper, silver, gold, carbon, zinc, iron, chromium, titanium, transition metals, natural graphite, synthetic graphite, boron doped diamond and glassy carbon, or particles thereof.

The polarity reversal frequency may be from 0.001 Hz to 3 MHz. The current density may be from 0.001 to 4.0 Acm⁻². The voltage may be from 2 volts to 240 volts.

Also featured is an apparatus for accomplishing polarity-reversal electrolysis, comprising a reactor that comprises at least one pair of spaced electrodes, a polarity-reversing power supply that is adapted to provide polarity-reversed power to the electrodes, and a controller that controls at least the current, and the polarity reversal frequency, of the power supplied to the electrodes by the power supply. The reactor may comprise multiple separate pairs of spaced electrodes, each such pair supplied with polarity-reversed power by the power supply. The polarity reversal frequency may be from 0.001 Hz to 3 MHz. The current density may be from 0.001 to 4.0 Acm⁻². The voltage may be from 2 volts to 240 volts. The apparatus may further comprise at least one mechanism to stir the contents of the reactor. The apparatus may comprise a flow-through reactor. The space between the electrodes may be from 0.1mm to 10 mm.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a description of the apparatus and process flow diagram illustrating a manufacturing process of the invention that may be used in a batch as well as continuous process.

Figure 2 is a description of the apparatus and process flow diagram illustrating a manufacturing process of the invention that may be used in a batch as well as continuous process where the reaction mixture is subjected to sonication or mechanical stirring to improve mass transfer.

Figure 3 is a description of the apparatus and process flow diagram illustrating a manufacturing process of the invention using multiple electrodes that may be used in a batch as well as continuous process to increase productivity.

Figure 4 is a description of the apparatus and process flow diagram illustrating a manufacturing process of the invention using electrodes that may be used in a flow through continuous process.

Figures 5-8 are data.

Detailed Description

Figure 1, describes the cylindrical reactor 10, with a silicone rubber sealable lid 12 for inserting the anode 14 and the cathode 16 that is separated by a fixed inert spacer 18 to maintain a fixed electrode separation between the electrodes. Leads, 20 and 22 from the power supply and function generator, 24, are connected to the two electrodes. The ammeter 26 is connected in series to measure current and the voltmeter 28 is connected to the electrodes, 14 and 16, to

measure the applied voltage. Ports, **30**, **31**, **32** and openings, **34**, **36** are provided or made as needed on the lid **12** for inserting a reflux condenser **38**, ports for thermometers and thermocouples, **40**, ports **34** for removing carbon dioxide and hydrogen generated during the reverse polarity electrolysis, ports for monitoring probes and sensors, **32**, ports for introducing reactants **30**, ports for removal of products **36**, and ports **31** for introducing nitrogen or other inert gas as needed to flush the reactants. In addition, the reactor **10** is provided with a magnetic stirrer **44** for mixing the reactants during electrolysis. Additionally, the reactor can be inserted in a water or cooling bath **45** for reactor cooling and removing the heat of reaction. In addition, the reactor can be jacketed with a cooling jacket (not shown) for additional cooling if needed. This additional cooling most likely will be needed during scale up and manufacturing.

The port for product removal **36** allows for easy removal of final products. The port for reactants **30** allows for the introduction of fresh batch of reactants **46** that comprises the electrolyte solution. In addition to the batch mode operation, the apparatus described in Figure 1 may be used in a semi-continuous mode.

Figure 2, describes the cylindrical reactor **10** described in Figure 1, and in addition contains mechanical mixer –stirrer **60** and a sonicator **62** for additional product mixing, that will be useful during scale up and manufacturing. In addition, the reactor can be jacketed with a cooling jacket (not shown) for additional cooling if needed. This additional cooling most likely may be needed during scale up and manufacturing.

The port for product removal allows for easy removal of final products. The port **30** for reactants allows for the introduction of fresh batch of reactants. In addition to the batch mode operation, the apparatus described in Figure 2 may be used in a semi-continuous mode

Figure 3, describes a rectangular electrochemical reactor **100** containing multiple sets of anode-cathode pairs, **102-112**, **104-114**, **106-116**, **108-118**, connected to the Power Generator/Function Generator **130** using the common leads **110** and **120**, for carrying out the inventive process in a semi-continuous and continuous mode for scale up and manufacturing. Each of the anode-cathode electrode pairs are separated by insulating spacers, **132**, **134**, **136** and **138** and connected to a power supply and function generator **130** to provide the voltage and current necessary to carry out the reverse polarity reaction. Ports **142**, **144** and **146** are provided for introducing in a continuous, semi-continuous or batch mode, the reagents and for removing the reaction products, in a continuous, semi-continuous or batch mode. Additional ports are

provided for introducing any purging gases such as nitrogen **148** and for removing product gases **150** such as hydrogen, carbon dioxide and any other gases. Additional ports **152** are provided for thermometers, thermocouples and other sensors needed for monitoring the progress of the process. Additional cooling of the reactor may be provided by jacketing of the reactor (not shown). The reactant electrolyte **154** is contained in the reactor and immerses the electrodes.

Figure 4, describes a rectangular or tubular electrochemical reactor **200** containing a single set of anode-cathode pairs, **210** and **212**, for carrying out the inventive process in a semi-continuous and continuous mode for scale up and manufacturing. The anode-cathode electrode pairs, **210** and **212**, are separated by insulating spacers, **220** and **222** and connected to a power supply and function generator **230** using the leads **232** and **234** to provide the voltage and current necessary to carry out the reverse polarity reaction. Reactants enter through port **240** in a continuous, semi-continuous or batch mode, into the electrolysis chamber **270** between the electrodes and after the desired electrolysis and the reaction products exit, through port **242** in a continuous, semi-continuous or batch mode from the product out port, **242**. An additional port **250** is provided for removing carbon dioxide and hydrogen. Further ports may be introduced as needed for monitoring the reaction conditions. An ammeter, **260**, capable of measuring DC and AC current is connected in series, and a voltmeter, **262**, capable of measuring DC voltage and AC voltage is connected to the anode and cathode, **210** and **212**. The rate of reactant introduction will be determined by the rate of the electrolytic reaction and the variable used based in the desired outcomes.

In the above figures, the carboxylic acids partially or fully neutralized with the alkali metal hydroxides dissolved in the solvent is introduced into the electrolytic reactor containing the graphite or other electrodes and subjected to polarity reversing electrolysis, by applying the appropriate voltage using a function generator. The electrolytic current and applied voltage were measured. The electrolytic cell is cooled by using cold water or by allowing the solvent to reflux to remove the heat of the reaction and the heat generated by the electrical resistance. The current density is dependent on the electrical conductivity of the solution and the applied voltage, the electrode gap, the temperature and progress of the electrolysis. The reverse polarity function can be adjusted to meet the requirements of the desired reactions.

The figures illustrate the present process in what is believed to be a largely self-explanatory process and apparatus. Pure fatty acid feedstock can be used, as indicated or

produced by the hydrolysis of esters. Non-Kolbe polarity reversing electrolysis produces the novel and useful biofuels and chemicals of the invention, as described herein, typically including a hydrocarbon, ether or hydrocarbon alcohol mix. Alternatively, the novel biofuel produced by electrolysis undergoes separation, e.g. phase separation or fractionation to produce pure ethers, pure hydrocarbons, pure alkyl-aryl products or alcohols as desired. Those of skill in the art will appreciate that the ethers, hydrocarbons, and alcohols can be further processed into pure hydrocarbons, using any suitable process such as cleavage or catalysis, as is known in the art. The hydrocarbons can be used as diesel, jet fuel, aviation fuel, lubricants or similar chemical product, or can be conventionally or otherwise suitably refined to produce liquid propane gas, gasoline, or other desired chemical products. In addition, the process is very generic and can be used to produce different chemical intermediates and compositions by selecting the carboxylic acid, aliphatic, aromatic, cyclic, heterocyclic and produce new compounds and intermediate by free radical coupling and electrophilic reactions. The products of this invention can be difficult to produce chemicals, chemical intermediates and pharmaceutical intermediate and even new chemical entities that can be used as new drugs, that is difficult or uneconomical to synthesize.

For those skilled in the art, additional configurations can be constructed on order to optimize the inventive apparatus, the inventive process and variations in the product compositions.

EXAMPLES

The invention will now be illustrated by the following, non-limiting examples. Gas chromatography/mass spectrometry was used to confirm production of a hydrocarbons, an alkene, and ether composition suitable for use as a biofuel and as chemicals. The fatty acids used in the examples below have been derived from naturally occurring vegetable oils. The examples are non-limiting in that any carboxylic acid can be substituted for the fatty acid, and can generally be produced by the hydrolysis of fats, oils and lipids.

The control oleic acid, Laboratory Grade, Formula Weight 282.46, CAS 113-80-1, was obtained from Consolidated Chemical, Allentown, Pennsylvania 18109, and used as received. The GC/MS analysis results of the control oleic acid is given in Figure 5 and Table II. The predominant oleic acid methyl ester, 11-Octadecanoic acid methyl ester peak is at 9.72 min. Other peaks are impurities from the sample bottle and the lid of the sample bottle, especially the siloxanes, 2-butoxy ethanol and 13-Docosenamide, (Z) used as anti-static and release agents

and was found in the GC/MS analysis. The oleic acid methyl ester was absent from the products to electrolysis, but new hydrocarbon peaks appeared as shown in Figures 6, 7 and 8 and Identified in Tables III, IV and V in substantial amounts from the invention. In GC/MS, the GC separates compounds based on retention time, and each peak may contain more than one compound. The MS identified each peak and assigns a probability value for the compound based on comparison to chemical databases. The results clearly demonstrate the utility and efficiency of reverse polarity electrolysis compared to the direct current electrolysis. More compounds are formed and it is expected that reactions can be controlled by adjusting the electrolysis reaction conditions.

Table II . GC/MS Results of Fatty Acid and Peak Identities from Fig 5.

