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Jovanovic et al.

(54) MICROREACTOR PROCESS FOR MAKING BIODIESEL

(76) Inventors: **Goran Nadezda Jovanovic**, Corvallis, OR (US); **Brian Kevin Paul**, Corvallis, OR (US); **James Parker**, Corvallis, OR (US); **Ahmad Al-Dhubabian**, Jeddah (SA)

Correspondence Address:
KLARQUIST SPARKMAN, LLP
121 SW SALMON STREET, SUITE 1600
PORTLAND, OR 97204 (US)

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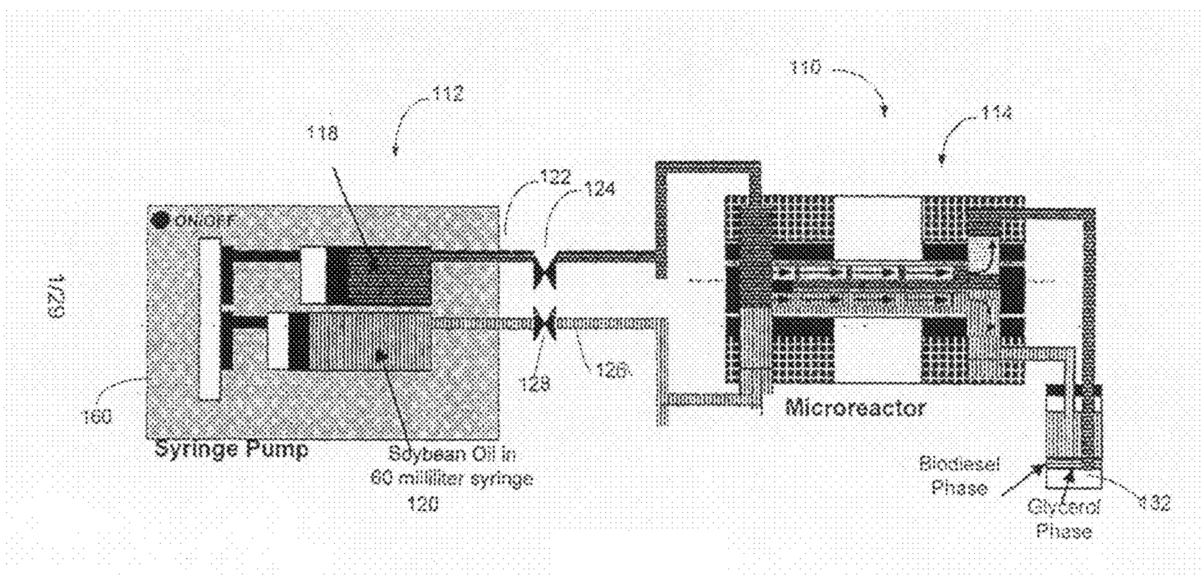
(52) **U.S. Cl.** **44/308**; 44/388

(57) ABSTRACT

Embodiments of a method for using a microreactor to produce biodiesel. For example, the method may comprise flowing a first fluid comprising an alcohol and a second fluid comprising an oil to the microreactor. Alcohols typically, but not necessarily, are lower aliphatic alcohols, including methanol, ethanol, amyl alcohol or combinations thereof. Biodiesel production can be under supercritical conditions, where such conditions typically are determined relative to the alcohol component. Suitable sources of oil products include soy, inedible tallow and grease, corn, edible tallow and lard, cotton, rapeseed, sunflower, canola, peanut, safflower, and combinations thereof. Catalysts can be used to facilitate biodiesel production, such as metal oxides, metal hydroxides, metal carbonates, alcoholic metal carbonates, alkoxides, mineral acids and enzymes. Oil conversion to biodiesel typically increases with increasing mean microreactor residence time. Certain embodiments of the present invention can include blending biodiesel produced by the method with petroleum-based products.



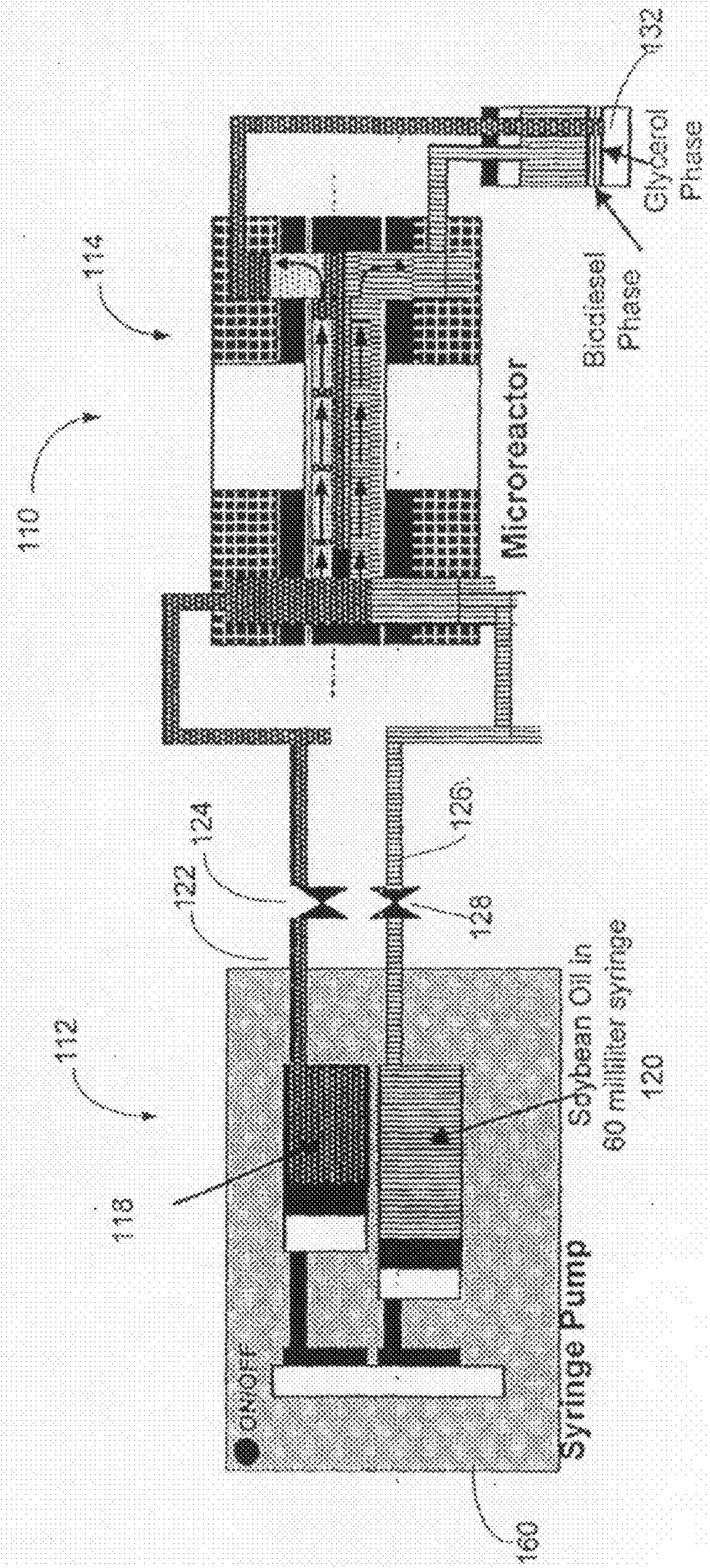

110
112
114
118
Soybean Oil In 60 milliliter syringe 120
122
124
126
128
132
Microreactor
Biodiesel Phase
Glycerol Phase
ON/OFF
Syringe Pump
160

FIG. 1

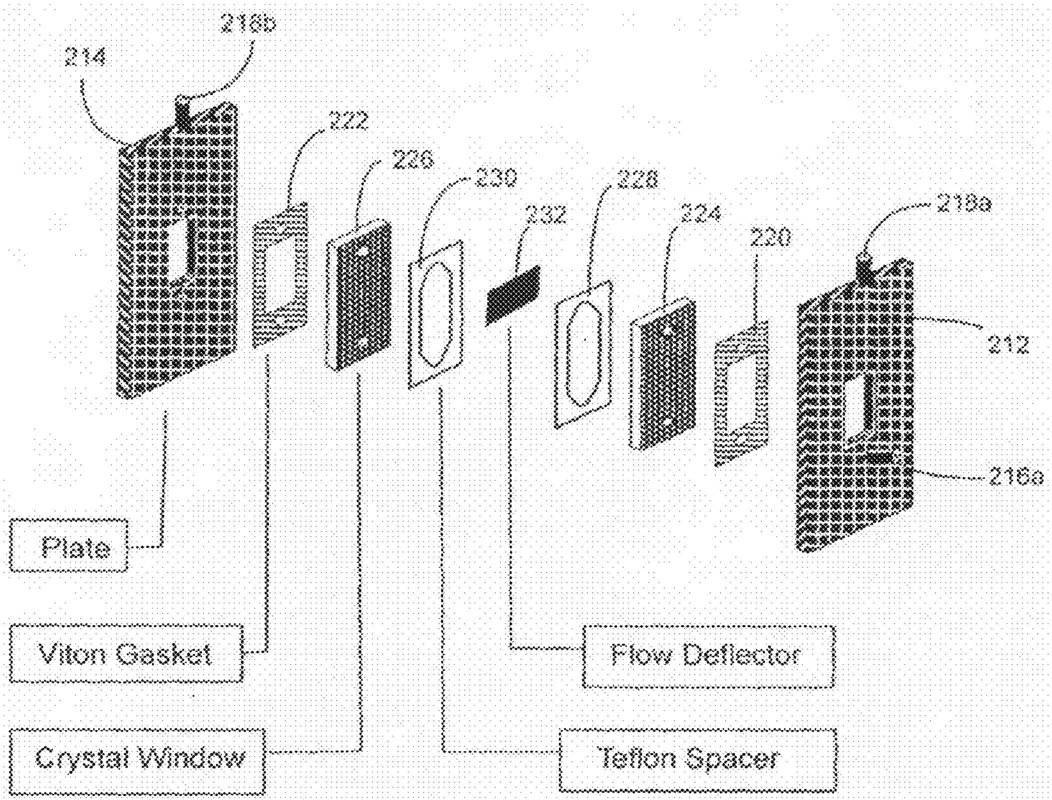

218b
214
222
226
230
232
228
224
220
218a
212
216a
Plate
Viton Gasket
Crystal Window
Flow Deflector
Teflon Spacer