Peak No.	GC-MS RT min	Fig 5 Fatty Acid Area % RT, Min	Fig 5 Fatty Acid Peak Identifier	Fig 5 Fatty Acid Peak Identifier CAS #	Peak Identifier Quality Probability %
1	4.378	9.86	Ethanol; 2-Butoxyethanol	000111-76-2	87, 72, 64
2	9.223	1.04	Benzenepropionic acid, 3,5- Prop acid bis (1,1-dimethyl ethyl)-4-hydroxy-, methyl ester)	006386-38-5	94
3	9.726	4.17	11-Octadecanoic Acid , methyl ester	052380-33-3	99
			9-Octanedeconic acid (Z) methyl ester	0000112-62-9	99
			cis-13-Octadecenoic acid, methyl ester	1000333-58-3	99
4	10.556	1.7	Hexanedioic Acid, bis(2-ethylhexyl) ester	000103-23-1	70
			Diisooctyl Adipate	0001330-86-5	64
			Hexanedioic Acid, bis(2-ethylhexyl) ester	000103-23-1	58
5	10.874	2.47	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	86
			Anthracene, 9,10-dihydro-9,9.10-trimethyl	014923-29-6	53
			2-Ethylacridine	055751-83-2	53
6	10.983	3.16	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	41
			3',8,8'-Trimethoxy-3-piperidyl-2,2'-binaphthalene-1,1',4.4'-tetrone	127611-84-1	38
			Phthalic acid, 4-methoxyphenyl 2-propyl ester		

				1000315-57-0	35
7	11.512	17.86	Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	59
			Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	59
			Cyclotrisiloxane, hexamethyl	0000541-05-9	58
8	11.646	51.57	13-Docosenamide, (Z)	000112-84-5	97
			13-Docosenamide, (Z)	000112-84-5	94
			13-Docosenamide, (Z)	000112-84-5	94
9	11.855	2.24	1,2 Bis(trimethylsilyl) benzene	017151-09-6	64
			Cyclotrisiloxane, hexamethyl	000541-05-9	52
			Cyclotrisiloxane, hexamethyl	000541-05-9	52
10	11.973	3.6	Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	64
			Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	64
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	41
11	12.023	2.34	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	64
			Cyclotrisiloxane, hexamethyl	000541-05-9	52
			1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)	001020-31-1	50
Total					
		100.01			

Example 1 (B6-31) Figure 6

Oleic Acid to Hydrocarbons Using Polarity Reversal

To 102 g of a 50/50 mixture by weight of oleic acid (0.18M) and methanol in a bottle with a magnetic stirrer and a lid added 4.2 g of a 10% (w/w) solution of sodium hydroxide in methanol and mixed well with the magnetic stirrer. A control sample of 5 g solution was removed for analysis. A pair of graphite electrodes, (EDM1-Poco, Saturn Industries, New York) 2.5 x15cm and 1 mm thickness, separated by 2mm, using polyethylene spacers was introduced to the bottle along with a thermocouple thermometer probe. The electrodes were immersed in the reactor such that 5 cm of the electrode pair was under the solvent solution. The electrodes were set so that the electrodes protruded through a silicone elastomer allowing for sealing the contents of the bottle as shown in Figure 1. The electrodes were then connected to a DC power supply and the voltage increased from 1.25V to 14.95V with the polarity reversal set at 2.6 sec with a polarity reversal switch (E-mechanical timing relay, Allied Electronics, USA) and the current measured. The current increased from 0.097A at 3.96 V to 0.39A at 12.69V to 0.46A at 14.95V. The voltage was then set to 12.69V and the polarity reversal switch was set to 0.6sec. The initial

temperature was 68 deg F. There was gas evolution from both electrodes and the temperature rose to 104 deg F within 50 minutes and the current increased to + and - 0.48 A. The solution was clear. After 29 hrs the voltage was 12.46V and the current + and - 0.36A. After 34 hrs the voltage was 12.59 V and the current + and - 0.19 A and there was gas evolution from both electrodes and the temperature 66 deg F. After 43 hrs, the temp was 66 deg F, voltage 12.59V and the current + or - 0.15 A. There was a white precipitate at the bottom covering to about 6 mm and there was gas evolution with stirring. After 48 hrs, there was an oil layer at the bottom, height 1.8 cm with a diameter of 5.4 cm corresponding to 41 cubic cm of oil with greatly reduced production of gas bubbles. After 72 hrs, the voltage was 12.63V and the current + or - 0.09A and the electrolysis was stopped. The oil at the bottom was removed and 32.6g of product oil was recovered. The measured yield from oleic acid from 50 g was 42.1 g, representing 79% of the theoretical yield. Balance was in the supernatant and as not reacted oleic acid. The supernatant was further electrolyzed, and the supernatant produced more oil that fell to the bottom of the electrolytic cell, and an additional 5 g of oil was recovered.

The initial fraction of product oil, was placed in a 40 ml glass bottle and placed in the freezer at -minus 12 deg C along with the control sample and oleic acid. The product oil was still liquid, oleic acid froze, and the control sample had at the bottom the frozen oleic acid and the methanol was at the top as a liquid.

The product Oil, Control Sample and Oleic Acid were analyzed by GC/MS. The results are given in figure 6.

The analysis showed that part of the oleic acid had been transformed with multiple product peaks at 8.23, 8.85 and 8.89 min, that was not present in Figure 5. When comparing the results with a Direct Current normal Kolbe and non-Kolbe results given in Example 4, figure 8, Table V, it shows that the amount of products with retention times of 8.23, 8.85 and 8.89 min were low for the normal Kolbe electrolysis. Additional compounds were formed that were not formed with the normal DC Kolbe electrolysis, Example 4, fig.8. Table I gives the GC/MS analysis by dissolving 0.1% by weight of the product in n-hexane analyzed by a third party independent analytical laboratory. The retention times are in minutes and the peak heights are normalized for the relative percentage of each component. Each retention time and each peak

Table III . GC/MS Results from Reverse Polarity Electrolysis and Peak Identities from Fig 6.

Peak No.	GC-MS RT min	Fig 6 B6-31 Area %	Fig 6 B6-31 Peak Identifier	Fig 5 Fatty Acid Peak Identifier CAS #	Peak Identifier Quality Probability %
1	4.376	4.76	Ethanol; 2-Butoxyethanol	000111-76-2	91, 86, 72
2	7.455	0.63	Cyclododecene	001501-82-2	94
			E-1,9-Tetradecadiene	1000245-70-7	83
			E-7-Dodecen-2-o1=acetate	1000131-35-3	80
3	7.513	0.61	1-Pentadecane	013360-61-7	98
			1-Pentadecene	013360-61-7	98
			Cyclopentadecene	000295-48-7	94
4	8.234	15.83	E-1,9-Tetradecadiene	1000245-70-7	96
			Cyclododecene	001501-82-2	94
			cis-9-Tetradecen-1-01	035153-15-2	74
5	8.284	3.07	1,9-Tetradecadiene	112929-06-3	87
			Cyclododecene	001501-82-2	76
			cis-9-Tetradecen-1-01	035153-15-2	74
6	8.335	1.58	Cyclododecene	001501-82-2	89
			1,9-Tetradecadiene	112929-06-3	76
			cis-9-Tetradecen-1-01	035153-15-2	74
7	8.41	4.79	Spiro(4,5) decane	000176-63-6	87
			8-Hexadecyne	019781-86-3	86
			9.12-Octadecadienoic acid (Z,Z)	000060-33-3	80
	8.63			1000131-10-4	
8	8.804	0.57	Z,E-3,13-Octadecadien-1-o1	1000131-10-2	83
			E-2-Octadecadecen-1-o1	028054-91-3	81
			Bicyclo(3.3.2) decan-9-one	1000185-19-1	78
9	8.854	4.68	(4-Methyl-pent-3-enyl)-cyclohexane	1000131-10-2	70
			Bicyclo(2.2.2) octane, 2-methyl-9,17-Octadecadienal, (Z)	056554-35-9	55
					47

			8.863			
10	8.896	5.47	(4-Methyl-pent-3-enyl)-cyclohexane	1000185=19-1	38	
			1,11-Dodecadiene	005876-87-9	38	
			E-1,9-Hexadecadiene	1000245-71-4	38	
			8.913			
11	9.081	2.34	1,11-Dodecadiene	005876-87-9	95	
			Oleyl alcohol, methyl ether	1000352-68-0	95	
			1,13-Tetradecadiene	021964-49-8	95	
12	9.223	0.89	Benzenepropionic acid, 3,5- Prop acid bis (1,1-dimethyl ethyl)-4-hydroxy-, methyl ester)	006386-38-5	94	
			8-(2,5-Dimethylanilino)naphtho-1,2-quinone	1000058-06-6	46	
			3,5-Di-tert-butyl-4-trimethylsiloxytoluene	018510-49-1	40	
13	9.718	6.27	8-Octadecanoic acid Methy; Ester	002345-29-1	99	
			11-Octadecenoic acid, methyl ester	052380-33-3	99	
			9-Octadecenoic acid, methyl ester	001937-62-8	99	
			9.726			
			10.556			
14	10.564	0.62	1,2-Benzisothiazol-3-amine tbdms	1000332-57-2	38	
			1,2-Bis(trimethylsilyl) benzene	017151-09-6	38	
			Silane, trimethyl (5-methyl-2-(1-methylethyl)phenoxy)-	055012-80-1	38	
			10.816			
15	10.866	3.12	Erucic acid	000112-86-7	56	
			Fumaric acid, 2-chloropropyl dodecyl ester	1000348-57-0	53	
			Erucic Acid	000112-86-7	53	
			10.874			
			10.983			
16	10.992	5.25	Cycloheptadecanol	004429-77-0	48	
			9-Octadecenoic acid, (Z)-2,3 dihydroxypropyl ester methyl ester		45	
				000111-03-5		
			1-Cyclohexylnonene	114614-84-5	41	
17	11.051	0.63	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	90	
			Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	81	
			Silane, trimethyl (5-methyl-2-(1-	055012-80-1	53	

			methylethyl)phenoxy)-		
	11,227				
18	11.243	6.17	Benzene, 2-(tert-butyldimethylsilyl) oxy)-1-isopropyl-4-methyl-	330455-64-6	38
			6-Octadecenoic acid(Z)	000593-39-5	38
			9-Octadecenoic acid(Z)-,0-octadecenyl ester,)Z)	003687-45-4	38
19	11.344	0.43	Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	59
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	53
			Cyclotrisiloxane, hexamethyl	000541-05-9	52
20	11.411	0.61	Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	59
			Cyclotrisiloxane, hexamethyl	000541-05-9	58
			Cyclotrisiloxane, hexamethyl	000541-05-9	50
21	11.486	0.34	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59
			Cyclotrisiloxane, hexamethyl	000541-05-9	58
			Cyclotrisiloxane, hexamethyl	000541-05-9	58
	11.495				
	11.512				
22	11.646	26.92	13-Docosenamide, (Z)	000112-84-5	98
			9-Octadecenamide, (Z)	000301-02-0	97
			13-Docosenamide, (Z)	000112-84-5	93
	11.855				
	11.864				
	11.939				
	11.973				
	12.023				
23	12.107	4.41	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	53
			Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	50
			Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	47
Total		99.99			

Example 2 (B3-25)**Oleic Acid 60 Hz Sine Wave Electrolysis**

To 104 g of a 50/50 mixture by weight of oleic acid (0.18M) and methanol in a reactor with a magnetic stirrer and a lid added 5 g of a 10% (w/w) solution of sodium hydroxide in methanol and mixed well with the magnetic stirrer. A control sample of 5 g solution was

removed for analysis. A pair of graphite electrodes, 2.5 x 15cm and 1 mm thickness, separated by 2mm, using spacers was introduced to the reactor along with a thermocouple thermometer probe. The electrodes were immersed in the reactor and 5 cm of the electrode pair was under the solvent solution. The electrodes were set so that the electrodes protruded through a silicone rubber elastomer allowing for sealing the contents of the bottle as shown in figure 1. The electrodes were then connected to a AC power supply using a rheostat and the AC sine wave voltage increased to 32.5V AC. The AC current was 2.2 A. The temperature increased from 25 deg C to 66 deg C in 5 minutes. The power was turned off and the rheostat adjusted to decrease the voltage to 14.5 V AC giving 1.02A. The voltage was decreased to 11.5V and the current decreased to 0.75A AC. There was no gas evolution from either electrode. The current decreased from 0.75A AC to 0.3A AC within 48 hrs and upon electrolysis for 7 days dropped to 0.05A AC. However, the solution was clear and there was no oil at the bottom and there was no gas evolution. This result was different from the reverse polarity example 1.

The final product, of was placed in a 40 ml glass bottle and placed in the freezer at minus 12 deg C. along with the control sample and oleic acid. The product showed a precipitate, and the control sample had at the bottom the frozen oleic acid and the methanol was at the top as a liquid.

Example 3 (B5-49) Fig.7

Oleic Acid and Polarity Reversing Square Wave Electrolysis

To 100 g of a 50/50 mixture by weight of oleic acid (0.18moles) and methanol in a bottle with a magnetic stirrer and a lid was added 4.0 g of a 10% (w/w) solution of sodium hydroxide in methanol to provide a 1.4M solution of oleic acid and mixed well with the magnetic stirrer. A control sample of 4 g solution was removed for analysis. A pair of graphite electrodes, 2.5 x15cm and 1 mm thickness, separated by 2mm using spacers was introduced to the bottle along with a thermocouple thermometer probe. The electrodes were immersed in the bottle such that 5 cm of the electrode pair was under the solvent solution with a gap for the magnetic stirrer. The electrodes were set so that the electrodes protruded through a silicone rubber outside the reactor allowing electrical connections and for sealing the contents of the reactor as shown in Figure 1. The electrodes were then connected to a Function Generator Maetec Model SFG 1000 set at symmetrical square wave at 0.11 Hz, 20.5 Vpp. The voltage as measured at the electrode

initially at the start of the electrolysis was + 4.77 V and -4.69V and there was gas evolution at both electrodes. After 96 hrs there was a white gel at the bottom and the voltage was + and – 7.36 V with oil drops floating. At 120 hrs, the white gel had turned into oil, and the oil layer was 1.5 cm thick. At 144 hrs, the voltage was + and – 8.03 V and current + or – 0.04A and it was stopped at + or – 8.04 volts with current + or - 0.04A. The oil layer at the bottom was 1.8cm corresponding to a volume of 3.142x2.682.68x1.8 cubic cm or 38.2 ml of product oil or 29.8 g of product. The theoretical yield from 50 g of oleic acid, allowing for decarboxylation is $0.85 \times 50 = 42.5$ g. This gives a theoretical yield of $29.8/42.5$, 70% yield, comparable to example 1 yield of 79% from example 1.

The recovered product oil from the bottom of the cell was removed and transferred into a 40 ml glass bottle and placed in the freezer at minus 12 deg C. along with the control sample and oleic acid. The product oil was still liquid, oleic acid froze, and the control sample had at the bottom the frozen oleic acid and the methanol was at the top as a liquid.

The product Oil, Control Sample and Oleic Acid were analyzed by GC/MS and the results are given in Figure 7 and the peaks identified in Table IV.

The analysis showed that greater part of the oleic acid had been transformed with multiple product peaks at 8.23, 8.85 and 8.89 min, and at 8.41 min, with the height of the 8.23 min peak increasing substantially, that were not present in Figure 5. When comparing the results with a Direct Current normal Kolbe and non-Kolbe results given in Example 4, Figure 8, Table V, it shows that the amount of products with retention times of 8.23, 8.85 and 8.89 min were low for the normal Kolbe electrolysis. Additional compounds were formed that were not formed with the normal DC Kolbe electrolysis in this invention.

Table IV . GC/MS Results from Reverse Polarity Electrolysis and Peak Identities from Fig 7.

Peak No.	GC-MS RT min	Fig 7 B5 1-49 Area %	Fig 7 B5 1-49 Peak Identifier	Fig 7 B5 1-49 Peak Identifier CAS #	Peak Identifier Quality Probability %
1	4.378	5.01	Ethanol; 2-Butoxyethanol	000111-76-2	91, 91, 72

2	7.446	0.8	Z-11,6-Y=Tridecadiene	1000230-98-3	94
			Z-1,8-Dodecadiene	1000245-70-7	83
			E-7-Dodecen-1-ol acetate	1000131-35-3	80
3	7.513	0.84	1-Pentadecane	013360-61-7	98
			1-Pentadecene	013360-61-7	98
			Cyclopentadecene	000295-48-7	94
4	8.234	21.47	E-1,9-Tetradecadiene	1000245-70-7	96
			Cyclododecene	001501-82-2	94
			cis-9-Tetradecen-1-ol	035153-15-2	74
5	8.284	4.19	1,9-Tetradecadiene	112929-06-3	87
			Cyclododecene	001501-82-2	76
			cis-9-Tetradecen-1-ol	035153-15-2	74
6	8.335	2.06	Cyclododecene	001501-82-2	89
			1,9-Tetradecadiene	112929-06-3	76
			cis-9-Tetradecen-1-ol	035153-15-2	74
7	8.41	7.12	Spiro(4,5) decane	000176-63-6	87
			8-Hexadecyne	019781-86-3	86
			9.12-Octadecadienoic acid (Z,Z)	000060-33-3	80
	8.63				
8	8.804	1.06	Z,E-3,13-Octadecadien-1-ol	1000131-10-4	83
			E-2-Octadecadecen-1-ol	1000131-10-2	81
			Bicyclo(3.3.2) decan-9-one	028054-91-3	78
9	8.854	7.16	(4-Methyl-pent-3-enyl)-cyclohexane	1000185-19-1	70
			Bicyclo(2.2.2) octane, 2-methyl-	1000131-10-2	55
			9,17-Octadecadienal, (Z)	056554-35-9	47
	8.863				
10	8.896	7.59	(4-Methyl-pent-3-enyl)-cyclohexane	1000185-19-1	38
			1,11-Dodecadiene	005876-87-9	38
			E-1,9-Hexadecadiene	1000245-71-4	38
	8.913				
11	9.072	3.23	1,11-Dodecadiene	005876-87-9	95
			Oleyl alcohol, methyl ether	1000352-68-0	95
			1,13-Tetradecadiene	021964-49-8	95
12	9.223	0.97	Benzenepropionic acid, 3,5- Prop acid bis (1,1-dimethyl ethyl)-4-hydroxy-, methyl ester)	006386-38-5	94
			8-(2,5-Dimethylanilino)naphtho-1,2-quinone	1000058-06-6	46
			3,5-Di-tert-butyl-4-trimethylsiloxytoluene	018510-49-1	40
13	9.718	3.85	8-Octadecanoic acid Methyl Ester	002345-29-1	99

			11-Octadecenoic acid, methyl ester	052380-33-3	99
			9-Octadecenoic acid, methyl ester	001937-62-8	99
	9.726				
	10.556				
14	10.564	0.7	1,2-Benzisothiazol-3-amine tbdms	1000332-57-2	38
			1,2-Bis(trimethylsilyl) benzene	017151-09-6	38
			Silane, trimethyl (5-methyl-2-(1-methylethyl)phenoxy)-	055012-80-1	38
15	10.766	0.34			
	10.816				
16	10.866	2.93	Erucic acid	000112-86-7	55
			Erucic acid	0000112-86-7	53
			cis-10-Nonadecenoic acid	073033-09-7	46
	10.874				
17	10.984	4.25	Phthalic acid, neopentyl 2-propyl ester	1000315-56-3	25
			Trimethyl (4-(2-methyl-4-oxo-2-pentyl) phenoxy)silane	1000233-56-9	25
			1,2-Benzenedicarboxylic acid, diisooctyl ester		22
	10.992				
	11.051				
18	11.118	0.18	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59
			Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	59
			5-methyl-2-phenylindolizine	036944-99-7	52
19	11.243	3.34	Cyclotrisiloxane, hexamethyl	000541-05-9	46
			Cyclotrisiloxane, hexamethyl	000541-05-9	46
			Trimethyl (4-tert-butylphenoxy) silane	025237-79-0	43
20	11.336	0.34	2,4,6-Cycloheptatrien-1-one, 3,5-bis-trimethyl silyl-	1000161-21-8	59
			Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	59
			Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	59
	11.344				
21	11.411	0.55	Trimethyl (4-(1-methyl-1-methoxyethyl)phenoxy) silane	1000283-54-8	59
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59
			Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	59
			Cyclotrisiloxane, hexamethyl	000541-05-9	58
	11.486				
22	11.487	0.34	Trimethyl (4-(1-methyl-1-methoxyethyl)phenoxy) silane	1000283-54-8	59
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59
			Cyclotrisiloxane, hexamethyl	000541-05-9	52