FIG. 2

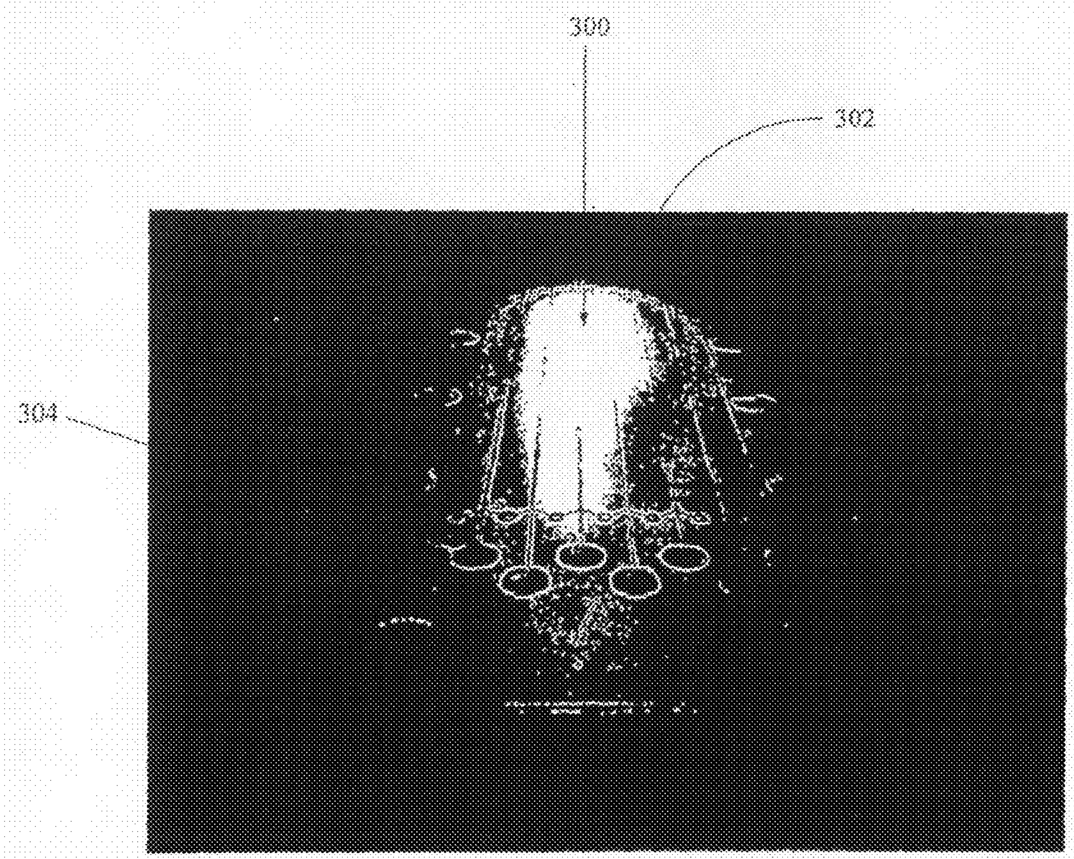


FIG. 3

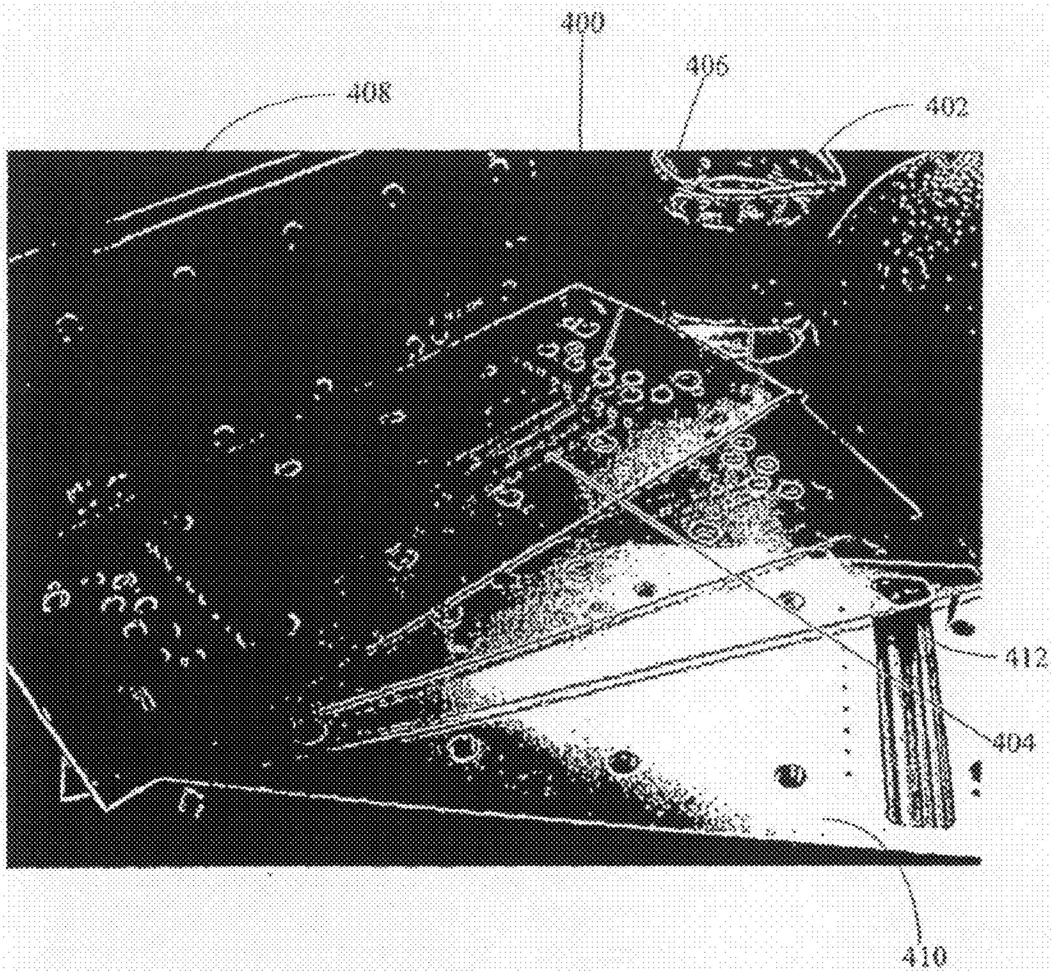


FIG. 4

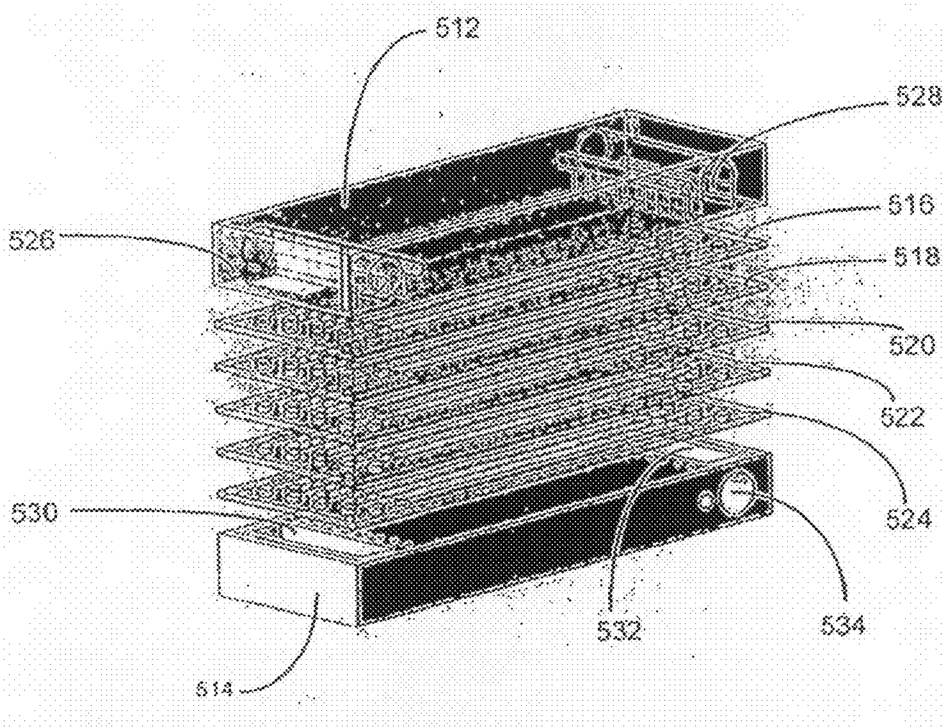


FIG. 5

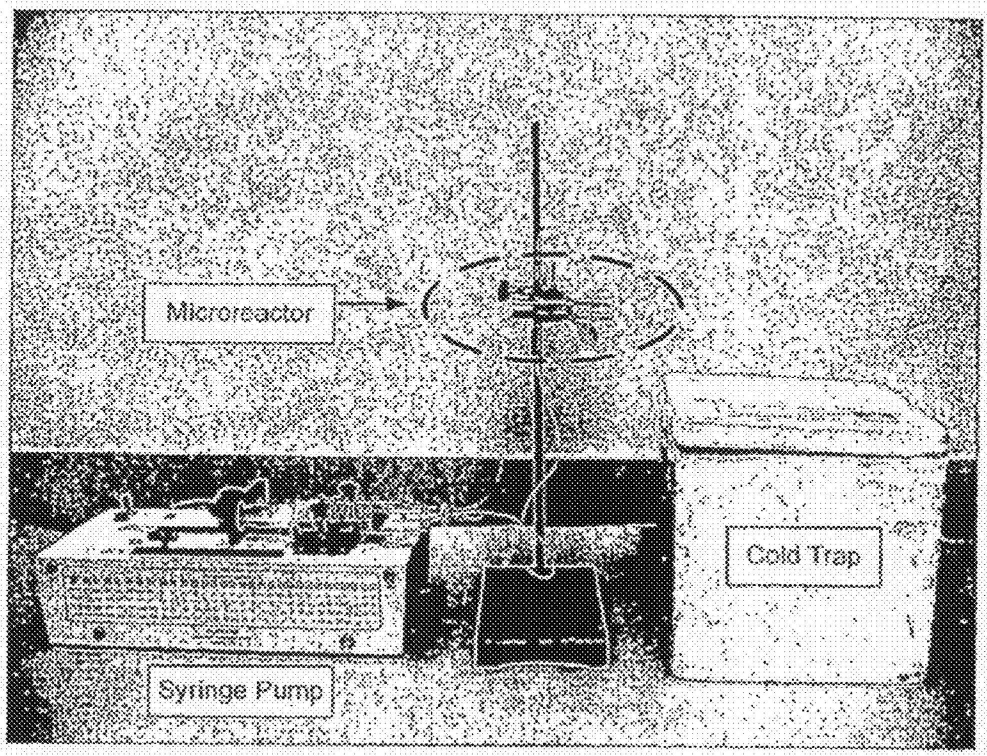


FIG. 6

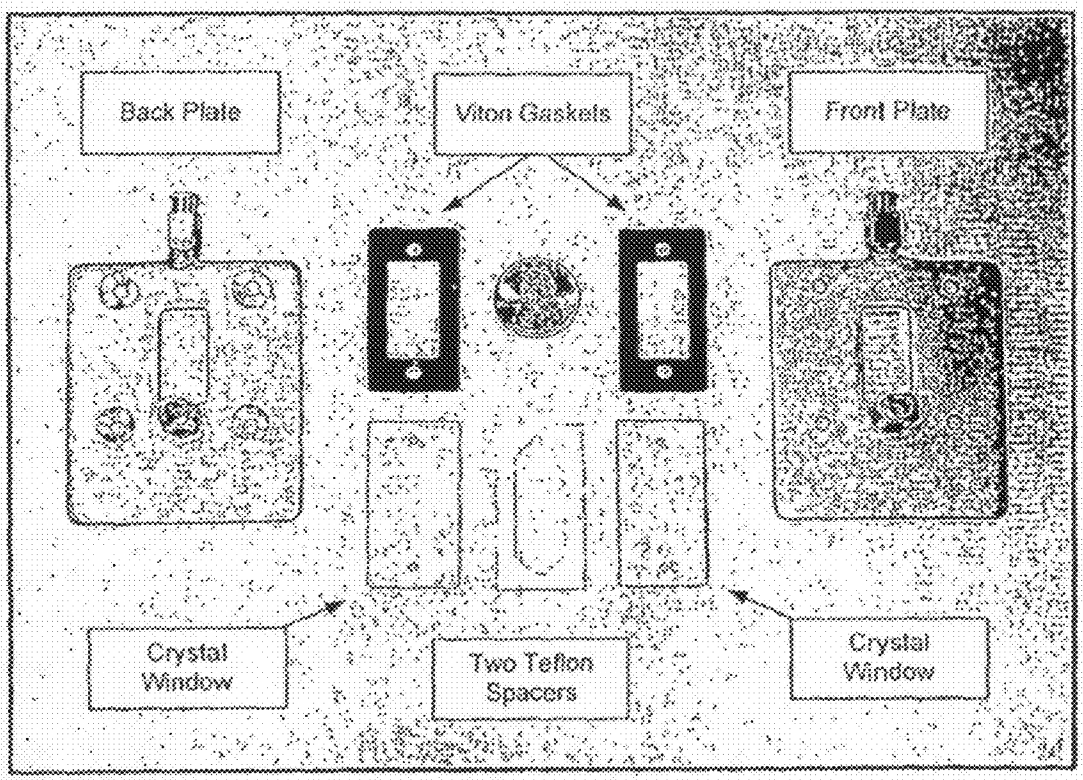

Back Plate
Viton Gaskets
Front Plate
Crystal Window
Two Teflon Spacers
Crystal Window

FIG. 7

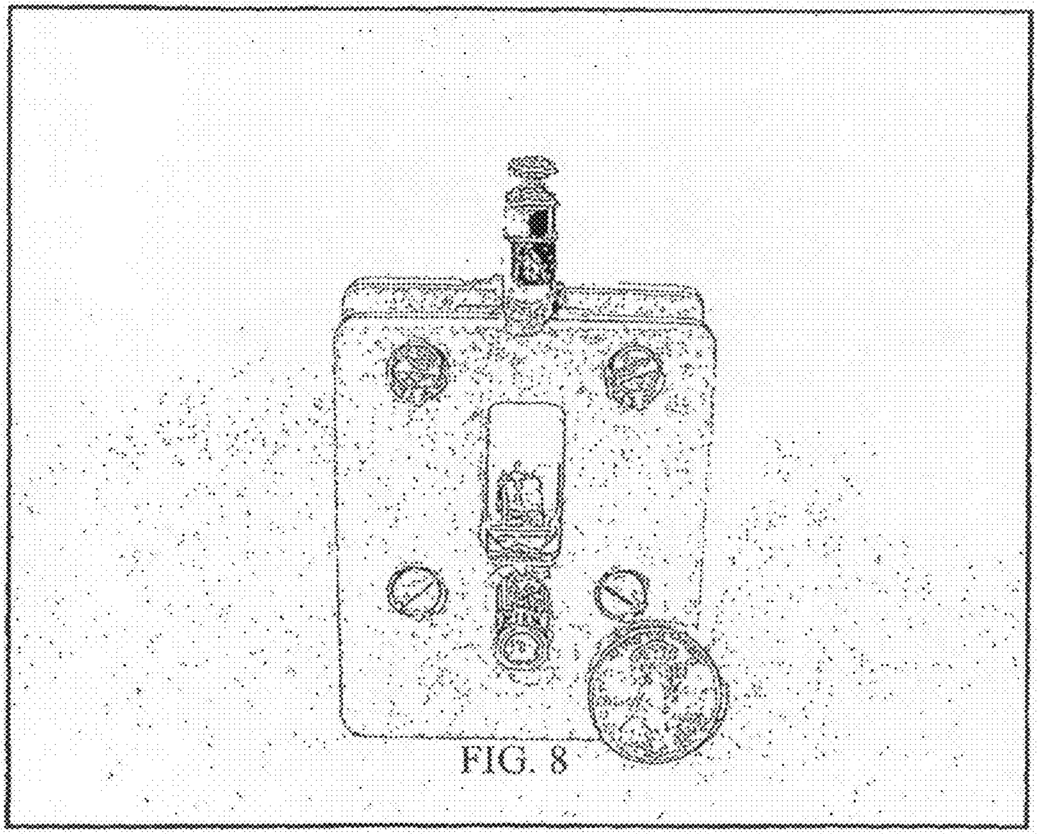


FIG. 8

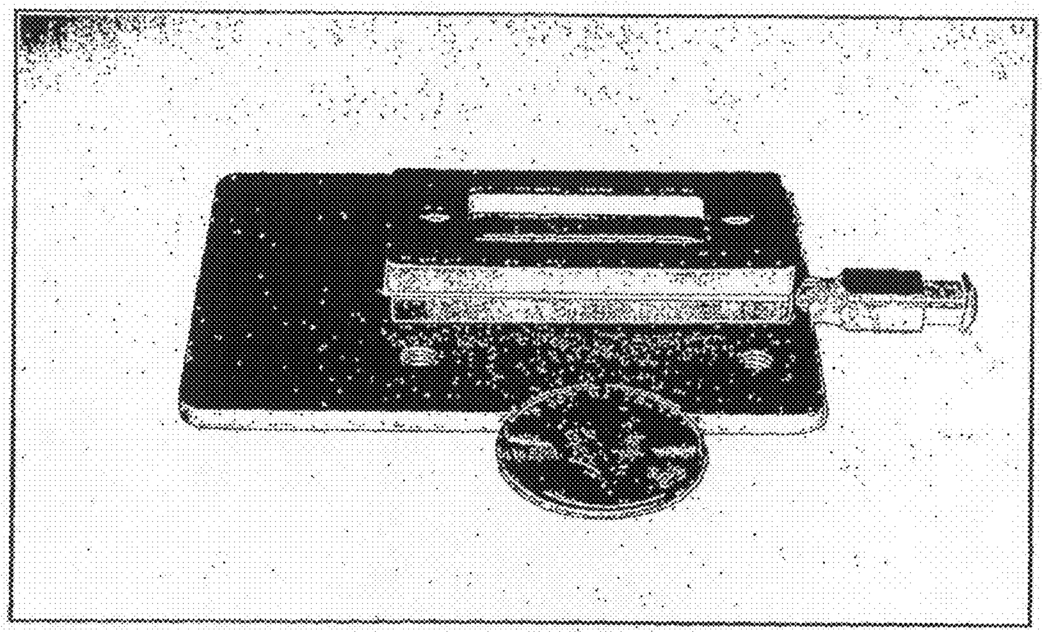


FIG. 9

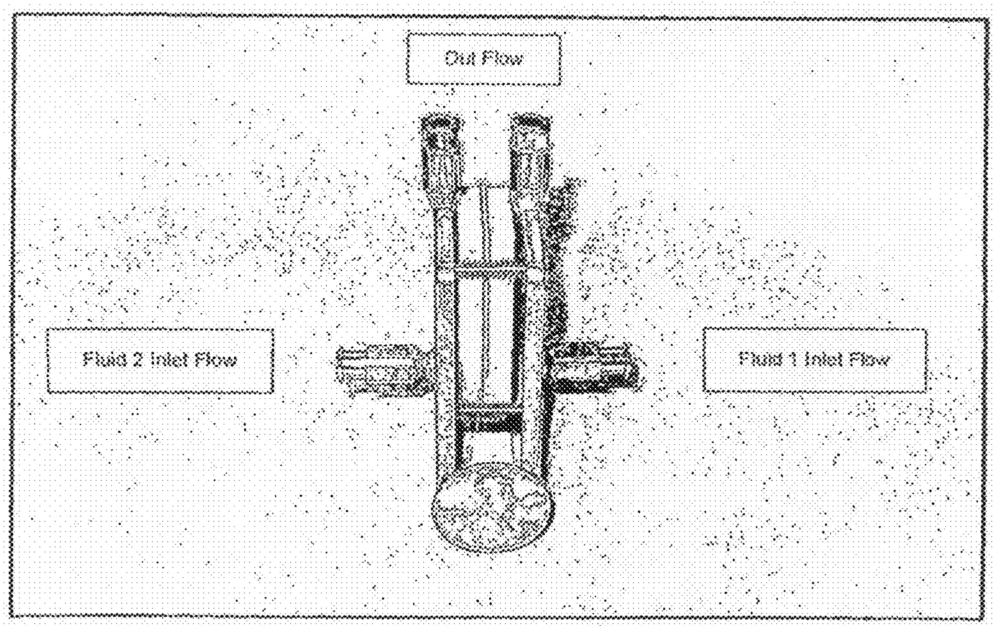


FIG. 10

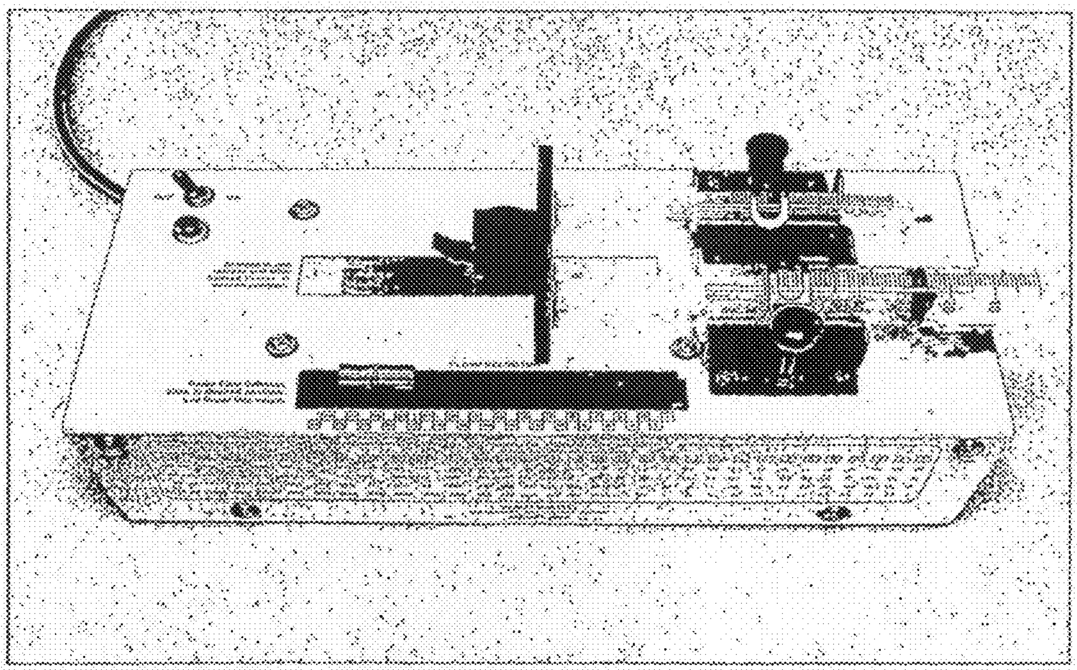


FIG. 11

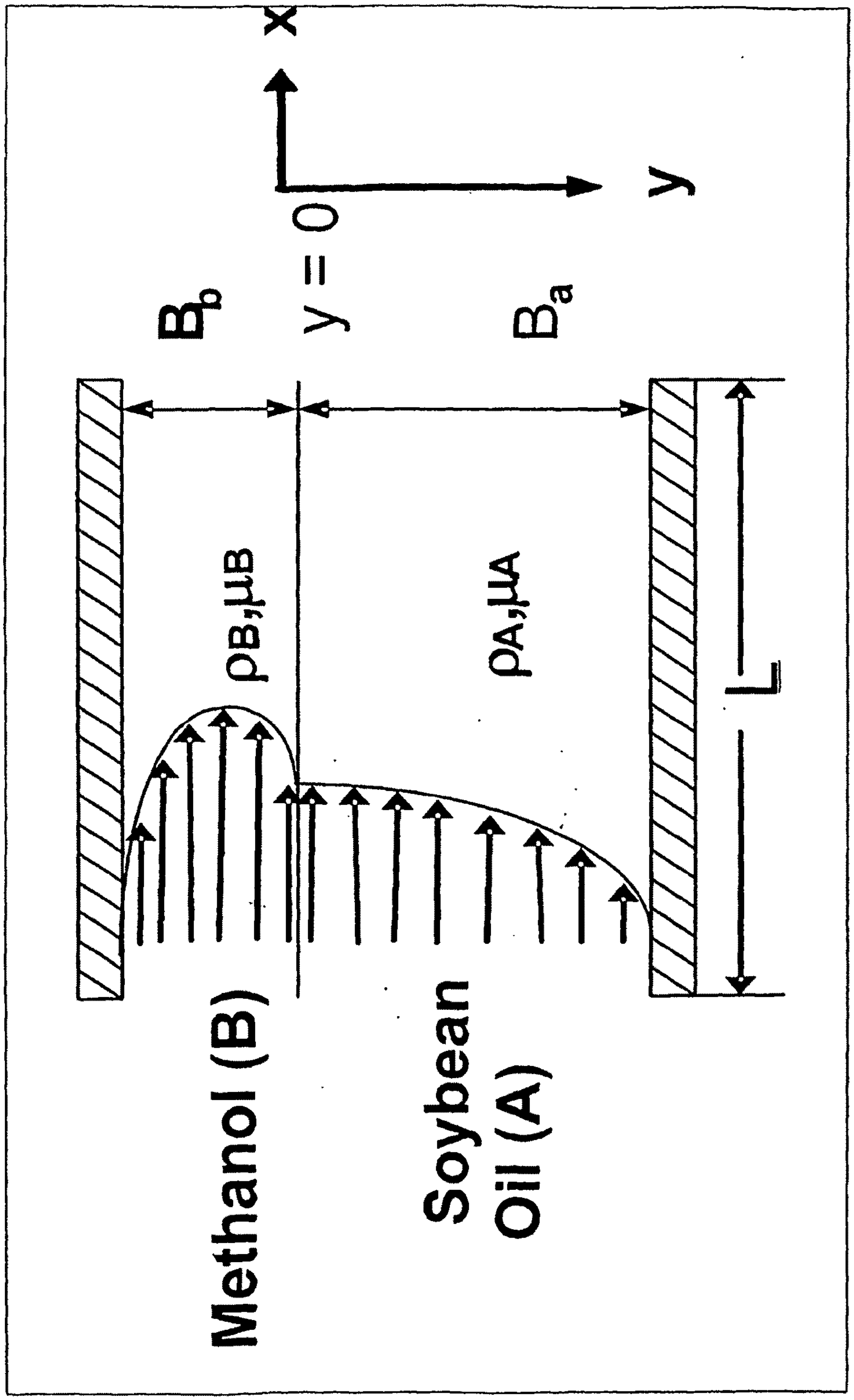


FIG. 12

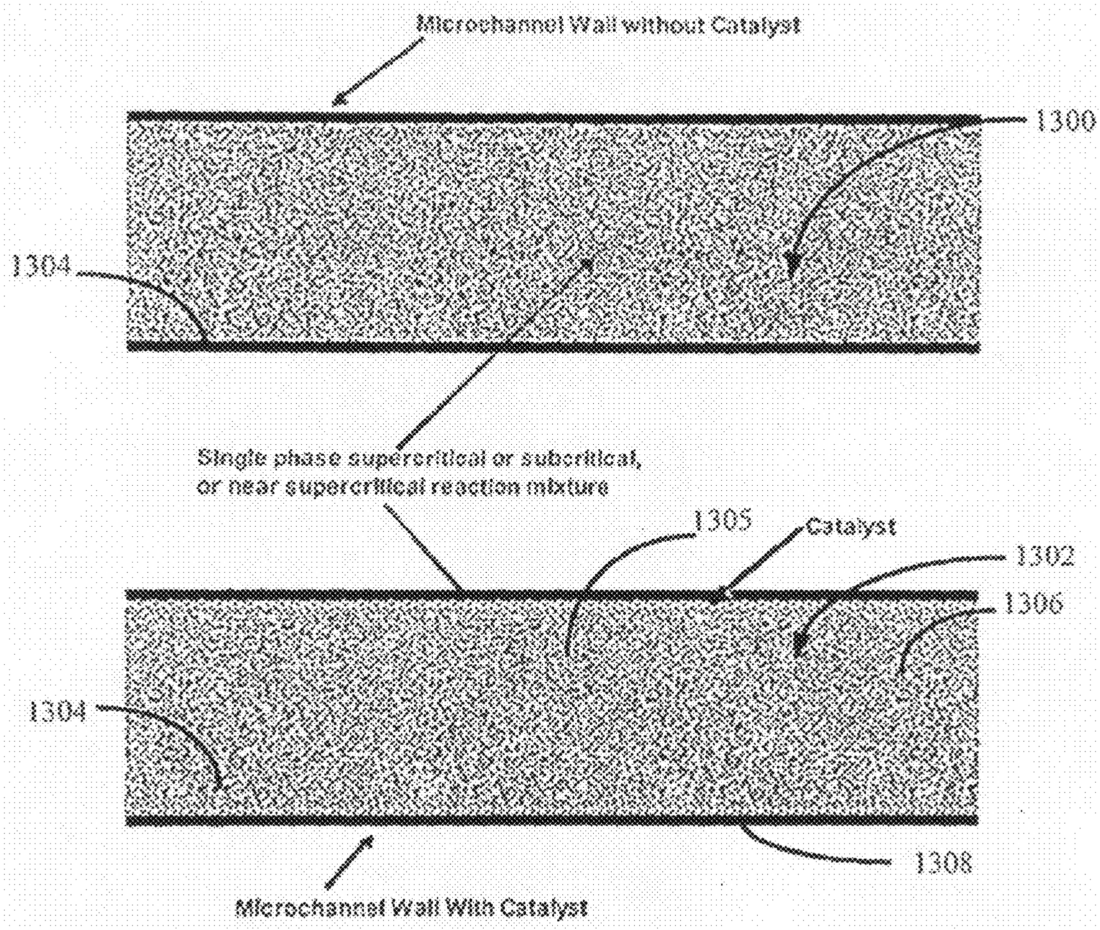

Microchannel Wall without Catalyst
1300
1304
Single phase supercritical or subcritical,
or near supercritical reaction mixture
1305
Catalyst
1302
1306
1304
1308
Microchannel Wall With Catalyst

FIG. 13

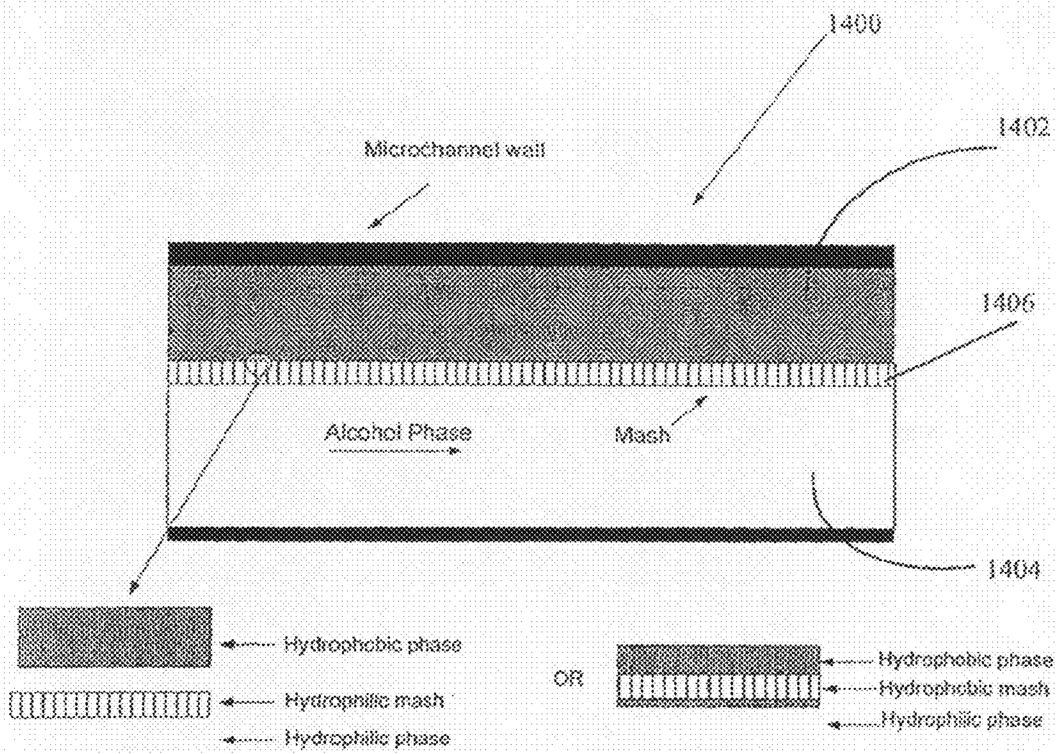

1400
Microchannel wall
1402
1406
Alcohol Phase
Mash
1404
Hydrophobic phase
Hydrophilic mash
Hydrophilic phase
OR
Hydrophobic phase
Hydrophobic mash
Hydrophilic phase

FIG. 14

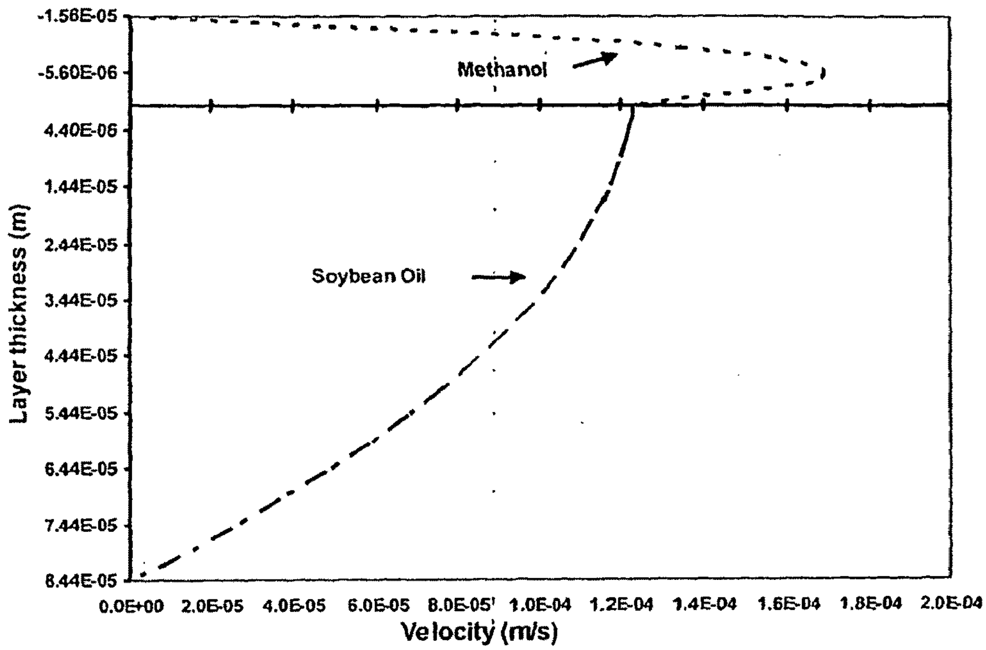

-1.56E-05
-5.60E-06
4.40E-06
1.44E-05
2.44E-05
3.44E-05
4.44E-05
5.44E-05
6.44E-05
7.44E-05
8.44E-05
Layer thickness (m)
Methanol
Soybean Oil
0.0E+00
2.0E-05
4.0E-05
6.0E-05
8.0E-05
1.0E-04
1.2E-04
1.4E-04
1.6E-04
1.8E-04
2.0E-04
Velocity (m/s)

FIG. 15

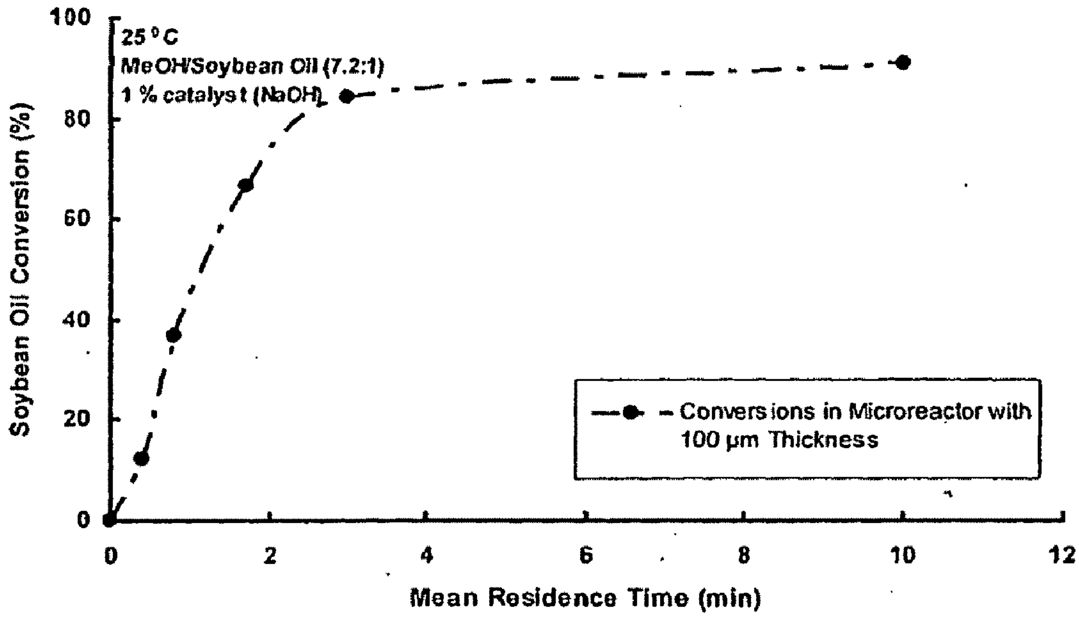

25 °C
MeOH/Soybean Oil (7.2:1)
1 % catalyst (NaOH)
Soybean Oil Conversion (%)
100
80
60
40
20
0
0
2
4
6
8
10
12
Mean Residence Time (min)
Conversions in Microreactor with 100 µm Thickness

FIG. 16

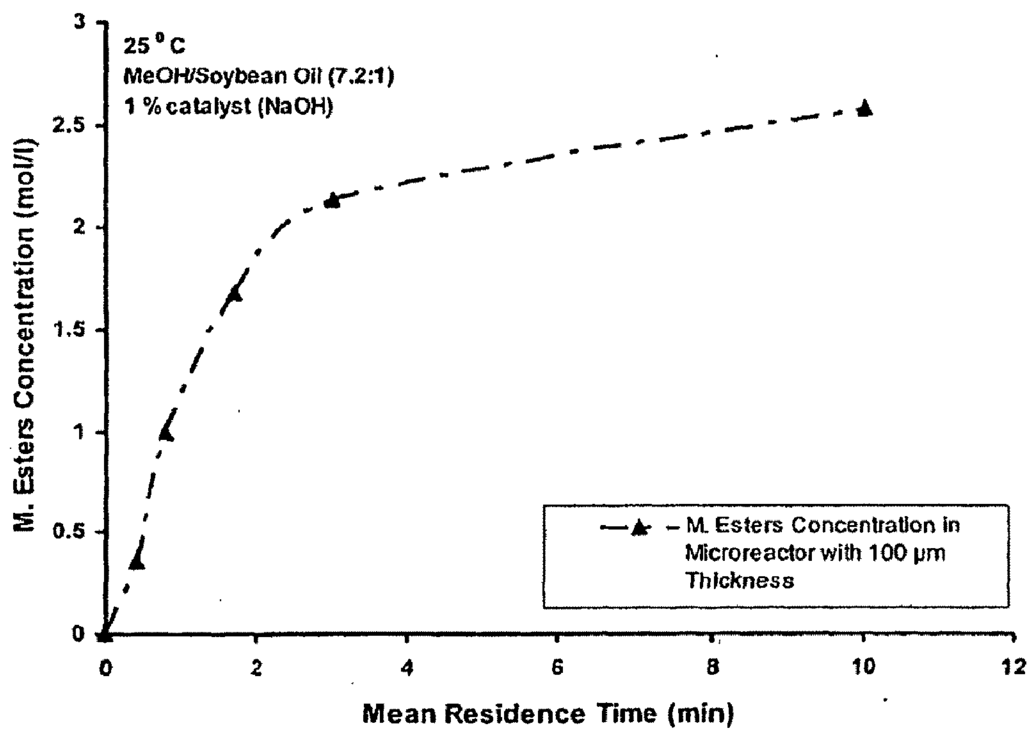

25 °C
MeOH/Soybean Oil (7.2:1)
1 % catalyst (NaOH)
M. Esters Concentration (mol/l)
Mean Residence Time (min)
M. Esters Concentration in Microreactor with 100 μm Thickness
0
0.5
1
1.5
2
2.5
3
0
2
4
6
8
10
12

FIG. 17

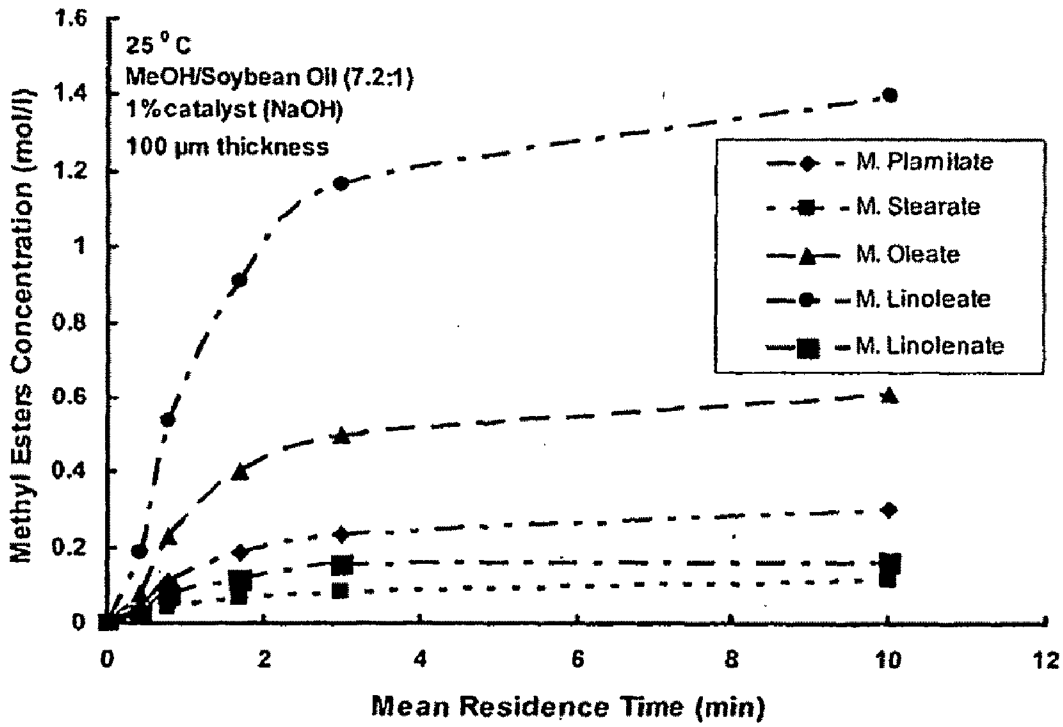

25 °C
MeOH/Soybean Oil (7.2:1)
1%catalyst (NaOH)
100 µm thickness
M. Plamitate
M. Stearate
M. Oleate
M. Linoleate
M. Linolenate
Methyl Esters Concentration (mol/l)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
Mean Residence Time (min)