	11.495					
	11.512					
23	11.646	18.86	13-Docosenamide, (Z)	000112-84-5	97	
			9-Octadecenamide, (Z)	000301-02-0	95	
			13-Docosenamide, (Z)	000112-84-5	93	
	11.855					
	11.864					
	11.939					
	11.973					
	12.023					
23	12.107	2.85	Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane	1000283-54-9	64	
			Cyclotrisiloxane, hexamethyl	000541-05-9	58	
			Cyclotrisiloxane, hexamethyl	000541-05-9	52	
Total		100.03				

Example 4: Direct DC Electrolysis Control, figure 8

Oleic Acid Direct Current Electrolysis -Normal Kolbe and non-Kolbe Electrolysis

To 52 g by weight of oleic acid (0.18 molar) and 52 g methanol (1.70 molar) in a reactor with a magnetic stirrer and a lid added 4.4 g of a 10% (w/w) solution of sodium hydroxide in methanol and mixed well with the magnetic stirrer. A control sample of 5 g solution was removed for analysis. A pair of graphite electrodes, 2.5 x 15cm and 1 mm thickness, separated by 2mm, using spacers was introduced to the bottle along with a thermocouple thermometer probe. The electrodes were immersed in the bottle such that 5 cm of the electrode pair was under the solvent solution. The electrodes were set so that the electrodes protruded through a silicone rubber elastomer allowing for sealing the contents of the bottle as shown in figure 1. The electrodes were then connected to a direct current power supply and the voltage and current were measured. The voltage was then set at 12.6 volts, and the current was measured at 0.20 A and direct current electrolysis performed while the solution was stirred by the magnetic stirrer continuously. After 11 hrs, the DC voltage was 12.91V with and 0.03 to 0.04 A with gas bubbles from the electrodes. After 24 hrs, voltage was 13.1V and 0.01A current with very little gas evolution. After 58 hours, the voltage was 13.03V with 0.01A current with no gas evolution and

phase separation with a clear solution. The final product was analyzed using GC/MS and the results are given in figure 8.

The final product, of was placed in a 40 ml glass bottle and placed in the freezer at –minus 12 deg C along with the control sample and oleic acid. The product showed a precipitate, and the control sample had at the bottom the frozen oleic acid and the methanol was at the top as a liquid.

The final product was analyzed using GC/MS and the results are given in Figure 8. A comparison of the results of Fig 8, with Figures 7, 6 and 5 shows that reverse polarity non-Kolbe electrolysis produces more products and more efficient in converting oleic acid to other hydrocarbons and chemicals. Furthermore, the drastic drop in the current and the very slow reaction rates makes it impractical to use the direct current Kolbe and non-Kolbe electrolysis likely due to the coating of the electrodes with the products.

Table V . GC/MS Results from Direct Current Electrolysis and Peak Identities from Fig 8

Peak No.	GC-MS RT min	Fig. 8 B7-1 DC Area %	Fig. 8 B7-1 DC Peak Identifier	Fig. 8 B7-1 DC Peak Identifier CAS #	Peak Identifier Quality Probability %
1	4.37	9.56	Ethanol; 2-Butoxyethanol	000111-76-2	76, 72, 64
	7.446				
	7.513				
	8.234				
2	8.243	4.46	Z-1,9-Tetradecadiene	100245-70-9	97
			Cyclododecene	001501-82-2	95
			E-2-Octadecadecen-1-o1	000506-42-3	93
	8.335				
	8.41				
3	8.63	1.44	1,13-Tetradecadiene	021964-49-8	91
			E-2-Methyl-3-tetradecadecen-1-o1 acetate	1000130-81-2	78
			Bicyclo(2.2.2) octane, 2-methyl-	000766-53-0	64
	8.804				
	8.854				

			8.863			
			8.896			
4	8.913	1.37	1,9-Tetradecadiene	112929-06-3	64	
			(S) (+)-Z-13-Methyl-11-pentadecen-1-01 Acetate	1000130-84-8	60	
			Z-8-Pentadecen-1-01 acetate	1000130-85-1	50	
			9.072			
5	9.223	1.52	Benzenepropionic acid, 3,5- Prop acid bis (1,1-dimethyl ethyl)-4-hydroxy-, methyl ester)	006386-38-5	94	
			Sarcosine, N-(3-phenylpropionyl)-isobutyl ester	1000321-41-2	46	
			Cyclohexanone, 2-((1,1'-biphenyl)-2-ylamino) methylene)	018510-49-1	38	
6	9.718	7.88	8-Octadecanoic acid Methy; Ester	002345-29-1	99	
			9-Octadecanoic acid Methy; Ester- E	052380-33-3	99	
			9-Octadecanoic acid Methy; Ester-E	001937-62-8	99	
			9.726			
			10.556			
7	10.564	1.41	1,2-Bis(trimethylsilyl) benzene	017151-09-6	42	
			Silane, 1,4 -phenylenebis (trimethyl)	013183-70-5	41	
			Cyclotrisiloxane, hexamethyl	000541-05-9	38	
			10.766			
8	10.816	0.58	Trimethyl (4-(2-methyl-4-oxo-2-pentyl) phenoxy)silane	1000233-56-9	59	
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59	
			Methyltris(trimethylsiloxy)silane	017928-28-8	59	
9	10.866	7	Erucic acid	000112-86-7	46	
			Erucic acid	0000112-86-7	53	
			cis-10-Nonadecenoic acid	073033-09-7	46	
			10.874			
10	10.984	2.77	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	004376-20-9	38	
			1,2-Benzenedicarboxylic acid, diisooctyl ester	027554-26-3	38	
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	38	
			10.992			
			11.051			
11	11.227	2.63	2,4,6-Cycloheptatrien-1-one, 3,5-bis-trimethyl silyl- Silane, 1,4-phenylenebis(trimethyl)	1000161-21-8	59	
			1,2 -Bis(trimethylsilyl) benzene	013183-70-5	59	
				017151-09-6	59	
			11.243	000541-05-9	46	
				000541-05-9	46	
				025237-79-0	43	
			11.336			
			11.344			

12	11.411	5.77	Silane, 1,4-phenylenebis(trimethyl)	013183-70-5	59
			1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59
			Cyclotrisiloxane, hexamethyl	000541-05-9	58
	11.486				
	11.487				
13	11.495	5.2	Trimethyl (4-(1-methyl-1-methoxyethyl)phenoxy silane	1000283-54-8	64
			5-Methyl-2-trimethylsilyloxy-acetophenone	097389-69-0	59
			Trimethyl (4-tert-butylphenoxy) silane	025237-79-0	53
	11.512				
14	11.646	47.32	13-Docosenamide, (Z)	000112-84-5	97
			trans -13-Octadecenamide	010436-09-6	91
			13-Docosenamide, (Z)	000112-84-5	89
	11.855				
15	11.864	0.9	1,2 -Bis(trimethylsilyl) benzene	017151-09-6	59
			2,4,6-Cycloheptatrien-1-one, 3,5-bis-trimethyl silyl-	1000161-21-8	59
			4-Methyl-2-trimethylsilyloxy-acetophenone	097389-70-3	53
16	11.939	0.2	Cyclotrisiloxane, hexamethyl	000541-05-9	52
			Trimethyl (4-2(2-methyl-4-oxo-2-pentyl) phenoxy) silane		
				1000283-54-9	50
			Cyclotrisiloxane, hexamethyl	000541-05-9	50
	11.973				
	12.023				
	12.107				
Total		100.01			

Example 5: Polarity Reversing Electrolysis with added water

To 240g of oleic acid added 184 g of methanol and mixed well using a magnetic stirrer and 60 g of a 10% w/w sodium hydroxide was then added slowly with mixing until the precipitated sodium salt dissolved. Distilled water, 15.3gm, was added drop wise with stirring using a pipette to produce a clear solution stock solution 5.

60 g of this stock solution 5 was added to a 150 ml electrolysis bottle reactor containing a pair of graphite electrodes, 2.5 x15cm and 1 mm thickness, separated by 2mm spacing and containing a thermocouple and a thermometer. The electrodes were immersed in the bottle such that 2.2 cm of the electrode pair was under the solvent solution with a gap for the magnetic stirrer. The electrodes were set so that the electrodes protruded through a silicon elastomer outside the bottle allowing electrical connections and for sealing the contents of the bottle as shown in Figure 1. The electrodes were then connected to a polarity reversing switch with a

timer that was fed by two sets of 30 Volt power supplies, set at 17.5V. The timer was set to change the polarity to the electrodes every 0.1 sec (10 Hz). The voltage as measured at the electrode initially at the start of the electrolysis measured as AC was 16.4 V, and the temperature rapidly rose from 83 d to 105 deg F, and there was gas evolution at both electrodes. The DC amps as measured at the power supply was 1.08 A and 1.10A. After 36hrs, the solution turned cloudy and the gas evolution between the electrodes, and at 40 hrs, there was phase separation with milky bottom layer and a cloudy top layer with the current at 0.46 amps. After 46 hrs, the current was 0.16 amps with the DC voltage at 17.3V, the measured AC voltage at 19.7V with 1.6cm of white bottom phase and 0.8cm of top cloudy supernatant phase. The yield of product oil from the bottom phase was 24.8 g.

The recovered product oil from the bottom of the cell was removed and transferred into three 15 ml centrifuge tubes, and placed in the freezer at minus 12 deg C. along with the control sample and oleic acid. The product oil froze unlike the product oil from the electrolysis in the absence of water.

Example 6: With Hexane as Additional Solvent

To 61 g of this stock solution 5, and 6 g of n-hexane were added to a 150 ml electrolysis bottle reactor containing a pair of graphite electrodes, 2.5 x15cm and 1 mm thickness, separated by 2mm spacing and containing a thermocouple and a thermometer. The electrodes were immersed in the bottle such that 2.2 cm of the electrode pair was under the solvent solution with a gap for the magnetic stirrer. The electrodes were set so that the electrodes protruded through a silicon elastomer outside the bottle allowing electrical connections and for sealing the contents of the bottle as shown in figure 1. The electrodes were then connected to a polarity reversing switch with a timer that was fed by two sets of 30 Volt DC power supplies, and the voltage was gradually increased from 2V to 14V. Gas evolution started at around 8V. The timer was set to change the polarity to the electrodes every 0.1 sec (10 Hz). The voltage as measured at the electrode initially at the start of the electrolysis measured as AC was 16.4 V, and the temperature rapidly rose from 83 to 105 deg F, and there was gas evolution at both electrodes. The DC amps as measured at the power supply was 1.08 A and 1.10A. After 36hrs, the solution turned cloudy and the gas evolution between the electrodes, and at 40 hrs, there was phase separation with milky bottom layer and a cloudy top layer with the current at 0.46 amps. After 46

hrs, the current was 0.16 amps with the DC voltage at 17.3V, the measured AC voltage at 19.7V with 1.6cm of white bottom phase and 0.8cm of top cloudy supernatant phase. The yield of product oil from the bottom phase was 24.8 g.