FIG. 18

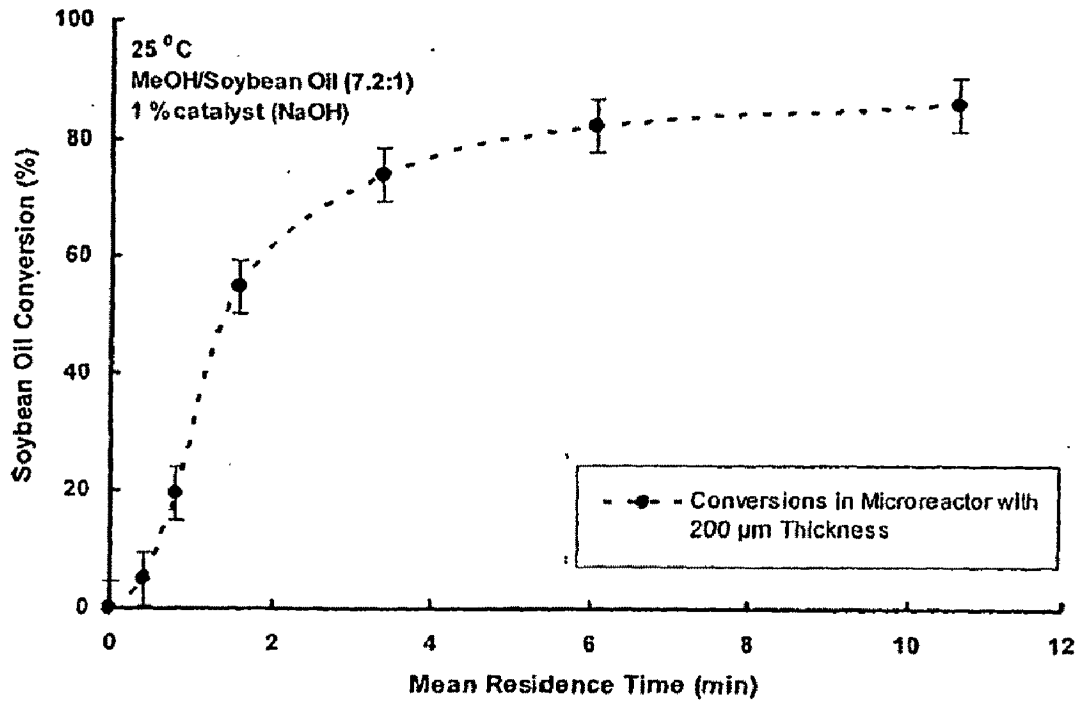
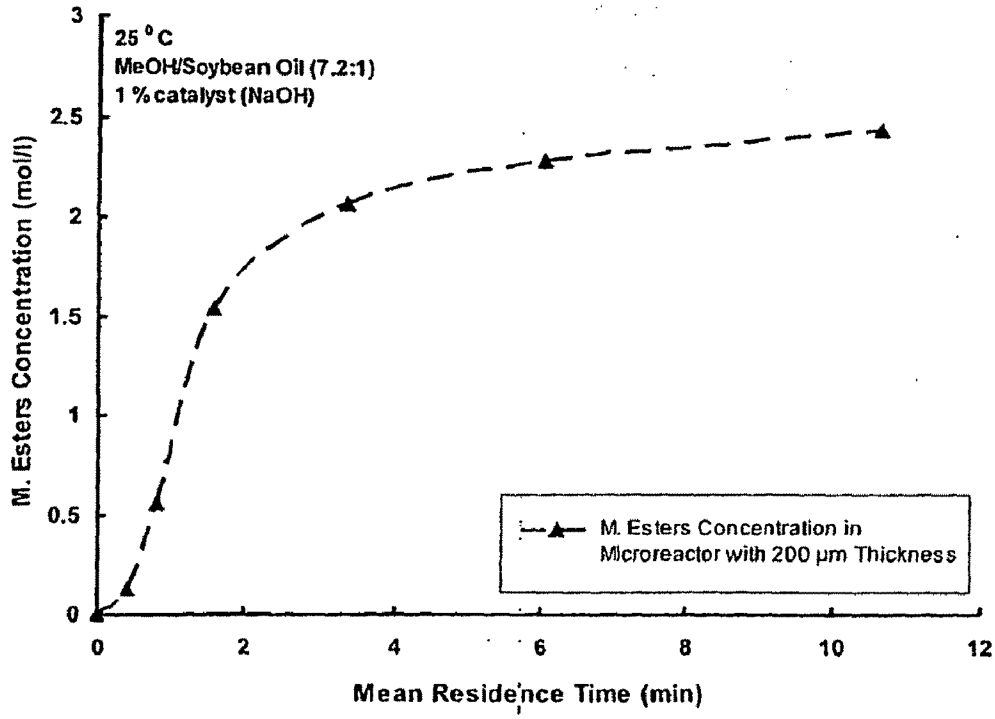

25 °C
MeOH/Soybean Oil (7.2:1)
1 % catalyst (NaOH)
Soybean Oil Conversion (%)
100
80
60
40
20
0
0
2
4
6
8
10
12
Mean Residence Time (min)
Conversions in Microreactor with 200 μm Thickness

FIG. 19



25 °C
MeOH/Soybean Oil (7.2:1)
1 % catalyst (NaOH)
M. Esters Concentration (mol/l)
0
0.5
1
1.5
2
2.5
3
M. Esters Concentration in Microreactor with 200 μm Thickness
0
2
4
6
8
10
12
Mean Residence Time (min)

FIG. 20

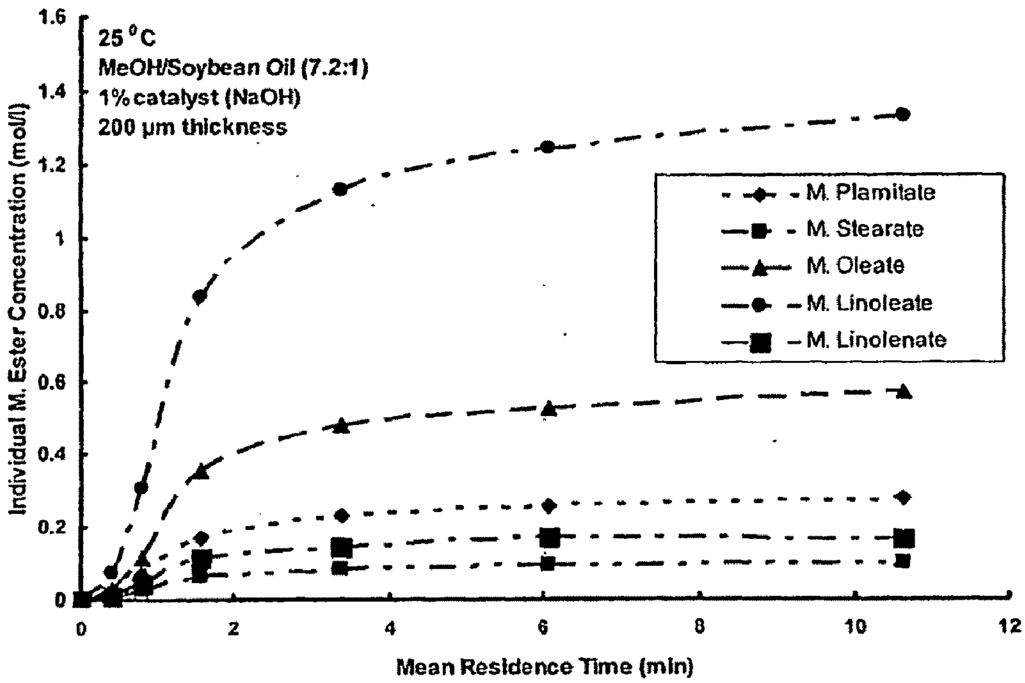
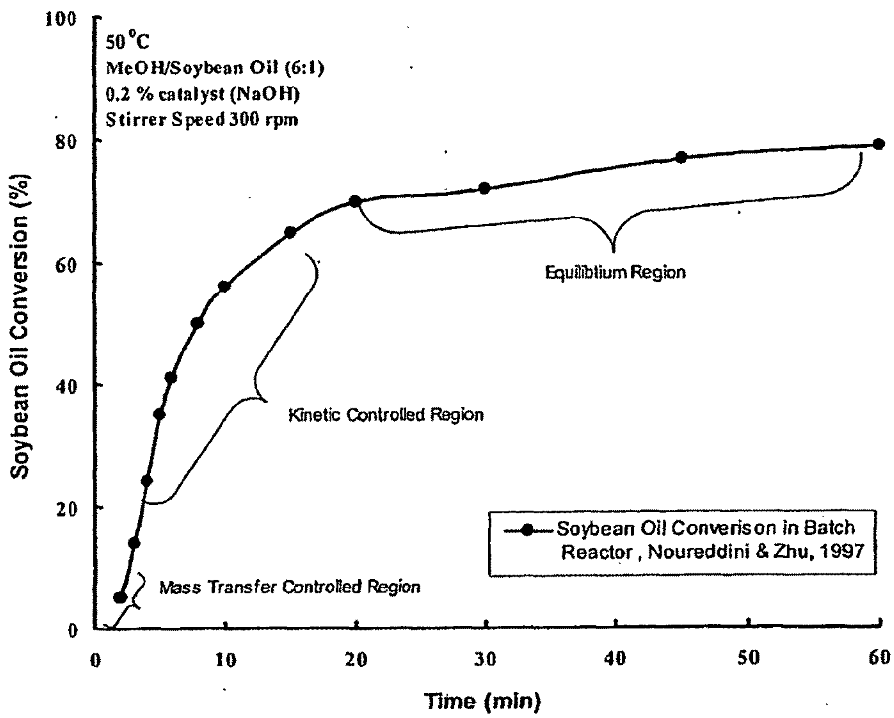

25 °C
MeOH/Soybean Oil (7.2:1)
1% catalyst (NaOH)
200 μm thickness
M. Plamitate
M. Stearate
M. Oleate
M. Linoleate
M. Linolenate
Individual M. Ester Concentration (mol/l)
Mean Residence Time (min)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
2
4
6
8
10
12

FIG. 21



100
80
60
40
20
0
50 °C
MeOH/Soybean Oil (6:1)
0.2 % catalyst (NaOH)
Stirrer Speed 300 rpm
Soybean Oil Conversion (%)
Equilibrium Region
Kinetic Controlled Region
Mass Transfer Controlled Region
Soybean Oil Converison in Batch Reactor, Noureddini & Zhu, 1997
0
10
20
30
40
50
60
Time (min)

FIG. 22

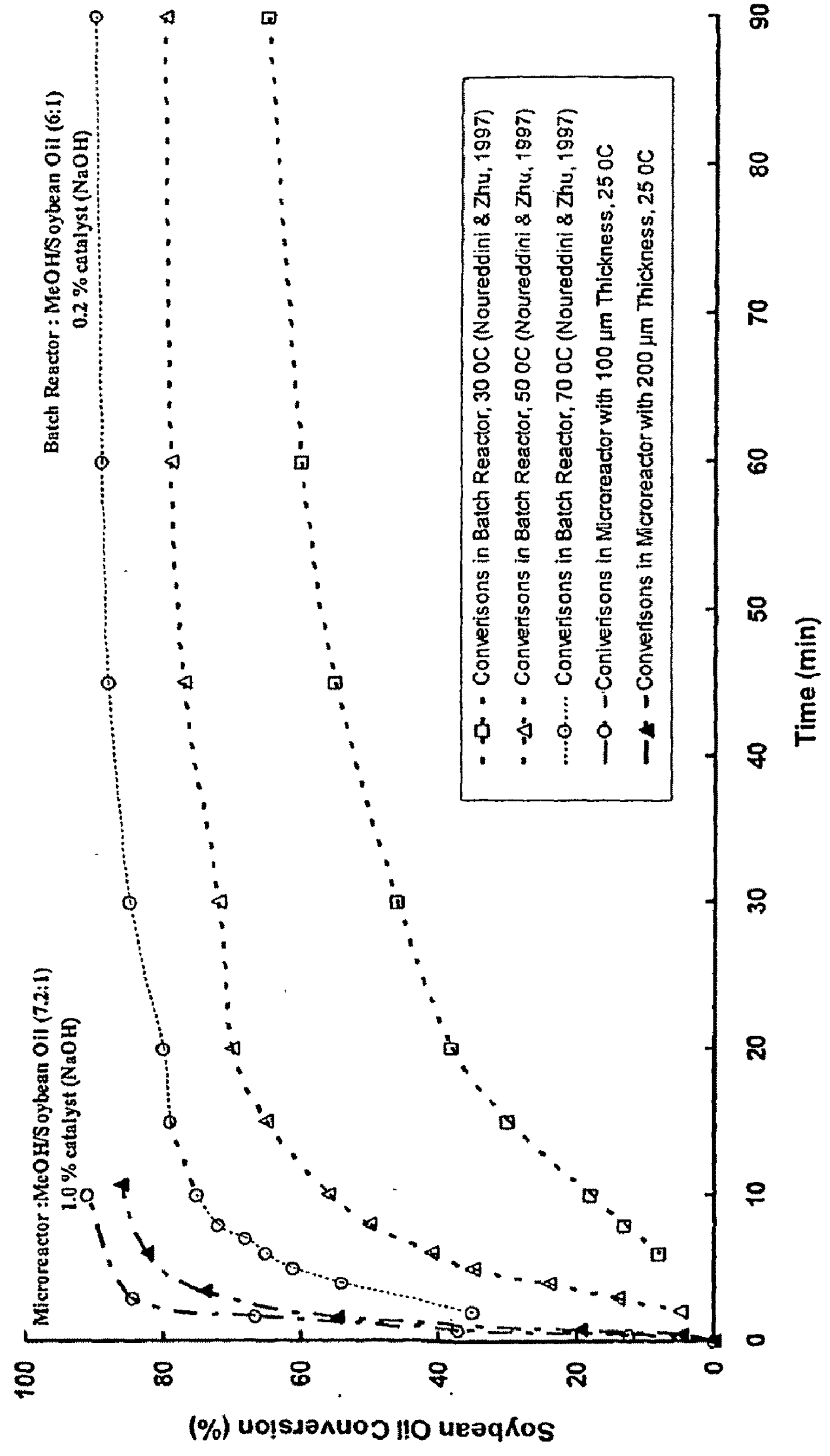

Microreactor :MeOH/Soybean Oil (7.2:1)
1.0 % catalyst (NaOH)
Batch Reactor : MeOH/Soybean Oil (6:1)
0.2 % catalyst (NaOH)
Converisons in Batch Reactor, 30 0C (Noureddini & Zhu, 1997)
Converisons in Batch Reactor, 50 0C (Noureddini & Zhu, 1997)
Converisons in Batch Reactor, 70 0C (Noureddini & Zhu, 1997)
Converisons in Microreactor with 100 μm Thickness, 25 0C
Converisons in Microreactor with 200 μm Thickness, 25 0C
Soybean Oil Conversion (%)
0
20
40
60
80
100
Time (min)
0
10
20
30
40
50
60
70
80
90

FIG. 23

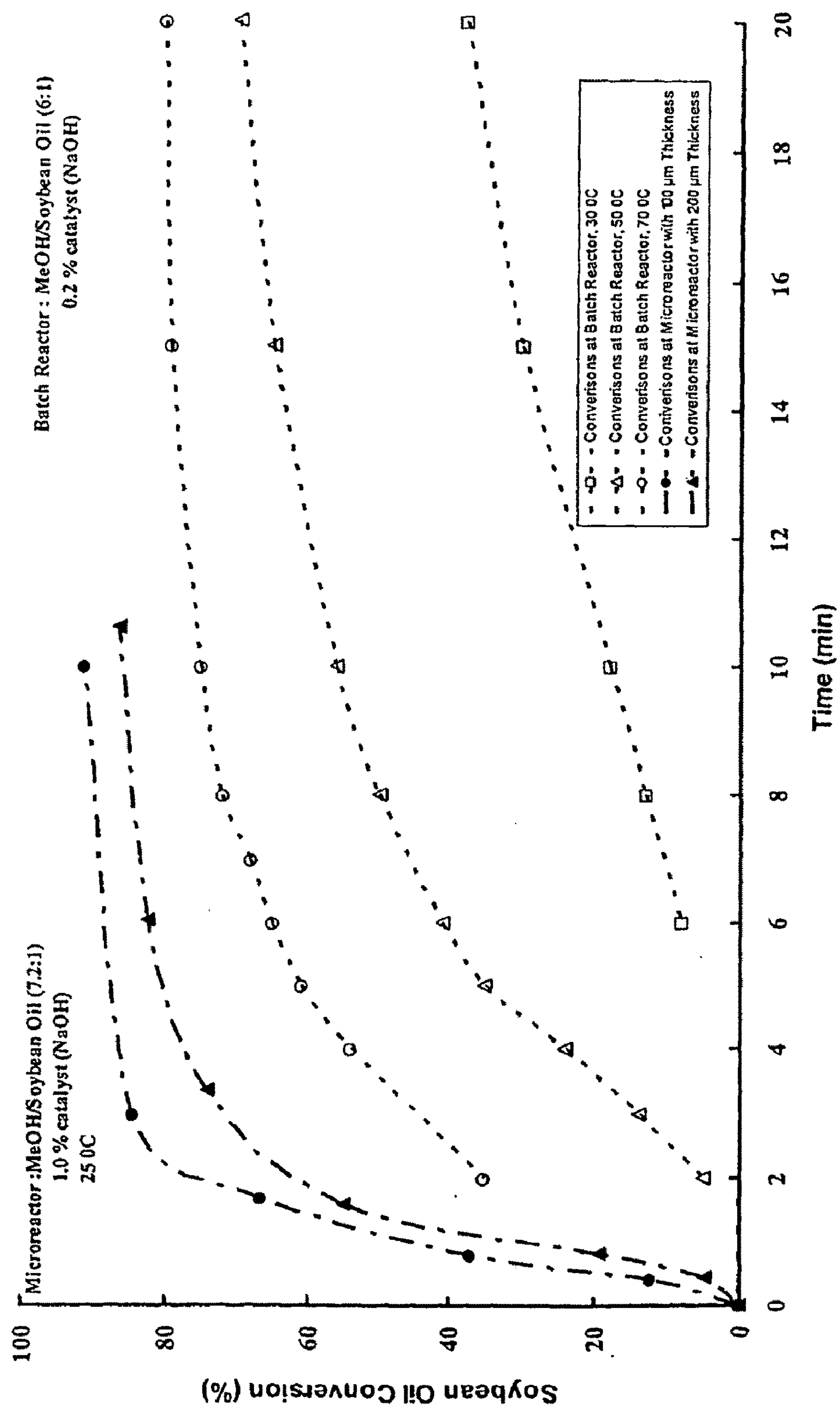

Batch Reactor : MeOH/Soybean Oil (6:1)
0.2 % catalyst (NaOH)
Microreactor :MeOH/Soybean Oil (7.2:1)
1.0 % catalyst (NaOH)
25 0C
Converisons at Batch Reactor, 30 0C
Conversions at Batch Reactor, 50 0C
Conversions at Batch Reactor, 70 0C
Coniversions at Microreactor with 100 μm Thickness
Conversions at Microreactor with 200 μm Thickness
Soybean Oil Conversion (%)
Time (min)
0
20
40
60
80
100
2
4
6
8
10
12
14
16
18
20

FIG. 24

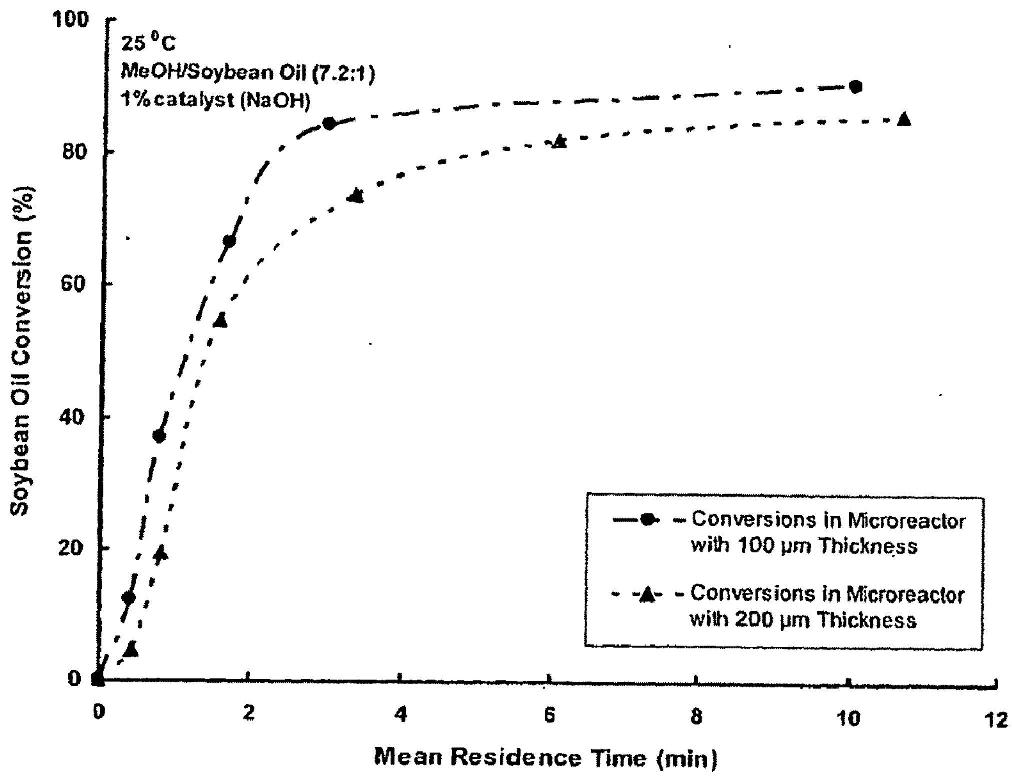

25 °C
MeOH/Soybean Oil (7.2:1)
1% catalyst (NaOH)
Soybean Oil Conversion (%)
Mean Residence Time (min)
0
20
40
60
80
100
0
2
4
6
8
10
12
Conversions in Microreactor with 100 μm Thickness
Conversions in Microreactor with 200 μm Thickness

FIG. 25

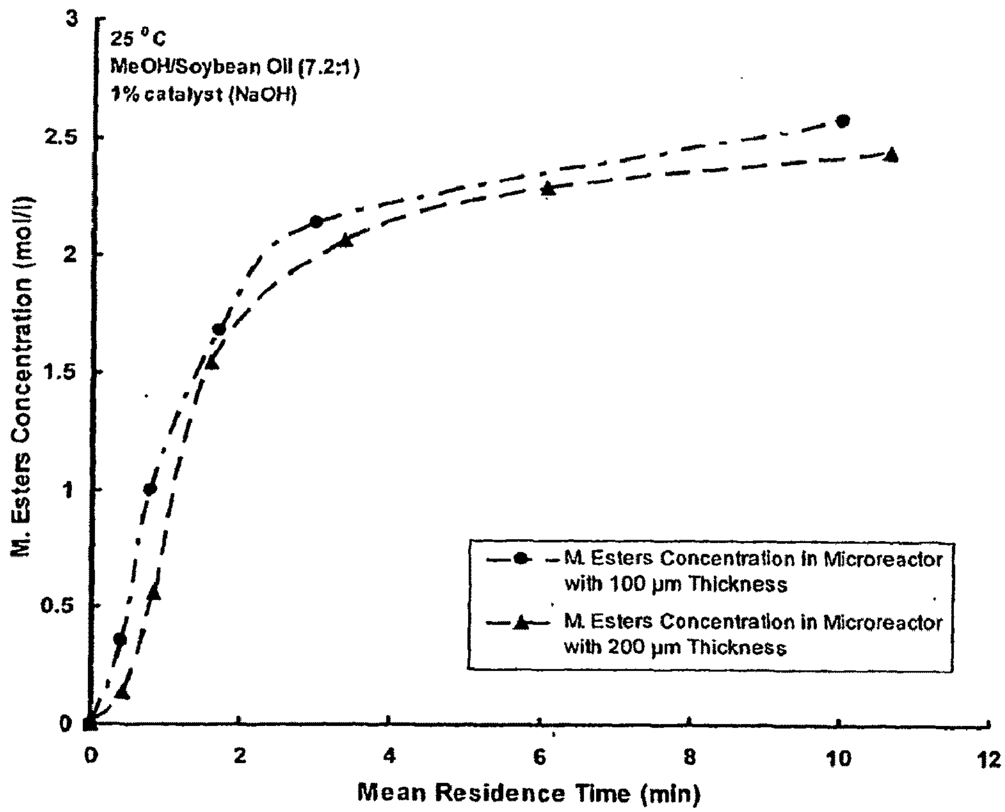

25 °C
MeOH/Soybean Oil (7.2:1)
1% catalyst (NaOH)
M. Esters Concentration (mol/l)
Mean Residence Time (min)
0
0.5
1
1.5
2
2.5
3
0
2
4
6
8
10
12
M. Esters Concentration in Microreactor with 100 μm Thickness
M. Esters Concentration in Microreactor with 200 μm Thickness

FIG. 26

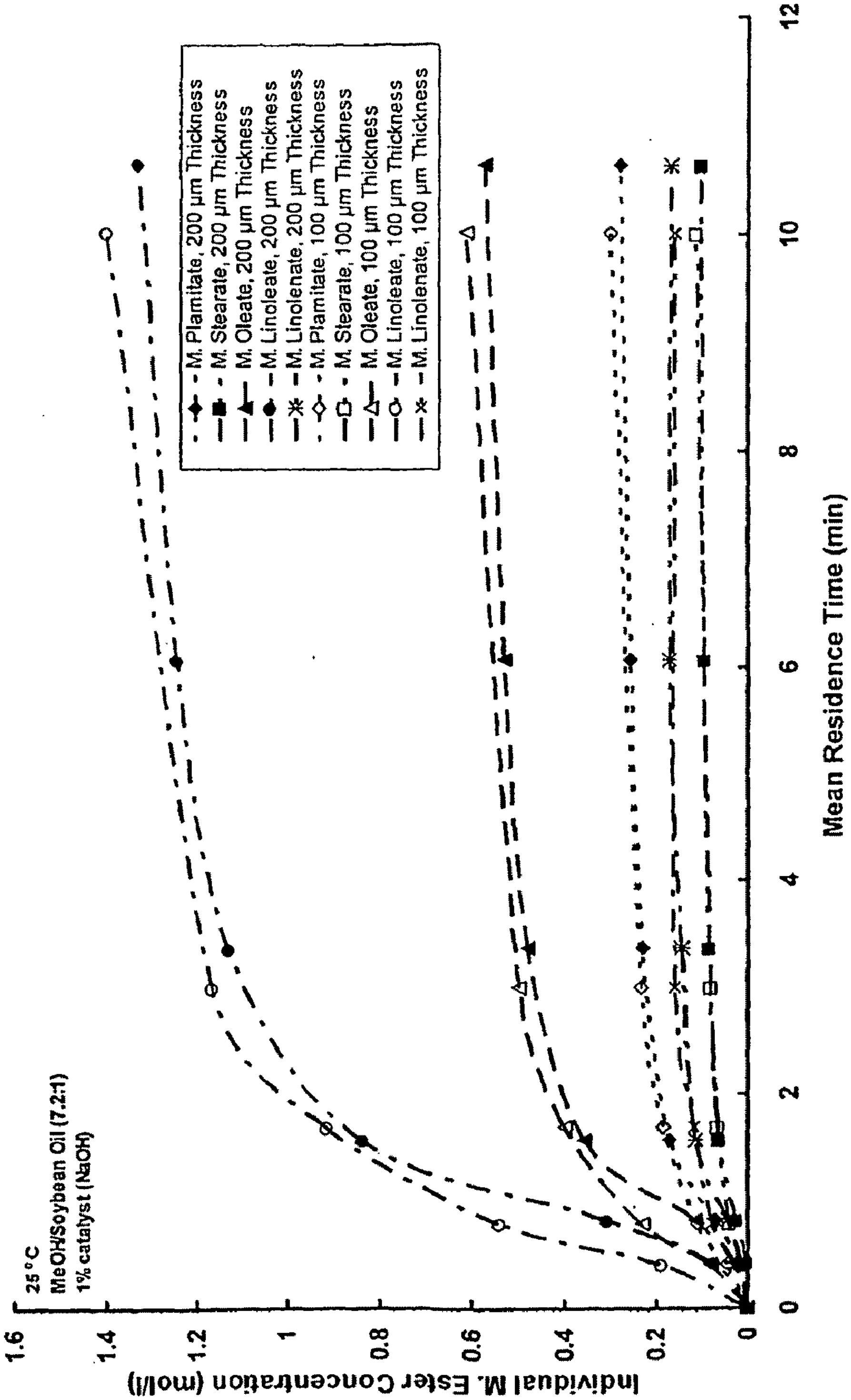

25 °C
MeOH/Soybean Oil (7.2:1)
1% catalyst (NaOH)
M. Plamitate, 200 µm Thickness
M. Stearate, 200 µm Thickness
M. Oleate, 200 µm Thickness
M. Linoleate, 200 µm Thickness
M. Linolenate, 200 µm Thickness
M. Plamitate, 100 µm Thickness
M. Stearate, 100 µm Thickness
M. Oleate, 100 µm Thickness
M. Linoleate, 100 µm Thickness
M. Linolenate, 100 µm Thickness
Individual M. Ester Concentration (mol/l)
Mean Residence Time (min)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
2
4
6
8
10
12

FIG. 27

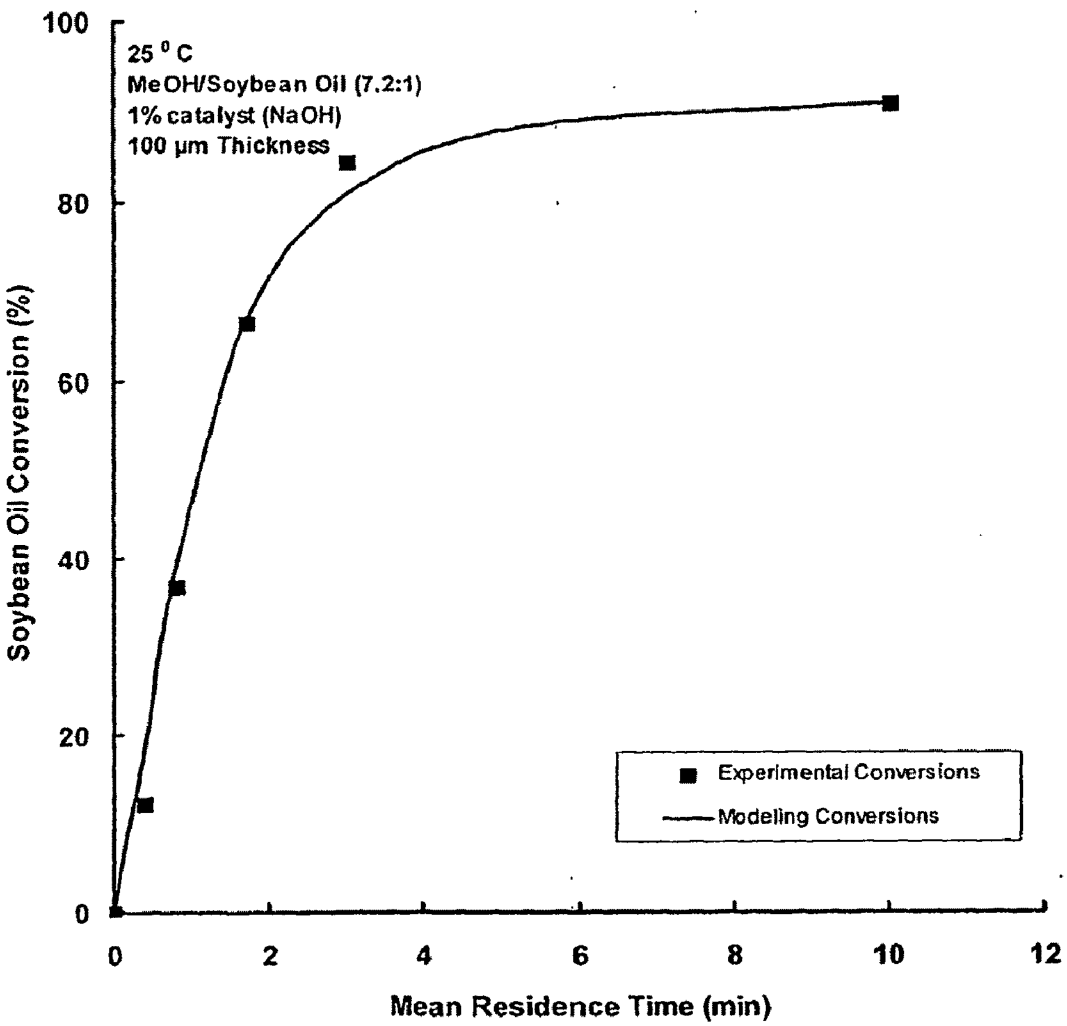
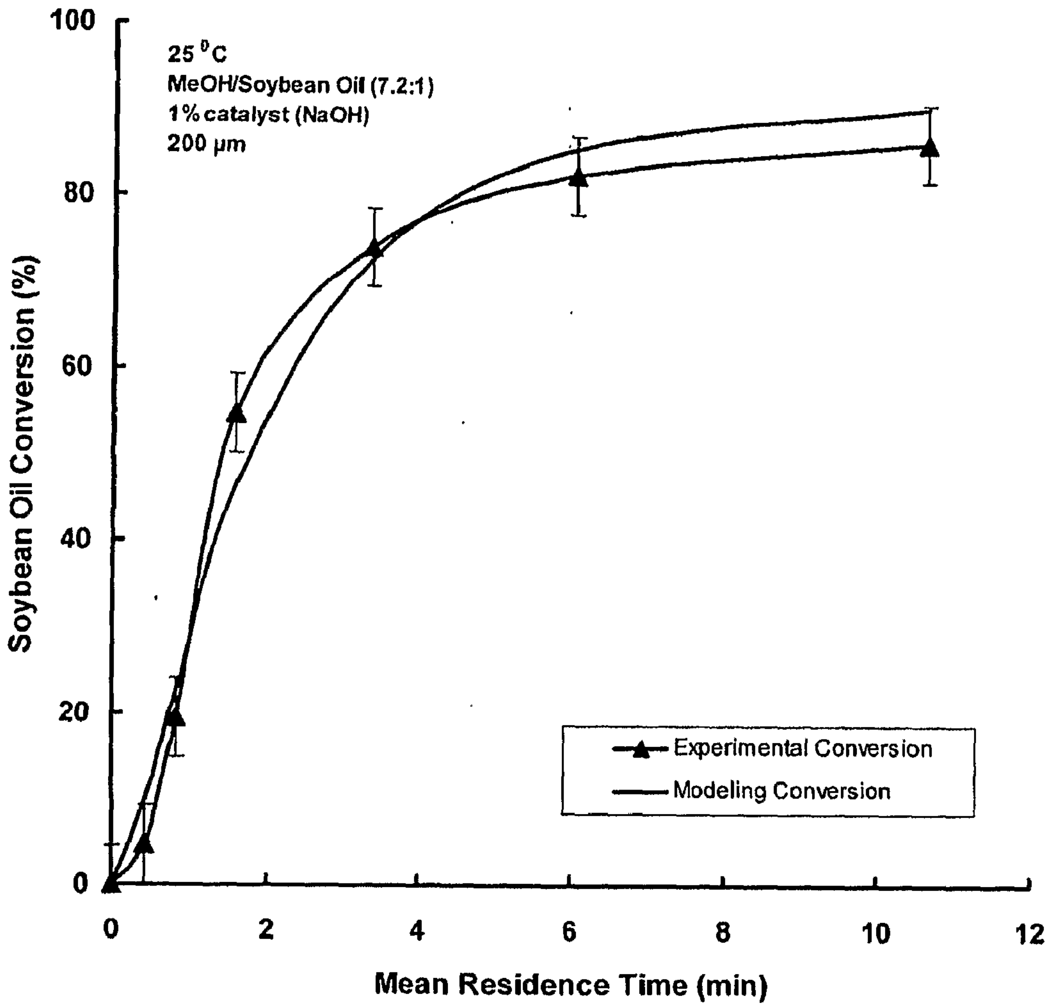

25 °C
MeOH/Soybean Oil (7.2:1)
1% catalyst (NaOH)
100 μm Thickness
Experimental Conversions
Modeling Conversions
Soybean Oil Conversion (%)
Mean Residence Time (min)
0
20
40
60
80
100
0
2
4
6
8
10
12

FIG. 28



25 °C
MeOH/Soybean Oil (7.2:1)
1% catalyst (NaOH)
200 μm
Soybean Oil Conversion (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
Mean Residence Time (min)
Experimental Conversion
Modeling Conversion

FIG. 29

MICROREACTOR PROCESS FOR MAKING BIODIESEL

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 60/810,569, filed on Jun. 1, 2006. The entire disclosure of the provisional application is considered to be part of the disclosure of the following application and is hereby incorporated by reference.