The recovered product oil from the bottom of the cell was removed and transferred into three 15 ml centrifuge tubes, and placed in the freezer at minus 12 deg C. along with the control sample and oleic acid. The product oil froze unlike the product oil from the electrolysis in the absence of water.

METHOD FOR ARYL-ALKYL COUPLING USING DECARBOXYLATION

In addition, the invention can be used for alkyl-aryl coupling by using the radicals produced by decarboxylation. In addition to using methanol, added water as a reactants, or using hexane as a solvent, aryl compounds and solvents can be used that are reactive to the generated radicals and carbanions during the reverse polarity electrolysis to produce alkylated aromatics and other alkyl-aryl compounds.

In this embodiment the radical, the carbocation can act as an electrophile and subsequently involved in the electrophoretic substitution reaction. In such a reaction,, the electrophile substitutes one of the substituents on an aromatic group, for example, hydrogen, instead of the hydrogen generated by the electro-reversal, as shown below as a non-limiting example with benzene.



The H^+ or the $H\cdot$ may then be consumed, further reacted, etc., in the reactor in the vicinity of the electrodes or in the bulk solution. In the embodiment shown above, benzene is shown as the aromatic solvent or additive, instead of water or n-hexane. Those skilled in the art will appreciate that other aromatic or non-aromatic organic solvent or additives may also be used, that will react with the radical or the carbocation.

Table VI. Summary of Reaction Conditions and Results						
Electrolysis Time	Electrode Area	12.5	sq.cm	Electrode Separation 2 mm		
	Electrode Reversing Frequency, Cycles/sec, Hz	Electrode Voltage Difference Volts	Electrolyzing Current Amps	Electrolyzing Current Density A/sq cm	Electrolyzing Current Density mA/sq cm	Electrolyzing Current Density/V mA/sq cm/V
Example 1	Example 1	3.96	0.097	0.00776	7.76	1.960
	0.40 Hz	12.69	0.39	0.0312	31.2	2.459
50 min	(2.6 sec/cycle)	14.95	0.46	0.0368	36.8	2.462
	Square Wave	12.69	0.48	0.0384	38.4	3.026
29 hrs		12.4	0.36	0.0288	28.8	2.323
24 hrs		12.59	0.15	0.012	12	0.953
72 hrs		12.63	0.09	0.0072	7.2	0.570
5 min	Example 2	32.5	2.2	0.176	176	5.415
	60 Hz	14.5	1.02	0.0816	81.6	5.628
	0.0167 sec/cycle)	11.5	0.75	0.06	60	5.217
48 hrs	Sine Wave	11.5	0.3	0.024	24	2.087
7 days		11.5	0.05	0.004	4	0.348
1 hr	Example 3	4.77	0.05	0.004	4	0.839
96 hrs	0.11 Hz	7.36	0.05	0.004	4	0.543
120 hrs	9.1 sec/cycle	7.5	0.05	0.004	4	0.533
144 hrs	Square Wave	8.03	0.04	0.0032	3.2	0.399
1 hr	Example 4	12.6	0.2	0.016	16	1.270
11 hrs	Direct Current	12.91	0.035	0.0028	2.8	0.217
24 hrs		13.1	0.01	0.0008	0.8	0.061
58 hrs		13.03	0.01	0.0008	0.8	0.061
1 hr	Example 5	17.5	0.2	0.016	16	0.914
1 hr	10 Hz	16.4	1.09	0.0872	87.2	5.317
36 hrs	0.1 sec/cycle	13.1	0.46	0.0368	36.8	2.809
40 hrs	Square Wave	17.3	0.16	0.0128	12.8	0.740
46 hrs		17.3	0.16	0.0128	12.8	0.740
1 hr	Example 6	2	0.2	0.016	16	8.000
1 hr	10 Hz	8	1.09	0.0872	87.2	10.900
	0.1 sec/cycle	14	0.46	0.0368	36.8	2.629
36 hrs	Square Wave	16.4	1.09	0.0872	87.2	5.317
40 hrs		17.3	0.46	0.0368	36.8	2.127
46 hrs		17.3	0.16	0.0128	12.8	0.740

Amines as Bases

In addition, the invention and the inventive process can be carried out by treating the solution of the carboxylic acid or derivative thereof with a tertiary amine, secondary amine, primary amine or ammonia.

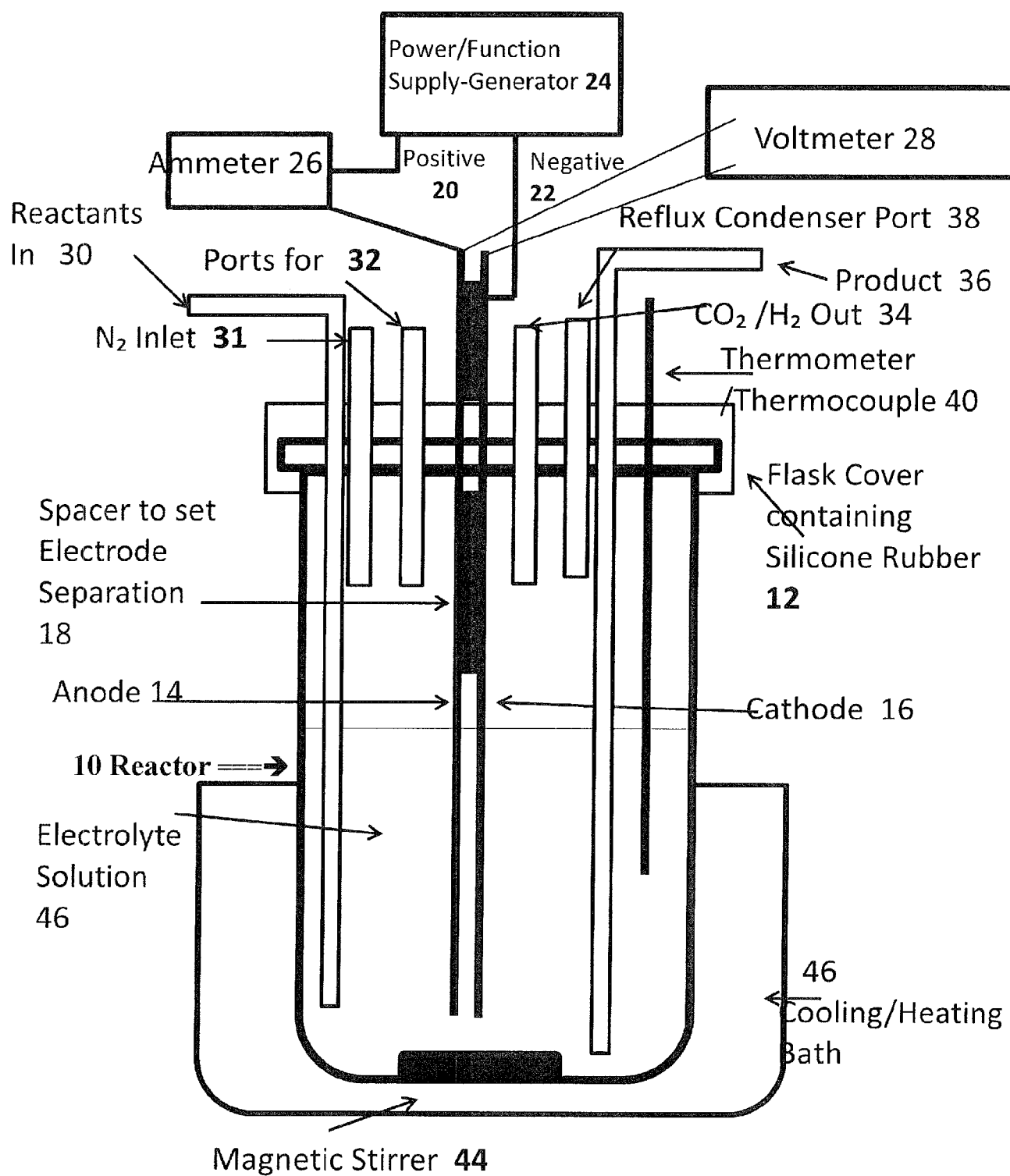
The invention can be carried out by replacing the alkali hydroxide with a tertiary amine, a secondary amine, a primary amine or ammonia salt in order to form the carboxylate salt. The amine base can be immobilized in a solid matrix and will allow for easy separation of products, such as using AMBERLYST A21 RESIN, a Divinyl Styrene copolymer with a tertiary amine functionality.

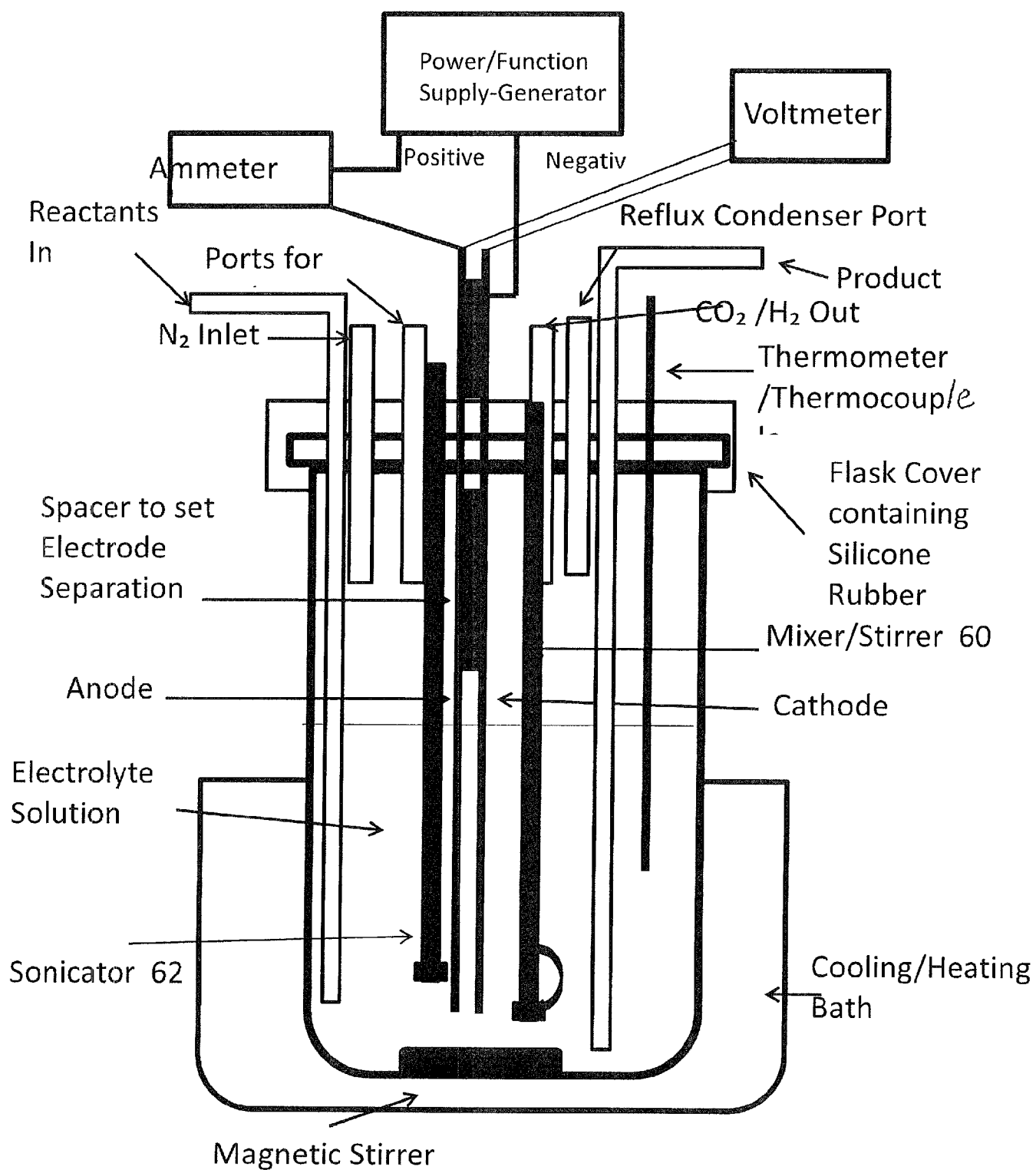
What is claimed is:

1. A polarity-reversal electrolysis process, comprising:
providing a reactor that comprises at least one pair of spaced electrodes;
providing a controlled polarity-reversing power supply that is constructed and arranged to provide polarity-reversed power to the electrodes;
providing to the reactor an electrically-conductive liquid reaction medium that comprises reactants, wherein the electrodes are at least partially immersed in the reaction medium; and
operating the power supply such that the polarity of the electrodes of the pair of electrodes reverses at a frequency rate.
2. A product produced by the process of claim 1.
3. The process of claim 1 wherein the reactor comprises multiple separate pairs of spaced electrodes, each such pair supplied with polarity-reversed power by the power supply.
4. The process of claim 1 wherein the reactants comprise a species that has an anion, and wherein the process produces a reactive radical intermediate at each electrode during the anodic cycle of each electrode.
5. The process of claim 4, wherein the reactants comprise a species that has a carboxylic acid group, and wherein the process produces a decarboxylated radical intermediate at each electrode during the anodic cycle of each electrode.
6. The process of claim 1 wherein the reactants comprise a species that has a cation, and wherein the process produces a reactive radical intermediate at each electrode during the cathodic cycle of each electrode.
7. The process of claim 6, wherein the cation comprises a hydrogen ion, and wherein the process produces a hydrogen radical intermediate at each electrode during the cathodic cycle of each electrode.
8. The process of claim 6, wherein the cation comprises a species that has an alkali cation, or an alkali earth cation, and wherein the process produces an alkali metal radical intermediate at each electrode during the cathodic cycle of each electrode.
9. The process of claim 1, wherein the process produces a hydrogen radical at the cathode electrode during the cathodic cycle of each electrode.

10. The process of claim 1, wherein the process produces carbonium ions at each electrode during the anodic cycle of each electrode.
11. The process of claim 1, wherein the process produces carbanion ions at each electrode during the cathodic cycle of each electrode.
12. The process of claim 1, wherein the said spaced electrodes comprise one or more materials selected from the group consisting of platinum, nickel, palladium, steel, copper, silver, gold, carbon, zinc, iron, chromium, titanium, transition metals, natural graphite, synthetic graphite, boron doped diamond and glassy carbon, or particles thereof.
13. The process of claim 1 wherein the polarity reversal frequency is from 0.001 Hz to 3 MHz.
14. The process of claim 7 wherein the current density is from 0.001 to 4.0 Acm⁻².
15. The process of claim 8 wherein the voltage is from 2 volts to 240 volts.
16. The process of claim 1 wherein reactive radical intermediates are produced at each electrode during the anodic cycle of each electrode or the cathodic cycle of each electrode, and the intermediates react with the reactants selected from a group of reactants consisting of compounds that contain an alkyl group, an alkene group, an alkoxy group, an aryloxy group, an aryl group, a hydroxyl group, a ketone group, an aldehyde group, a carboxyl group, a nitrogen group, a halogen group, an allylic group, or a nitrile group.
17. An apparatus for accomplishing polarity-reversal electrolysis, comprising:
 - a reactor that comprises at least one pair of spaced electrodes;
 - a polarity-reversing power supply that is adapted to provide polarity-reversed power to the electrodes; and
 - a controller that controls at least the current, and the polarity reversal frequency, of the power supplied to the electrodes by the power supply.
18. The apparatus of claim 17 wherein the reactor comprises multiple separate pairs of spaced electrodes, each such pair supplied with polarity-reversed power by the power supply.
19. The apparatus of claim 17 wherein the polarity reversal frequency is from 0.001 Hz to 3 MHz.

20. The apparatus of claim 17 wherein the current density is from 0.001 to 4.0 Acm⁻².
21. The apparatus of claim 17 wherein the voltage is from 2 volts to 240 volts.
22. The apparatus of claim 17 further comprising at least one mechanism to stir the contents of the reactor.
23. The apparatus of claim 17 comprising a flow-through reactor.
24. The apparatus of claim 17 wherein the space between the electrodes is from 0.1mm to 10 mm.

**Figure 1**

**Figure 2**

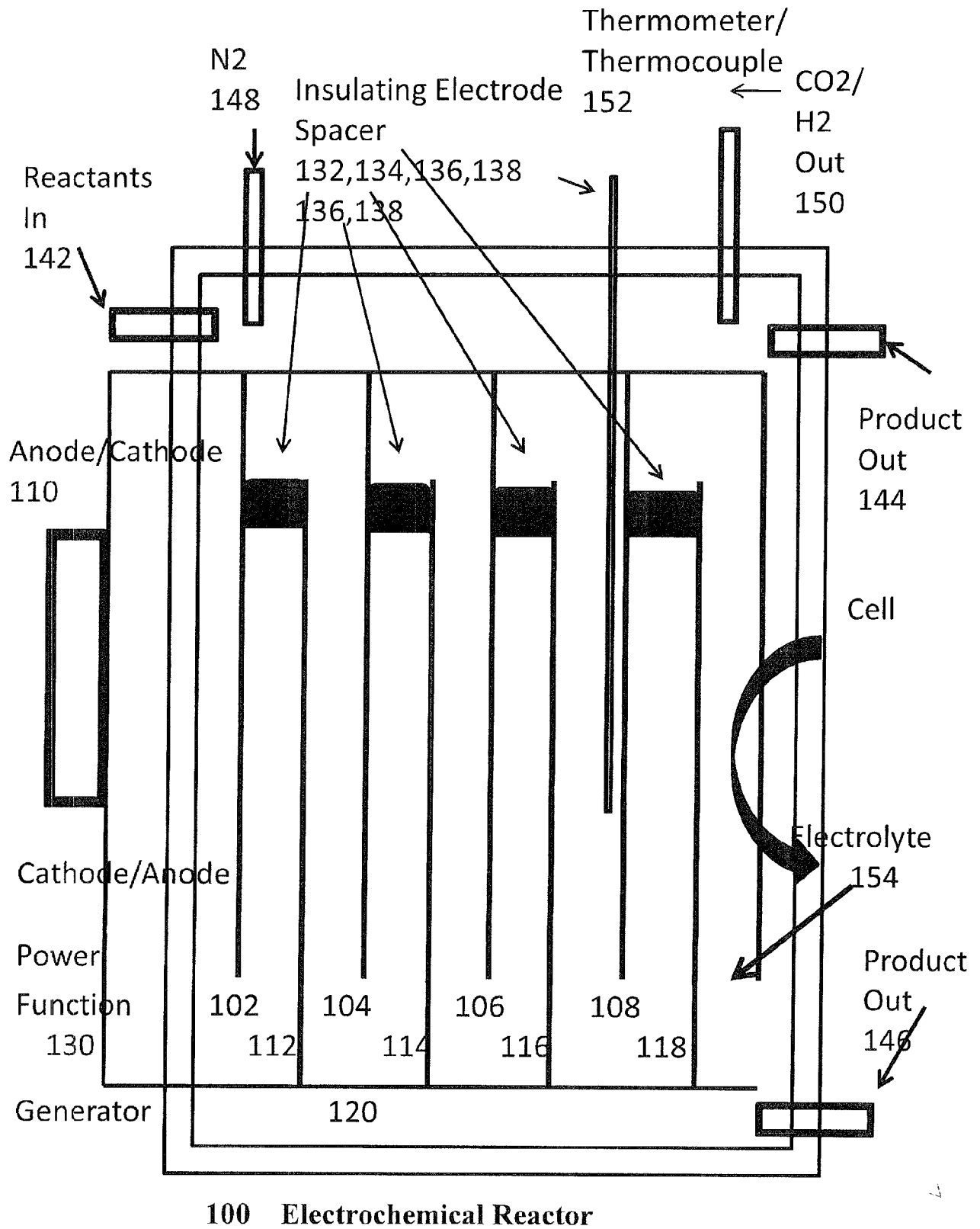
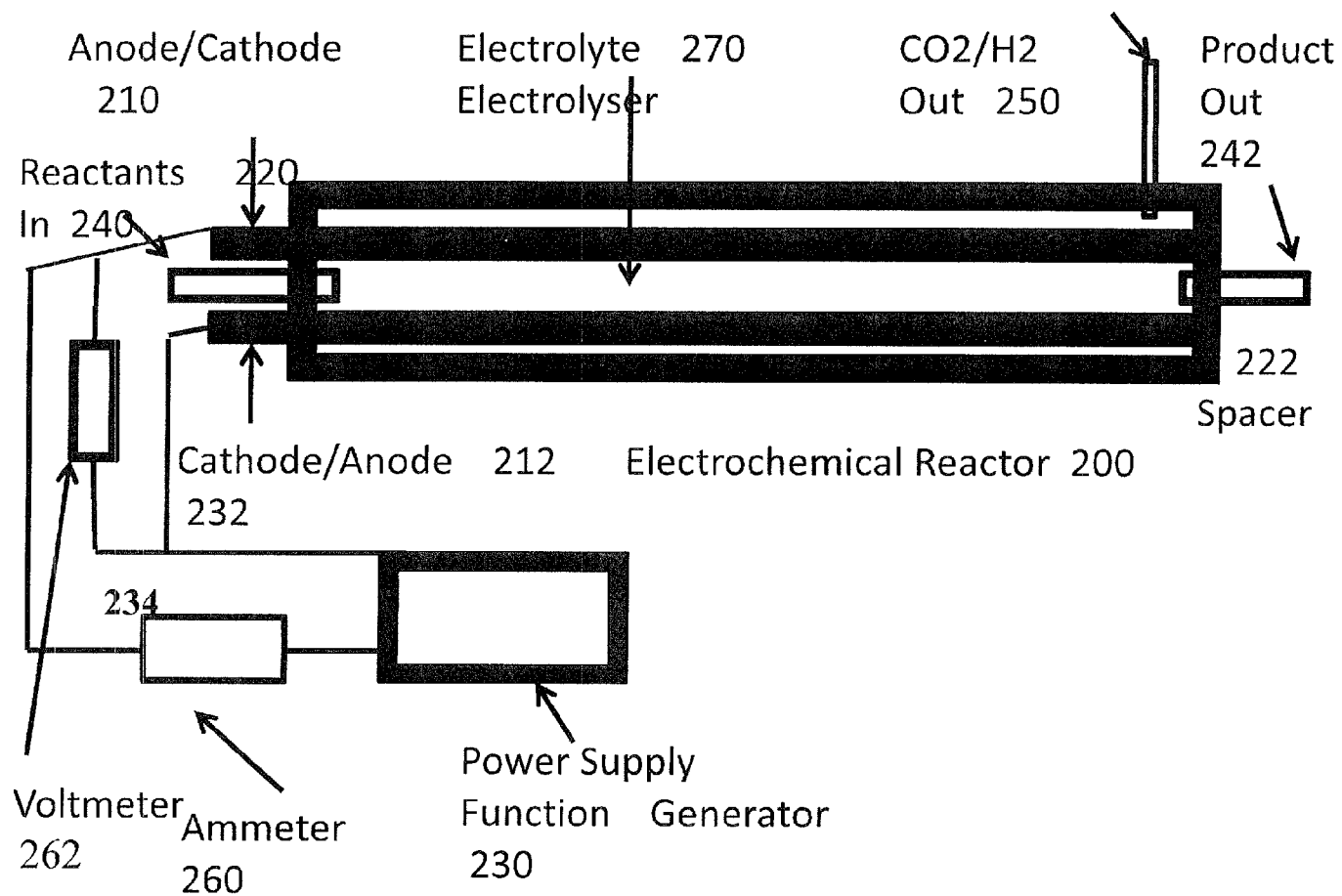