FIELD

[0002] The present disclosure concerns embodiments of a process for making biodiesel, particularly a process that utilizes at least one microreactor device.

BACKGROUND

A. Biodiesel Generally

[0003] Biodiesel is registered with the U.S. Environmental Protection Agency as a pure fuel or as a fuel additive, is a legal fuel for commerce, and meets clean diesel standards established by the California Air Resources. Its physical and chemical properties as they relate to operation of diesel engines are similar to petroleum-based diesel fuel as per the ASTM fuel tests shown in Table 1.

TABLE 1

ASTM Fuel Tests on # 2 Diesel Fuel and Methyl Soyate

Test Property	ASTM Method no.	# 2 Ref Diesel fuel	Methyl Soyate (Biodiesel)
Viscosity @ 40° C. (cSt)	D-445	2.39	4.08
Specific gravity @ 15.6° C.	—	0.847	0.884
Higher heating value (MJ/KG)	D-240	45.2	39.8
Cetane no.	D-613	45.8	46.2
Distillation 90% ° C.	D-86	296	342
Pour point (° C.)	D-97	−23	−1
Cloud point (° C.)	D-2500	−19	2
Flash point (° C.)	D-93	78	141
Sulfur (% mass)	D-129	0.25	0.01
Corrosion	D-130	1-a	1-a
Ash (% mass)	D-482	0.025	<0.01
Color (ASTM color code)	D-1500	L2.0	L2.0

Biodiesel can be used most effectively as a supplement for other energy liquid fuels such as diesel fuel. It is biodegradable and non-toxic, has low pollutant emission and therefore is environmentally beneficial.

[0004] Biodiesel has been considered as a fuel or fuel additive since the late 1970's. The oil embargo by the Organization of Petroleum Exporting Countries of 1973 resulted in significant biodiesel research by various universities, government agencies, and research organizations. The general conclusion is that biodiesel is a technically acceptable substitute, replacement, or blending stock for conventional petroleum diesel. It can be used at a 100-percent level (B100) or mixed with diesel in any proportion. The most common mixtures are B2 containing 2 percent biodiesel and B20 containing 20 percent biodiesel.

[0005] In 1999, only one million gallons of biodiesel were produced. In 2002, 25 million gallons of biodiesel were produced. Furthermore, biodiesel is the renewable fuel of choice in the European Union. Nearly 40 percent of the cars in Europe have diesel engines. Some cars are even fueled by B100, pure biodiesel. Germany uses the most biodiesel: 200 million gallons in 1991; 500 million gallons in 2001; and an estimated 750 million gallons in 2002. Most of Germany's biodiesel is made from rapeseed oil.

[0006] In 2000, biodiesel become the only alternative fuel to have successfully completed the EPA-required Tier I and Tier II healthy effects testing under the clean air act. These independent tests conclusively demonstrated biodiesel's significant reduction of virtually all regulated emissions and showed that biodiesel does not pose a threat to human health. Biodiesel contains no sulfur or aromatics, and using biodiesel in a conventional diesel engine substantially reduces unburned hydrocarbons, carbon monoxide and particulate matter. The EPA has surveyed biodiesel emissions studies and compared them with the testing results obtained in major studies of conventional fuels. The results are shown in Table 2.

TABLE 2

Average Biodiesel Emissions Compared to Conventional Diesel, According To EPA (Source, National Biodiesel Board)

Emission Type	B100	B20
Regulated Type		
Total Unburned Hydrocarbons	−67%	−20%
Carbon Monoxide	−48%	−12%
Particulate Matter	−47%	−12%
No_x	+10%	+2%
Non-Regulated		
Sulfates	−100%	−20%*
PAH (Polycyclic Aromatic Hydrocarbons)**	−80%	−13%
nPAH (nitrated PAH's)**	−90%	−50%***
Ozone potential of speciated HC	−50%	−10%

*Estimated from B100 result
**Average reduction across all compounds measured
***2-nitroflourine results were within test method variability

[0007] In 2000, the EPA released its new diesel regulations, which require over 90% reductions in both NO_x and particulate matter emissions from diesel engines beginning in the year 2007. After-treatment technologies (largely NO_x catalysts, particulate traps with catalysts, and exhaust gas recirculation) dramatically reduce diesel emissions only if the sulfur level in the fuel is significantly reduced. The EPA has mandated that the sulfur level in on-road diesel fuel be reduced from the current 500 ppm maximum to 15 ppm maximum (97% reduction) beginning in 2006. However, the increased removal of sulfur from diesel fuel has the unintended consequence of removing other components responsible for the fuel's lubricity. Decreased fuel lubricity results in increased engine wear, repair expense, and idle-time. Lubricity additives will have to be added to this new ultra-low sulfur diesel fuel to provide satisfactory protection for engines and high-pressure fuel injection equipment. Using biodiesel as a blending stock may help refineries meet future sulfur specifications. Biodiesel also has excellent lubricity characteristics and improves lubricity, even with a blend as low as 2% in conventional diesel fuel.

B. Biodiesel Production Methods

[0008] Biodiesel has been produced in different ways, including microemulsification, pyrolysis and transesterification. Microemulsification (forming a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally in the 1-150 nm range) reduces the high viscosity of vegetable oils by mixing them with solvents, such as methanol, ethanol and ionic or nonionic amphiphiles.

Microemulsions form spontaneously from two normally immiscible liquids. Short term performances of both ionic and nonionic microemulsions of aqueous ethanol in soybean oil were found to be similar to # 2 diesel fuel, in spite of the lower cetane number and energy content. In longer term testing (200 hours), no significant deteriorations in performance were observed.

[0009] Pyrolysis converts one substance into another using heat, or heat and a catalyst, typically in the absence of air or oxygen. SiO_2 and Al_2O_3 are typical pyrolysis catalysts. Animal fats can be pyrolyzed to produce many smaller chain compounds, and fat pyrolysis has been investigated for over a hundred years, especially in regions that lack petroleum deposits. Thermal decomposition of triglycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small amounts of gaseous products. Pyrolyzed oils are unacceptable in terms of ash content, carbon residues, and pour point. Additionally, oxygen removal during thermal processing eliminates any environmental benefits of using an oxygenated fuel.

[0010] Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The physical properties of chemicals related to the transesterification reaction are summarized in Table 3.

TABLE 3

Physical Properties of Chemicals Related to Transesterification

Name	Sp. gr., g/milliliter (° C.)	Melting point (° C.)	Boiling point (° C.)	Solubility (>10%)
Methyl Myristate	0.875 (75)	18.8	—	—
Methyl Palmitate	0.825 (75)	30.6	196.0	Acids, benzene, EtOH, Et_2O
Methyl Stearate	0.850	38.0	215.0	Et_2O, chloroform
Methyl Oleate	0.875	−19.8	190.0	Et OH, Et_2O
Methanol	0.792	−97.0	64.7	H_2O, ether, EtOH
Ethanol	0.789	−112.0	78.4	H_2O, ether
Glycerol	1.26	17.9	290.0	H_2O, EtOH

[0011] Biodiesel also has been produced using supercritical methanol [350° C. and 45 MPa] to produce methyl esters (biodiesel) by transesterification without using any catalyst. A study of rapeseed oil transesterification in supercritical methanol found that transesterification proceeds very effectively and produces the same methyl esters as those obtained in the conventional method using an alkali catalyst. Furthermore, the methyl ester yield in the supercritical methanol reaction is higher because the free fatty acids contained in crude oils and fat also are efficiently converted to methyl esters. According to kinetic analyses of the reactions in supercritical methanol, a reaction temperature of 350° C. and a methanol-to-rapeseed oil molar ratio of 42:1 produced the best reaction conditions. Increasing the reaction temperature increased ester conversion, but thermal degradation of hydrocarbons occurred at a temperature above 400° C.

SUMMARY

[0012] Embodiments of a method for producing biodiesel are disclosed. One embodiment of the method comprise providing a microreactor, and then using the microreactor to produce biodiesel. Reactants suitable for producing biodiesel are flowed to the microreactor. For example, the method may comprise flowing a first fluid comprising an alcohol and a second fluid comprising an oil to the microreactor. A person of ordinary skill in the art also will appreciate that other process steps, such as purification of products produced, can be accomplished "on chip" using a microseparator, for example, or "off chip," such as by using conventional purification techniques, such as precipitation, crystallization, distillation, chromatography, etc., and any and all combinations of such techniques.

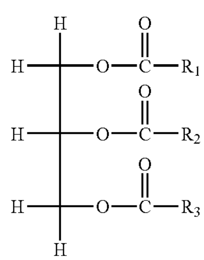
[0013] Alcohols useful for producing biodiesel typically, but not necessarily, are lower aliphatic alcohols, such as alcohols having 10 or fewer total carbon atoms and including alkyl, alkenyl or alkynyl alcohols. Specific examples of suitable alcohols include methanol, ethanol, propanol, butanol, amyl alcohol or combinations thereof. Suitable sources of oil products include soy, inedible tallow and grease, corn, edible tallow and lard, cotton, rapeseed, sunflower, canola, peanut, safflower, and combinations thereof.

[0014] Catalysts can be used to facilitate biodiesel production. Examples of suitable catalysts include metals, such as Pt, Pd, Ag, Ni, Zn, Fe etc., metal oxides, such as FeO, Fe_2O_3, Fe_3O_4, NiO, ZnO, SnO etc., metal hydroxides, metal carbonates, alcoholic metal oxides, alcoholic metal hydroxides, alcoholic metal carbonates, alkoxides, mineral acids and enzymes. Any and all combinations of such catalysts also can be used. Working embodiments typically used Group I metal hydroxides or alkoxides as catalysts, such as sodium or potassium hydroxides or alkoxides.

[0015] The conditions used to produce biodiesel can vary. For example, pressure and temperature both can be substantially ambient conditions, or can be elevated. For example, the temperature useful for producing biodiesel according to disclosed embodiments typically varies from about ambient (e.g. about 25° C.) to about the degradation temperature of either reactants or products, which typically is less than about 350° C., more typically less than about 250° C. Likewise pressure can be substantially ambient, or can be substantially greater than ambient. Particular working embodiments for producing biodiesel also can be conducted at supercritical conditions, typically supercritical conditions relative to any alcohol component used. These conditions will vary, as will be understood by a person of ordinary skill in the art, based on the reactants used. Relative reactant amounts also can be varied, but reactants typically were used in at least a 3:1 molar ratio of alcohol-to-oil, and more typically a larger excess of alcohol.

[0016] The method may result in forming two phases. Thus, the method can include separating two phases produced by the reaction, such as by using a distillation process, a centrifugation process, or combinations thereof.

[0017] Working embodiments for making biodiesel typically involved a transesterification process using an alcohol and a triglyceride having a formula

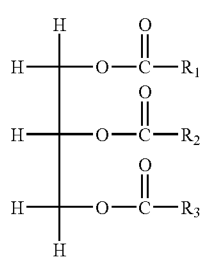


where R_1, R_2 and R_3 independently are fatty acids. Suitable fatty acids typically have carbon chain lengths ranging from at least as few as 10 carbon atoms to at least as many as 20 carbon atoms, and more typically chain lengths range from about 12 carbon atoms to about 18 carbon atoms. Examples of particular fatty acids include, without limitation, lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. These fatty acids can be saturated or unsaturated, and can include at least one site of unsaturation other than a carbon-carbon double bond.

[0018] An important feature of the present invention is using microreactors for the production of biodiesel. Various microreactor structures are suitable for making biodiesel according to the present invention, and the structures described herein are exemplary. For example, microreactors can be used that vary the oil and alcohol fluid layer thicknesses, such as thicknesses that range from about 10 μm to about 500 μm. Likewise, microreactors having microchannels with variable surface-to-volume ratios can be used, such as microchannels having surface-to-volume ratios that range from about 10,000 m^2/m^3 to about 50,000 m^2/m^3. Microreactors having a single microchannel might be used to make biodiesel, but increasing output may require using (1) devices having plural microchannels, (2) plural microreactors, or (3) both. Typical working embodiments of microreactors had plural laminae with at least one lamina defining at least one microchannel for receiving fluid. Microreactors useful for producing biodiesel also can include a manifold, or manifolds, for distributing fluid flow to individual microchannels. Commercial implementations of the disclosed method likely will use plural microreactors to provide suitable quantities of biodiesel.

[0019] Biodiesel can be blended with other materials. As a result, certain embodiments of the present invention include blending biodiesel produced by the method with petroleum-based products. For example, the biodiesel produced by the method can be blended with greater than zero weight percent petroleum product to less than 100 weight percent petroleum product.

[0020] A particular embodiment of the disclosed method for producing biodiesel comprises first providing a microreactor. A first fluid comprising a lower aliphatic alcohol is flowed to the microreactor, as is a second fluid comprising a triglyceride having a formula



where R_1, R_2 and R_3 independently are fatty acids. A reaction catalyst is then provided, such as an alcoholic solution comprising a reaction catalyst selected from the group consisting of metal oxides, metal hydroxides, metal carbonates, alcoholic metal oxides, alcoholic metal hydroxides, alcoholic metal carbonates, alkoxides, mineral acids, enzymes, or combinations thereof. The microreactor is then used to produce biodiesel, which is blended with petroleum-based products in an amount greater than zero weight percent petroleum product to less than 100 weight percent petroleum product.

[0021] A person of ordinary skill in the art will appreciate that reactants and reaction conditions suitable for making biodiesel are variable. For example, working embodiments include using soybean oil, methanol or ethanol, and the method further comprises using a metal hydroxide catalyst, such as a metal hydroxide catalyst used in an amount of about 1.0 weight % of the soybean oil used for the transesterification reaction. Oil and alcohol fluids have been pumped to the microreactor using a pump volume flow rate ratio of oil: alcohol of about 3.4, which resulted in a molar ratio of oil-to-alcohol of about 1:7.2.

[0022] Oil conversion to biodiesel typically increases with increasing mean microreactor residence time. So, for working embodiments that used a microchannel having a 100 μm thickness, soybean oil, and a transesterification processing temperature of about 25° C., conversion of soybean oil to biodiesel ranged from about 12% at about 0.4 MRT to about 91% at 10 minutes MRT, and total methyl ester concentration ranged from about 0.3 mole/l at about 0.4 minute MRT to about 2.5 moles/l at about 10 minutes MRT. For working embodiments using a microchannel having a 200 μm thickness, soybean oil, and a transesterification processing temperature of about 25° C., conversion of soybean oil to biodiesel ranged from about 4% at about an 0.4 MRT to about 86% at about 10 minutes MRT, and total methyl ester concentration ranged from about 0.1 mole/l at about 0.43 minute MRT to about 2.4 moles/l at about 10.6 minutes MRT.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. **1** is a schematic diagram of one embodiment of a microreactor used to produce biodiesel according to the present invention.

[0024] FIG. **2** is an exploded schematic view of a microreactor used in working embodiments of a process for making biodiesel.

[0025] FIG. **3** is a digital image showing a plate patterned to define microchannels and apertures for receiving fluid flow.

[0026] FIG. **4** is a digital image showing plural plates of FIG. **3** positioned adjacent end plates used to construct a working embodiment of the present invention.

[0027] FIG. **5** is a schematic perspective drawing illustrating positioning plural plates defining microchannels to collectively define one embodiment of a microreactor for producing biodiesel.

[0028] FIG. **6** is digital image of a working embodiment of a system comprising a microreactor useful for making biodiesel according to the present invention.

[0029] FIG. **7** is a digital image of one embodiment of a disassembled microreactor useful for making biodiesel according to the present invention adjacent a penny for size comparison.

[0030] FIG. **8** is a digital image providing a front perspective view of one embodiment of a microreactor useful for making biodiesel according to the present invention adjacent a penny for size comparison.

[0031] FIG. **9** is a digital image providing a perspective view of one embodiment of an end plate, adjacent a penny for size comparison, used in one embodiment of a microreactor useful for making biodiesel according to the present invention.

[0032] FIG. **10** is a digital image providing a side perspective view of one embodiment of a microreactor useful for making biodiesel according to the present invention adjacent a penny for size comparison.

[0033] FIG. **11** is a digital image providing a top perspective view of dual syringe pump used with one embodiment of a microreactor useful for making biodiesel according to the present invention.

[0034] FIG. **12** is a schematic diagram illustrating methanol and soybean oil flow through a microchannel.

[0035] FIG. **13** is a cross sectional schematic drawing illustrating a microchannel without a catalyst and a microchannel having catalyst disposed therein.

[0036] FIG. **14** is a schematic cross sectional drawing illustrating a microchannel having two fluids flowing therethrough.

[0037] FIG. **15** is a graph of fluid layer thickness (m) versus velocity (m/s) comparing fluid flow velocities of methanol and soybean oil in a microchannel.

[0038] FIG. **16** is a graph of soybean oil conversion (%) versus mean microchannel residence time (minutes) using a microreactor having a 100 μm microchannel thickness.

[0039] FIG. **17** is a graph of ester concentration (mol/l) versus mean microchannel residence time (minutes) using a microreactor having a 100 μm microchannel thickness.

[0040] FIG. **18** is a graph of methyl ester concentration (mole/l) versus mean microchannel residence time (minutes) using a microreactor having a 100 μm microchannel thickness.

[0041] FIG. **19** is a graph of soybean oil conversion (%) versus mean microchannel residence time (minutes) using a microreactor having a 200 μm microchannel thickness.

[0042] FIG. **20** is a graph of methyl ester concentration (mole/l) versus mean microchannel residence time (minutes) using a microreactor having a 200 μm microchannel thickness.

[0043] FIG. **21** is a graph of methyl ester concentration (mol/l) versus mean microchannel residence time (minutes) using a microreactor having a 200 μm microchannel thickness.

[0044] FIG. **22** is a graph of soybean oil conversion (%) versus time (minutes) providing a survey of the work of others, as reported by Noureddini & Zhu, (1997), showing that the conversion of soybean oil to methyl esters in a batch reactor is a reaction process with changing mechanisms reflected in a sigmoidal conversion curve for soybean oil conversion.

[0045] FIG. **23** is a graph of soybean oil conversion (%) versus time (minutes) comparing batch reactors to microreactors.

[0046] FIG. **24** is a graph of soybean oil conversion (%) versus time (minutes) comparing batch reactors to microreactors.

[0047] FIG. **25** is a graph of soybean oil conversion (%) versus time (minutes) comparing microreactors having 100 μm and 200 μm microchannels.

[0048] FIG. **26** is a graph of methyl ester concentration (mol/l) versus time (minutes) comparing microreactors having 100 μm and 200 μm microchannels.

[0049] FIG. **27** is a graph of methyl ester concentration (mol/l) versus mean residence time (minutes) comparing microreactors having 100 μm and 200 μm microchannels.

[0050] FIG. **28** is a graph of soybean oil conversion (%) versus mean residence time (minutes) comparing production results to modeling results for a 100 μm microchannel.

[0051] FIG. **29** is a graph of soybean oil conversion (%) versus mean residence time (minutes) comparing production results to modeling results for a 200 μm microchannel.

DETAILED DESCRIPTION

I. Biodiesel, Fats, Oils and Alcohols

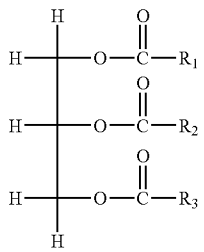
[0052] Biodiesel is defined as a mixture of mono alkyl esters of long chain fatty acids derived from renewable lipid sources. Fats and oils, also referred to as triglycerides, are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom comprising one mole of glycerol and three moles of fatty acids. Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats may contain small amounts of free fatty acids and water. Vegetable oils generally are liquids at room temperature while fats typically are solids at room temperature because they contain a larger percentage of saturated fatty acids. Table 4 summarizes the fatty acid compositions found in common sources of vegetable oils and fat.

TABLE 4

Typical Fatty Acid Composition of Common Oil Sources

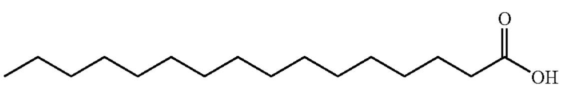
Vegetable Oil & Fat	Fatty acid composition, % by weight Lauric 12:00	Myristic 14:00	Palimitic 16:00	Stearic 18:00	Oleic 18:01	Linoleic 18:02	Linolenic 18:03
Soybean	0.1	0.1	10.2	3.7	22.8	53.7	8.6
Cottonseed	0.1	0.7	20.1	2.6	19.2	55.2	0.6
Palm	0.1	1.0	42.8	4.5	40.5	10.1	0.2
Lard	0.1	1.4	23.6	14.2	44.2	10.7	0.4
Tallow	0.1	2.8	23.3	19.4	42.4	2.9	0.9
Coconut	46.5	19.2	9.8	3.0	6.9	2.2	0.0

[0053] General chemical structural formulas and chemical schemes involving triglycerides and exemplary fatty acids are provided below.

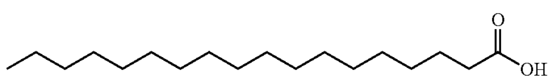


Triglycerides

With reference to this general triglyceride formula, R_1, R_2 and R_3 independently are fatty acids. Fatty acids vary in carbon chain length and in the number of sites of unsaturation. For example, the fatty acids may have carbon chain lengths ranging from at least as low as 10 carbon atoms to at least 20 carbon atoms, and more typically about 12 carbon atoms, such as with lauric acid, up to at least 18 carbon atoms, such as with stearic, oleic, linoleic or linolenic acid. Sites of unsaturation typically are double bonds, although compounds having different sites of unsaturation, such as triple bonds, also potentially are useful fuel sources. Numerical indications used herein adjacent fatty acids, e.g. 18:2 for linoleic acid, indicate the number of carbon atoms (18 in this example), and the number of sites of unsaturation (2, in this example). Examples of saturated fatty acids include, but are not limited to:

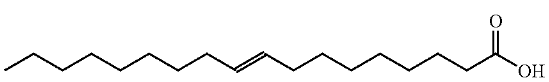


Palmitic Acid (16:00): $CH_3(CH_2)_{14}CO_2H$

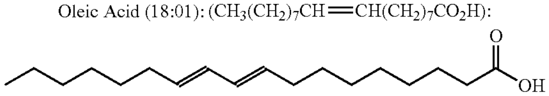


Stearic Acid (18:00): $(CH_3(CH_2)_{16}CO_2H)$

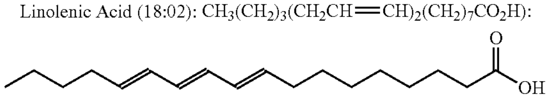
[0054] Examples of unsaturated fatty acids include, but are not limited to:



Oleic Acid (18:01): $(CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H)$:



Linolenic Acid (18:02): $CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7CO_2H)$:

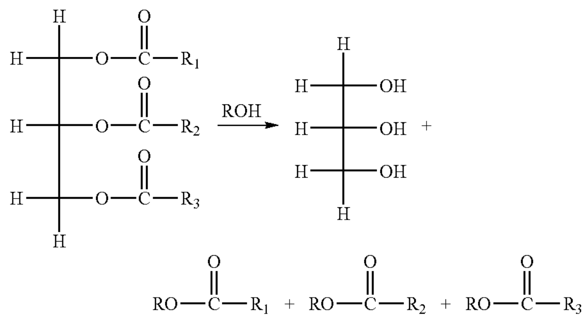


Linolenic Acid (18:03): $CH_3(CH_2CH{=}CH)_3(CH_2)_7CO_2H)$:

[0055] The primary sources of oils and fats for use in biodiesel production are soy, inedible tallow and grease, corn, edible tallow and lard, cotton, sunflower, canola, peanut, rapeseed and safflower. Soy oil accounts for about 58% of the total oil and fat production, and is by far the largest available product for biodiesel production. Much of the research and promotion for biodiesel production has come from national and state soybean associations.

[0056] Scheme 1 illustrates one embodiment of a method for making biodiesel according to the present invention. This embodiment involves transesterification of vegetable oil or animal fat with an alcohol. Transesterification can be accomplished according to the present invention using a microreactor and any suitable process, such as by using a catalyst or not, and/or using supercritical conditions, to yield glycerin and biodiesel according to Scheme 1.

Scheme 1



[0057] Scheme 1 also illustrates the use of an alcohol, ROH, for transesterification. Any alcohol suitable for performing the transesterification reaction can be used to practice embodiments of the present invention. The alcohol generally is a lower aliphatic alcohol, i.e. an alcohol having 10 or fewer total carbon atoms. Thus, R typically is a C1-C10 aliphatic chain, more typically an alkyl, alkenyl and/or alkynyl group. Specific examples of suitable alcohols include, but are not limited to, methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. Ethanol is a useful alcohol, at least in part, because it is derived from agricultural products, is renewable and less environmentally objectionable than other commonly used alcohols. However, methanol is primarily used because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Methanol quickly reacts with triglycerides, and typical catalysts, such as metal hydroxides, are more readily soluble in methanol than other alcohols.

[0058] Theoretically, to complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol-to-triglycerides is needed. In practice, this ratio needs to be higher to shift the equilibrium to product side to provide maximum ester yield. A higher molar ratio results in a greater ester conversion in a shorter time. Many oils, including soybean, reach their highest conversions (93-98%) at a 6:1 alcohol/triglyceride molar ratio.

[0059] A catalyst may be used to improve the reaction rate and yield. Any suitable catalyst can be used. Exemplary classes and species of catalysts include metals, such as Pt, Pd, Ag, Ni, Zn, Fe etc.; metal oxides, such as FeO, Fe_2O_3, Fe_3O_4, NiO, ZnO, SnO etc.; alkaholic metal hydroxides and carbonates, particularly methanolic or ethanolic NaOH or KOH; sodium and potassium alkoxides, such as sodium methoxide, which is more effective than sodium hydroxide, although sodium hydroxide is cheaper; zeolites; Lewis bases generally; acidic catalysts, such as sulfuric acid (H_2SO_4); enzymatic catalysts; and combinations thereof. Alkali-catalyzed transesterification proceeds approximately 4,000 times faster than that catalyzed by the same amount of an acidic catalyst; thus, alkali-catalyzed transesterification is a preferred embodiment. However, if a triglyceride has a higher free fatty acid content (>0.5%) and more water, acid-catalyzed transesterification is preferred. For an alkali-catalyzed transesterification, the triglycerides and alcohol must be substantially anhydrous to avoid soap production, which lowers the yield of esters. Furthermore, separating ester and glycerol, and the water washing steps, are performed with difficulties. The product stream of the transesterification reaction consists mainly of esters, glycerol and traces of alcohol, catalyst and tri-, di-, and monoglycerides.

[0060] Transesterification can occur at different temperatures, depending on the oil. Typically, higher temperatures increase the reaction rate and yield of esters. Thus, the temperature at which the transesterification reaction is conducted can vary from at least as low as ambient (about 25° C.) to at least as high as the degradation temperature of reactants and/or products, typically less than about 400° F., more typically less than about 350° F., and even more typically less than about 250° F., and any temperature within this range.

[0061] Certain embodiments also can be conducted at supercritical conditions relative to the alcohol component. For example, transesterification can be conducted using supercritical methanol at a temperature of about 350° C. A person of ordinary skill in the art will appreciate that pressure also can influence supercritical conditions, and further that there is a relationship between the temperature and pressure and whether a fluid is supercritical. For methanol the pressure can be at least as high as 45 MPa. A person of ordinary skill in the art also will appreciate that the conditions resulting in supercritical fluid depend on the fluid itself. Hence if an alcohol other than methanol is used for supercritical fluid transesterification, then the supercritical conditions will be other than that stated for methanol to exemplify this process. Supercritical conditions can be determined by consulting a phase diagram for particular compounds.

II. Microreactors

[0062] Microreactors are usually defined as miniaturized reaction vessels fabricated, at least partially, by methods of microtechnology and precision engineering. The characteristic dimensions of the internal structure of microreactor fluid channels can vary substantially, but typically range from the sub-micrometer to the sub-millimeter range. Microreactors most often are designed with microchannel architecture. These structures contain a large number of parallel channels, often with common inlet/outlet flow regions. Each microchannel is used to convert a small amount of material. Increased fluid throughput using microreactors is facilitated usually by a numbering-up approach, rather than by scale-up approach, although both numbering up and/or scale up processes can be used to increase throughput. Numbering-up guarantees that desired features of a basic unit remain unchanged when increasing the total system capacity.

[0063] The benefits of miniaturized systems, designed with dimensions similar to microreactors, compared to a large-scale process include, but are not limited to: large-scale batch process can be replaced by a continuous flow process; smaller devices need less space, fewer materials, less energy and often shorter response times; cost per device can be kept low by parallel microfabrication and automated assembly; and system performance is enhanced by decreasing the component size, which allows integration of a multitude of small functional elements. Smaller linear dimensions of microreactors increase the respective gradient for a given difference in some important physical properties in the chemical reactor such as temperature, concentration, density and pressure. Consequently, microreactors significantly intensify heat transfer, mass transport, and diffusional flux per unit volume or unit area. Typical thickness of the fluid layer in a microreactor can be set to few tens of micrometers (typically from about 10 to about 500 μm) in which diffusion plays a major role in the mass/heat transfer process. Due to a short diffusional distance, the time for a reactant molecule to diffuse through the interface to react with other molecular species is reduced to milliseconds and, in some cases, to nanoseconds. Therefore, the conversion rate is significantly enhanced and the chemical reaction process appears to be more efficient. Diffusion is no longer a rate determining step. Also, a decrease in fluid layer thickness increases the surface-to-volume ratio of microchannels to the range of 10,000 to 50,000 m^2/m^3, whereas typical laboratory and production vessels do not usually exceed 1000 m^2/m^3 and 100 m^2/m^3, respectively. Other potential benefits of microreactors include earlier production start at lower costs and safer operation; easier production scale-up; smaller plant size for distributed production; lower transportation, materials and energy costs; and more flexible response to market demands.

[0064] Coinventor, Dr. Brian Paul, also is a coinventor named on several United States patents and applications concerning devices, including microreactors, that are made using microlamination technology. Embodiments of these devices can be used to practice embodiments of the present invention for making biodiesel. These patents and applications include U.S. Pat. No. 6,672,502 and No. 6,793,831, application Ser. Nos. 11/086,074 and 11/243,937, as well as PCT application No. PCT/US2004/035452. Each of these patents and applications is incorporated herein by reference.

[0065] A particular working embodiment of a microreactor system **110** used to produce biodiesel according to the present invention is illustrated schematically in FIG. **1**. System **110** includes a fluid delivery system **112** and a microreactor system **114**. Certain working embodiments of the present invention used a dual syringe pump **116** for fluid delivery to microreactor system **114**, such as mechanical syringe pump model 975 from Harvard Apparatus Company. This pump has a 30-speed mechanical gear box with a positive locking mechanism. The pump's syringe holder can hold either one or two syringes of any size from 5 milliliters to 100 milliliters. System **110** has been used to deliver an alcohol and soybean oil to microreactor system **114**. For these embodiments, a first syringe **118**, typically a 10 milliliter syringe, was used to deliver alcohol, and a second syringe **120**, typically a 60 milliliter syringe, was used to deliver soybean oil. Alcohol was delivered by syringe **118** to the microreactor system **114** through a fluid conduit **122** having an in-line stop valve **124**. Similarly, soybean oil was delivered by syringe **120** to the microreactor system **114** through a fluid conduit **126** having an in-line stop valve **128**.

[0066] The illustrated microreactor **110** had three channels in a rectangular cross section—one 100 mm wide by 0.8 mm deep, another 100 mm wide by 1.7 mm deep, and the third 135 mm wide by 135 mm deep. Alcohol and soybean oil were mixed in the microreactor for varying mean residence times, as discussed further below in the working examples. Transesterification produced biodiesel and glycerol, collected in cold trap **132**, which allowed effective separation of the two phases.

[0067] FIG. **2** is a schematic, exploded view of one embodiment of a microreactor **210** used in working embodiments of the present invention for making biodiesel. FIG. **2** also illustrates that the microreactors typically are assembled using plural laminae that, when appropriately assembled, collectively define the working microreactor. Certain components used to make microreactor **210** were purchased from International Crystal Laboratories (Garfield, N.J.). For example, microreactor **210** includes a front plate **212** and a back plate **214**. Working embodiments of plates **212** and **214** were sealed liquid cells (model SL-3) having two 304 stainless steel plates (front plate **212** and back plate **214**). Plates **212** and **214** allow accurate visual alignment of the other cell (microreactor) components. Each plate **212**, **214** has an inlet **216***a* (inlet **216***b* of plate **214** is not shown) and an outlet **218***a*, **218***b* having lure type connectors.

[0068] Microreactor **210** also includes two gaskets **40** and **42**. A working embodiment of microreactor **210** included two viton gaskets **220**, **222**, each 38.5×19.5×4 mm. Gaskets **220** and **222** cushion and form seals with metal and optic components.

[0069] Microreactor **210** also includes two optic windows **224** and **226**. A working embodiment of microreactor **210** included two polished crystal optics (CAF2), each 38.5×19.5×4 mm, which serve as windows.

[0070] Microreactor **210** also includes spacers **228** and **230**. A working embodiment included two teflon spacers, each 38.5×19.5 mm. Each spacer **228**, **230** had different thicknesses (50 μm or 100 μm each). Spacers **228**, **230** create space between windows **220**, **224** of the microreactor **210** for the reactant liquids and to enable assembly of microreactor **210** with accurate pathlengths.

[0071] FIGS. **3-6** are digital images illustrating microchannels formed in individual lamina. For example, FIG. **3** is an end perspective view of a single lamina **300** having plural microchannels **302** extending axially along the long axis of the lamina. Plural fluid ports **304** also are illustrated, with each microchannel **302** having a fluid port through which fluid, such as an alcohol or an oil, flows for reaction in the microreactor **300**.

[0072] FIG. **4** is a digital image illustrating a dissembled view of a microreactor **400** comprising plural laminae **402**, each of which defines plural fluid microchannels **404** and plural fluid ports **406** for delivering fluid to the microchannels, as described for the single lamina illustrated by FIG. **3**. FIG. **4** also indicates that plural such laminae can be used, each having the same microfeatures, so that increased fluid throughput, and hence increased biodiesel production, is realized by a numbering up approach, as opposed to a feature-size scale up approach. FIG. **4** also illustrates two end plates **408**, **410** positioned adjacent the plural microchannel laminae **402**. The two end plates **408**, **410** also include a manifold portion **412** formed therein for distributing fluid flow to the individual microchannels **404**.

[0073] FIG. **5** is a schematic perspective exploded view illustrating positioning plural laminae, each defining microchannels, to collectively define one embodiment of a microreactor **510** for producing biodiesel as with the embodiment of FIG. **4**. Microreactor **510** includes end plates **512** and **514**, and plural laminae **516**, **518**, **520**, **522** and **524**, each defining plural microchannels. Microreactor **510** also includes plural manifolds, such as manifolds **526** and **528** for end plate **512**, and manifolds **530** and **532** in end plate **514**. Fluids enter and exit the manifolds through fluid ports. For example, fluids may enter or exit manifold **532** through fluid port **534**.