Figure 3

**Figure 4**

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Figure 5

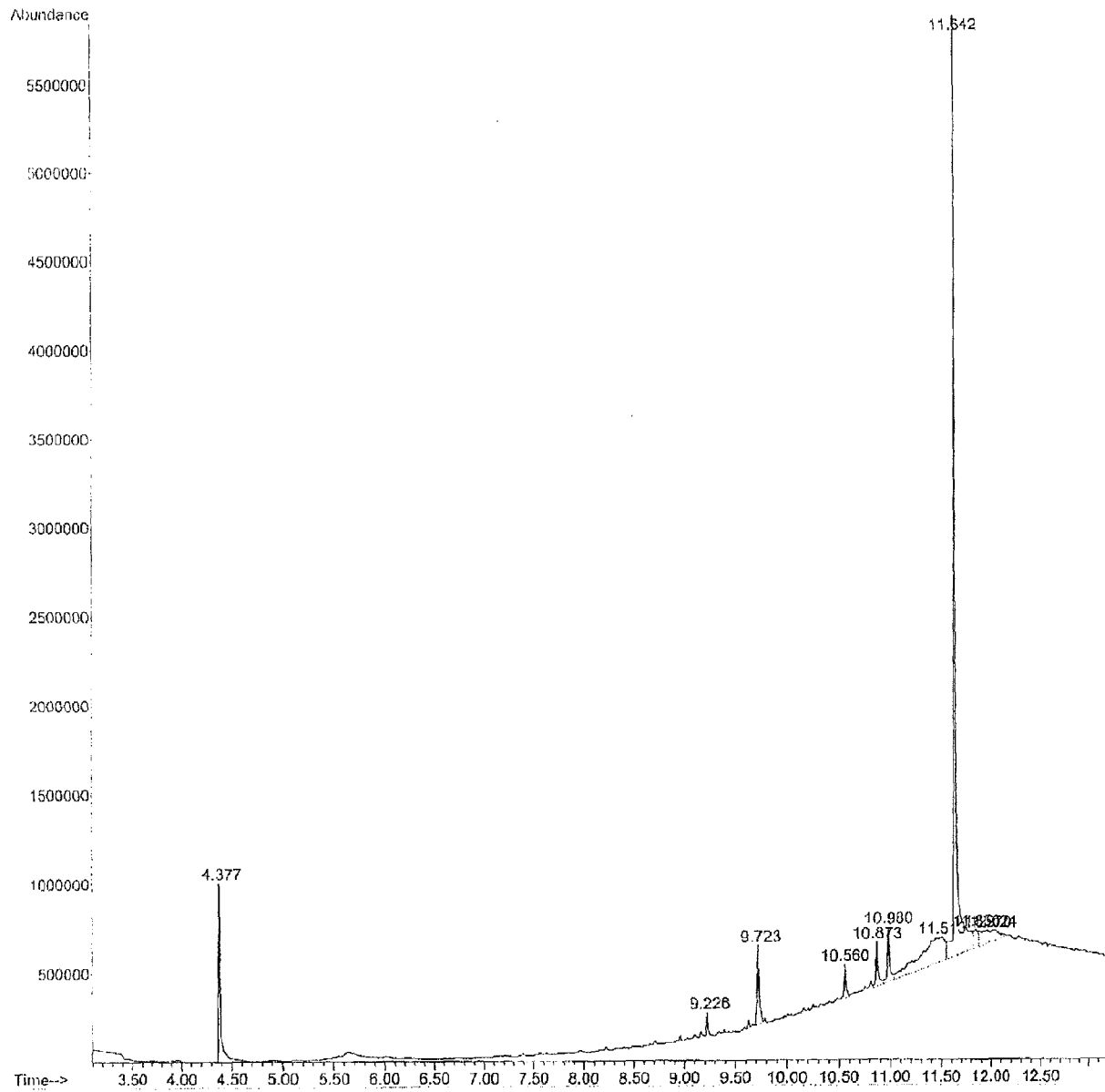


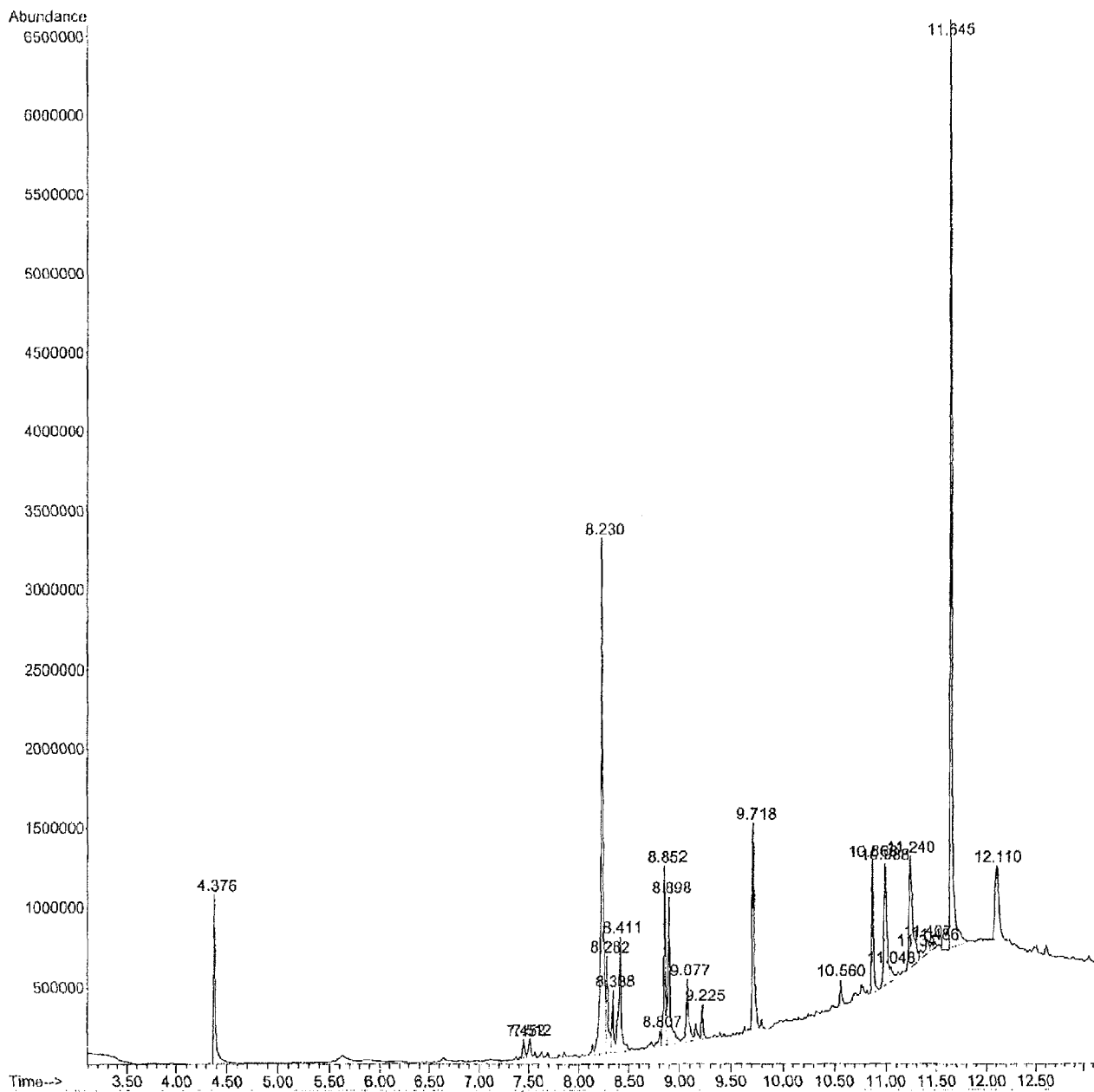
Figure 6

Figure 7

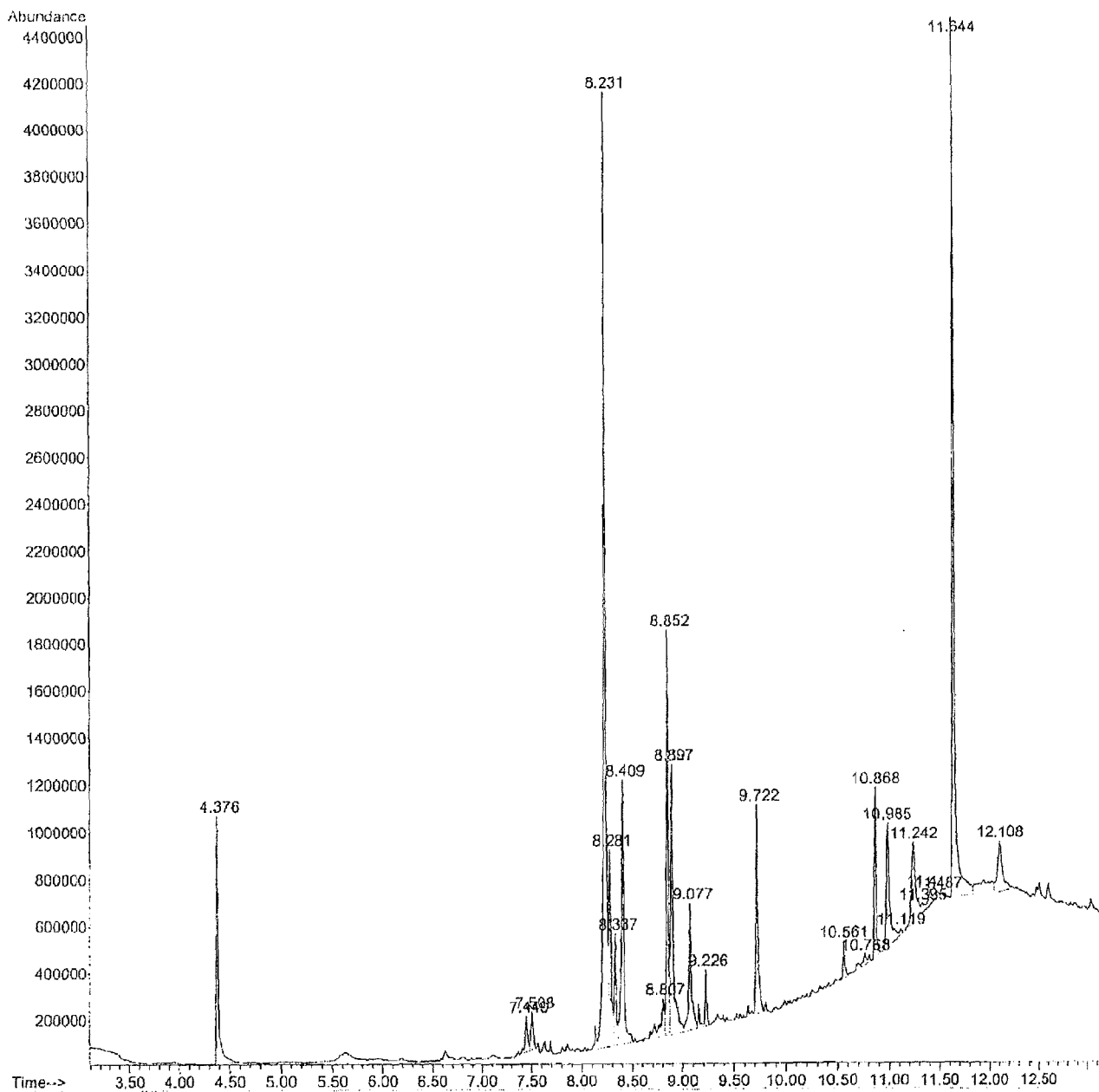
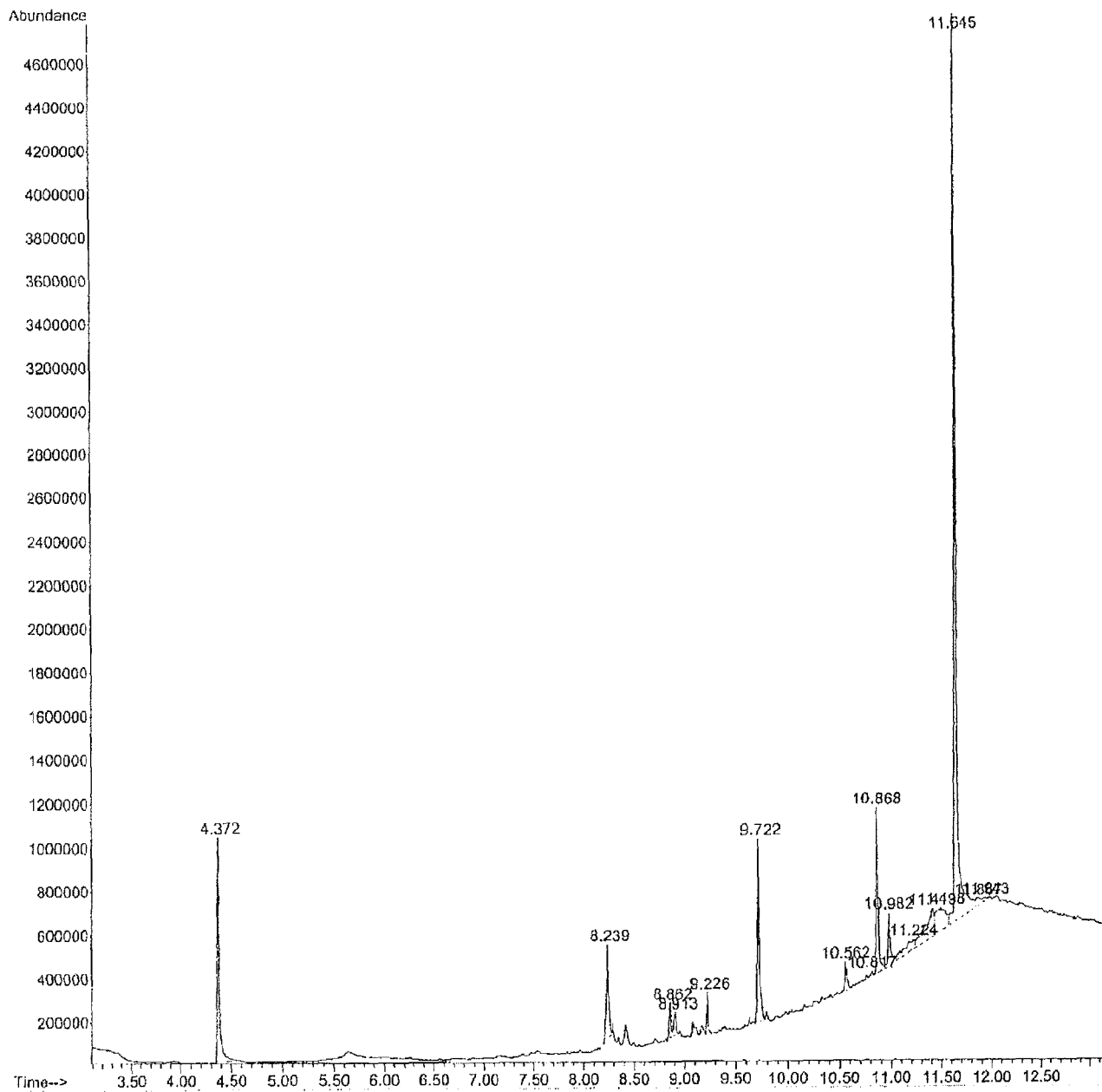


Figure 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/41531

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C25C 3/08 (2014.01)

CPC - C25C3/08; C25C3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CPC: C25C3/08; C25C3/06

IPC(8): C25C 3/08 (2014.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

CPC: C25B11/0473; C25B3/04 (keywords limited; search terms below)

USPC: 205/378,561 (keywords limited; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST(PGPB, USPT, EPAB, JPAB); PatBase; Google Scholar; Google Patents

Search terms: polarity electrolysis "polarity reversing" "polarity reversal" "current density" "reversal frequency" "polarity reversal electrolysis" "polarity reversing electrolysis" electrodes pairs "power supply" carboxylic decarboxylated decarboxylat\$5 "hydrogen ion?"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2011/0034625 A1 (Grassl et al.) 10 February 2011 (10.02.2011), especially, para [0014], [0016], [0018], [0019], [0022], [0024], [0025], [0032], [0033], [0055]-[0057], [0120] and [0124].	1-5, 12, 13, 16-24 ----- 6-11, 14, 15
Y	US 3,193,479 A (Baizer) 6 July 1965 (06.07.1965), especially, claim 8; col 2, ln 56-61; col 5 ln 24-27; and col 11, ln 5-7.	6-11, 14, 15

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

2 September 2014 (02.09.2014)

Date of mailing of the international search report

30 SEP 2014

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