[0074] FIGS. **6-12** are digital images of working embodiments of microreactor systems useful for making biodiesel according to the present invention.

[0075] A person of ordinary skill in the art will appreciate that microreactors suitable for biodiesel synthesis can operate with and without solid catalysts. Furthermore, the reaction conditions can be operated either under subcritical or supercritical operating conditions. The reaction also can be accomplished using cosolvents. For example, microreactors can be used that operate at supercritical conditions with addition of a cosolvent. One example, without limitation, of a suitable cosolvent for supercritical conditions is CO_2. CO_2 is added as co-solvent to mediate the temperature and/or pressure of the reaction mixture, whereas the supercritical conditions otherwise are determined by the alcohol component used in the reaction mixture.

[0076] FIG. **13** illustrates a first microchannel **1300** and a second microchannel **1302** having a single phase reaction mixture **1304**, either under subcritical or supercritical conditions, therein. Microchannel **1300** does not include a catalyst. As an alternative embodiment, microchannel **1302** does include a catalyst **1305** positioned effectively for catalyzing the production of biodiesel. Microchannel **1302** includes both a first wall **1306** and a second wall **1308**. The illustrated embodiment includes catalyst **1305** associated with both walls. For example, the catalyst **1305** may be deposited at the reactor walls for use in subcritical or supercritical operating conditions. Moreover, the illustrated embodiment of microchannel **1302** has catalyst substantially uniformly distributed along the length of walls **1306**, **1308**. A person of ordinary skill in the art will appreciate that it may not be necessary to have catalyst associated with both walls of a microchannel, nor that the catalyst be substantially uniformly distributed on a wall, or walls.

[0077] Oil and alcohol are hydrophobic/hydrophilic respectively to each other and are immiscible for all practical purposes. One way to control the interface between oil and alcohol in a reaction mixture is to use inserts that have a relative small size, such as from about 20 μm to about 60 μm thick with micrometer size openings. This interface material can be made from a variety of materials, such as polymers, metals, and combinations thereof. Wicking material, woven fabrics or otherwise mashed fiber-like materials also can be used for this purpose. Without being limited to a theory of operation, such interface materials use natural surface tension effects to create a stable interface.

[0078] FIG. **14** is a schematic drawing of a microchannel **1400**. Microchannel **1400** has a first oil phase **1402** and a second alcohol phase **1404** flowing therethrough. Microchannel **1400** also includes an interface supporting material **1406**. Interface mesh **1406** can also serve as a substrate for solid catalyst. Mesh material, for example metals, with stainless steel being one example, can be coated with solid catalyst materials, such as catalysts particularly useful for supporting biodiesel synthesis. These materials typically are used as relatively small particles, such as nanometer-scale particles.

Also the mesh material may have nanoparticles incorporated into its structure even before the mesh is produced.

III. Biodiesel Production

[0079] A. Simulation

[0080] FIG. **15** illustrates the velocity profile of the two immiscible reactants, such as methanol and soybean oil, in a microchannel. As a result of the different physical properties of these reactants, the thickness of each fluid layer depends on the volumetric ratio and the ratio of viscosities of the two substances. The thickness of the oil layer may be important for modeling and for determining process rate.

[0081] Several assumptions were made to construct the model, including, the system is under steady state conditions, velocity in the z direction (u_z) and y direction (u_y) are equal to 0, velocity in the x direction (u_x) is not 0, and is only a function of y, the gravity (g) in the x and z directions is equal to zero (g_x=g_z=0.0); and pressure drop along the x direction is constant [ΔP=P (x=L)−P (x=0)]. Using these assumptions, the following equations were derived.

$$u_A = V_{A,x} = m\left[1+\left(\frac{b^2-a}{aB_a(1+b)}\right)y-\left(\frac{a+b}{aB_aB_b(b+1)}\right)y^2\right] \tag{4}$$

$$u_B = V_{B,x} = m\left[1+\left(\frac{b^2-a}{B_a(1+b)}\right)y-\left(\frac{a+b}{B_aB_b(b+1)}\right)y^2\right] \tag{5}$$

$$\text{Where } m = \frac{\Delta PB_aB_b}{2\mu_BL}\left(\frac{1+b}{a+b}\right)$$

[0082] Starting with these equations for soybean oil/methanol, the laminar velocity profile and the definition of the volumetric rate are:

$$Q_A = w\int_0^{Ba} u_A\,dy \Rightarrow \frac{Q_A}{w} = \int_0^{Ba} u_A\,dy \tag{6}$$

$$Q_B = -w\int_0^{-Bb} u_B\,dy \Rightarrow \frac{Q_B}{w} = -\int_0^{-Bb} u_B\,dy$$

$$\frac{Q_A}{w} = m\int_0^{Ba}\left[1+\left(\frac{b^2-a}{aB_a(1+b)}\right)y-\left(\frac{a+b}{aB_aB_b(1+b)}\right)y^2\right]dy$$

$$\frac{Q_A}{wm} = B_a\left[1+\left(\frac{b^2-a}{2a(1+b)}\right)-\left(\frac{a+b}{3a(1+b)}\right)b\right]$$

$$\frac{Q_B}{w} = -m\int_0^{-Bb}\left[1+\left(\frac{b^2-a}{B_a(1+b)}\right)y-\left(\frac{a+b}{B_aB_b(1+b)}\right)y^2\right]dy \tag{7}$$

$$\frac{Q_B}{wm} = B_b\left[1-\left(\frac{b^2-a}{2b(1+b)}\right)-\left(\frac{a+b}{3b(1+b)}\right)\right]$$

After dividing Eq (6) with Eq (7) we obtain,

$$\frac{Q_A}{Q_B} = b\left[\frac{1+\left(\frac{b^2-a}{2a(1+b)}\right)-\left(\frac{a+b}{3a(1+b)}\right)b}{1-\left(\frac{b^2-a}{2b(1+b)}\right)-\left(\frac{a+b}{3b(1+b)}\right)}\right] \tag{8}$$

The thickness layer ratio "b" is calculated by replacing the viscosity ratio "a" and appropriate values of "b" into equation (8). Since the equation is nonlinear and implicit, a trial and error method was used to determine "b," which will yield the correct ratio of

$$\frac{Q_A}{Q_B} = 3.4:$$

Soybean oil (μ_A)=5.825*10^{-2} Pa·S (25° C.)
Methanol (μ_B)=5.47*10^{-4} Pa·S (25° C.) Where

[0083]

$$a = \frac{\mu_A}{\mu_B} = 106.5$$

TABLE 5

Soybean oil/Methanol Phases Thickness Ratio (b)

Thickness Layer Ratio "b"	Q_A/Q_B
1	0.062
2	0.349
3	0.933
4	1.797
5	2.883
5.43	3.402

The obtained thickness layer ratio is b = 5.43
For a 100 μm μ-channel thickness: B_a = 84.4 * 10^{-6} m (84.4 μm) and B_b = 15.6 * 10^{-6} m (15.6 μm).
For a 200 μm μ-channel thickness, B_a = 168.75 * 10^{-6} m (168.75 μm), and B_b = 31.25 * 10^{-6} m (31.25 μm).

[0084] B. Chemical Reactions

[0085] Production of biodiesel by transesterification reactions, such as transesterification of soybean oil (A) with methanol (B), consists of several consecutive, reversible reactions. Without being limited to a particular theory of operation, one reaction pathway involving consecutive reversible reactions is shown below. The first proposed step is converting soybean oil, which is a triglyceride, to diglycerides (DG). This conversion is then followed by conversion of diglycerides to monoglycerides (MG), and finally by conversion of monoglycerides to glycerol (GL). After the conversions, three moles of methyl esters (M) are obtained for each triglyceride reacted.

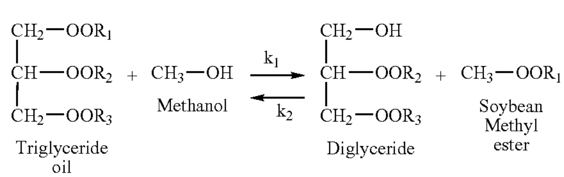
Triglyceride (*A*)+Methanol (*B*)$\leftrightarrow$Diglyceride (*DG*)+ Methyl ester (*M*)

Diglyceride (*DG*)+Methanol (*B*)$\leftrightarrow$Monoglyceride (*MG*)+Methyl ester (*M*)

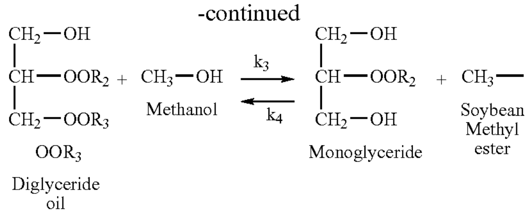
Monoglyceride (*MG*)+Methanol (*B*)$\leftrightarrow$Glycerol (*GL*)+Methyl ester (*M*)

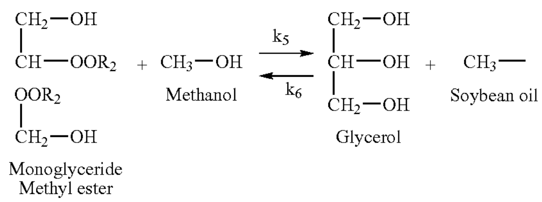
Step Reactions:

[0086]



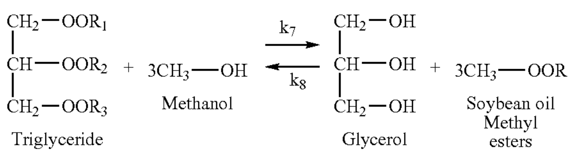
-continued





Overall Reaction:

[0087]



EXAMPLES

[0088] The following examples are provided to exemplify particular features of working or hypothetical examples. A person of ordinary skill in the art will appreciate that the invention is not limited to the specific features recited in these examples.

Materials

[0089] Refined, bleached, and deodorized soybean oil (Crisco Brand) was obtained from J. M. Smucker Company (Orrville, Ohio). Reference standards, such as methyl linoleate, methyl linolenate, methyl stearate, methyl palmitate, and methyl oleate, having a minimum purity of 99%, were purchased from Sigma-Aldrich Company (Saint Louis, Mo.). Analytical grade methanol was purchased from EMD Chemicals Inc. (Canada). Sodium Hydroxide Pellets, 99% pure, were purchased from Mallinckrodt Baker, Inc. (Paris, Ky.).

Example 1

[0090] This example concerns transesterification of soybean oil at room temperature (25° C.) and at atmospheric pressure using a working embodiment of a microreactor as described above. A 10-milliliter syringe was filled with a stock solution comprising dried sodium hydroxide dissolved in 10 milliliters of methanol. Two steps were required to prepare a stock solution of methanolic sodium hydroxide (NaOH). First, the amount of NaOH required for the transesterification reaction had to be calculated. Second, NaOH was dried before being dissolved in methanol. The amount of NaOH used for transesterification represented 1.0 wt % of the soybean oil used for the transesterification reaction. The amount of sodium hydroxide to be used was calculated according to the following formula:

$$\begin{aligned}\text{NaOH amount (g)} &= 1\% * \text{volume of soybean oil in 60 milliliter syringe} * \text{sp gr.}\\ &= 0.01 * 34 \text{ milliliters} * 0.885\\ &= 0.3 \text{ g to be dissolved in each 10 milliliters of methanol}\end{aligned}$$

1.8 grams of NaOH were dried for a few hours at a temperature of about 106° C. After drying, NaOH was dissolved in 60 milliliters of methanol. This stock solution was filtered to remove small particles that potentially might obstruct flow in the microreactor. For the transesterification reaction, a 10 milliliter syringe was filled with methanolic NaOH stock solution.

[0091] A second 60-milliliter syringe was filled with 34 milliliters of soybean oil. The soybean oil/methanol molar ratio calculation was performed using the following data: soybean oil molecular weight=872.4; specific gravity of soybean oil=0.885 g/milliliter; methanol molecular weight=32, methanol specific gravity=0.792 g/milliliter; the weight of one mole of soybean oil=1*872.4=872.4; the volume of one mole of soybean oil=872.4÷0.885=985.76 milliliters. The pump volume flow rate ratio for a 60 milliliter syringe and a 10 milliliter syringe of soybean oil/methanol is 3.4. This value was used to calculate the methanol volume from the soybean oil volume.

$$\text{Volume of methanol} = \frac{985.76}{3.4} = 290 \text{ milliliters}$$

$$\text{Weight of methanol} = 290 * 0.792 = 229.7 \text{ g}$$

$$\text{Moles of methanol} = \frac{229.7}{32} = 7.2 \text{ moles}$$

As a result, the molar ratio of soybean oil/methanol provided by using a 60 milliliter syringe and a 10 milliliter syringe was 1:7.2.

[0092] Both the 10-milliliter and the 60-milliliter syringes were installed in the syringe pump. The syringe pump delivered the two solutions to the microreactor at a constant volumetric flow rate ratio of soybean oil-to-methanol of 3.4:1, which corresponds to the calculated 1:7.2 soybean oil/alcohol molar ratio. Six syringe pump flow positions were used. Flow position numbers 20, 22, 24, 26, 28 and 30 were used for the 100 μm μ-channel thickness. These flow positions correspond to the following mean residence times (MRT): 0.41, 0.79, 1.69, 3, 5.3, and 10 minutes. Flow position numbers 18, 20, 22, 24, 26 and 28 were used for the 200 μm μ-channel thickness, which correspond the following MRT: 0.43, 0.82, 1.58, 3.37, 6.05, and 10.63 minutes. In both cases the MRT was based on the soybean oil phase since it had a higher flow rate than the methanol. Syringe pump flow rates are summarized below in Table 6.

TABLE 6

Pump Flow Position	Syringe Pump Flow Rate 60 milliliter syringe flow Rate (Q_A, milliliter/min)	10 milliliter Syringe Flow Rate (Q_B, milliliter/min)	Flow rate Ratio (Q_A/Q_B)
18	0.107	0.032	3.34
20	0.0559	0.0164	3.4
22	0.02915	0.0085	3.42
24	0.01363	0.00394	3.46
26	0.00760	0.0022	3.45
28	0.004328	0.0013	3.33
30	0.002314	0.0006615	3.49
Average Ratio			3.4

[0093] Fluids from both syringes were pumped into a microreactor μ-channel, where they formed two layers with different thicknesses as shown in the soybean oil/methanol laminar velocity profile, FIG. **15**. The layer thicknesses of the soybean oil and methanol inside the microreactor were determined by their viscosities and flow rate ratios as calculated above. The microreactor reaction channel dimensions were 2.33 cm length, 1.05 cm width, and 100 or 200 μm in height, depending on the spacer thickness used.

[0094] Fluid flowed out of the microreactor as a two-phase stream and was collected in a cold trap (0° C.), mainly to stop any further reaction in the test tube. The two phases in the test tube were further separated by centrifuge. The volumes of both phases were recorded and then parts of both phases were stored in vials for methyl esters analysis by gas chromatography (GC). Gas chromatographic HP model 5890 Series II was used to determine methyl ester concentrations. A Nukol capillary column (30 m×0.53 mm ID, 1.0 μm film) with an operating temperature limitation (60° C. to 200° C.) was used, along with a pre-installed flame ionization detector (FID). Liquid samples (1 μl each) were injected using a splitless injection method. Data was collected using the HP Integrator model 3396 Series II.

[0095] Five compounds were used as methyl ester standards: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. These standards were used to identify biodiesel (methyl ester) peaks in the recorded chromatographs. Identifications were established by comparing retention times of both reference standards with eluted sample peaks. The biodiesel peaks were eluted in the following retention times: methyl palmitate (9 minutes), methyl stearate (16.3 minutes), methyl oleate (17.5 minutes), methyl linoleate (20.5 minutes), methyl linolenate (25.3 minutes).

[0096] Four steps were required to calculate the soybean oil conversions. First, Relative Response Factors (RRFs) were determined for each methyl ester standard. Second, the methyl ester moles at the biodiesel phase in the experimental sample were determined. Third, the soybean oil reacted from the total methyl esters moles existing at the biodiesel phase of the experimental sample were calculated. Fourth, the soybean oil entered in the transesterification reaction was calculated. Each step is explained in detail in the following paragraphs.

[0097] To determine the RRF of each methyl ester standard, five methyl ester concentrations were prepared from standard methyl ester samples having a minimum purity of 99%. 5 μl or equivalent weight from each methyl ester standard was diluted into 6,000 μl of hexane to give a 0.000833 μl mole ester/μl hexane concentration. These five methyl ester standards were analyzed in the GC twice, before and after running the biodiesel samples, to check for any inconsistencies or shifts over the duration of the analysis. The differences in the GC standard areas for both runs (before and after analyzing the experimental samples) ranged from 1% to 4.7%. The RRF (concentration over GC standard area) for each methyl ester standard was calculated and was used to determine the corresponding methyl ester concentration in the biodiesel phase. RRFs are provided below in Table 7.

TABLE 7

Standard Methyl Ester Relative Response Factors (RRFs)

Methyl Ester Name	Methyl Standard Concentration	GC Methyl Standard Area	RRFs
Methyl palmitate	0.000833	2278422	3.656e−10
Methyl stearate	0.000833	2290152	3.637e−10
Methyl oleate	0.000833	2225547	3.743e−10
Methyl linoleate	0.000833	2272309	3.666e−10
Methyl linolenate	0.000833	2304266	3.615e−10

[0098] To determine the methyl ester moles at the biodiesel phase in a typical analysis, 5 μl of the biodiesel phase experimental sample at each MRT was diluted with a solvent (hexane). The amount of solvent (1,000 to 4,000 μl) used depended on the biodiesel concentration in the sample. One μl of the diluted sample was injected into the GC to obtain the chromatographic record. To calculate the concentration of each methyl ester in one μl of the diluted sample, the peak area obtained in the chromatograph was multiplied by the corresponding RRF of the standard methyl ester. Once the concentration of each methyl ester was determined, the moles of each methyl ester in the biodiesel phase sample was calculated.

[0099] The overall transesterification reaction showed that three moles of methyl esters were obtained for each soybean oil (triglyceride) milliliter reacted. To calculate the amount of soybean oil reacted at each MRT, the total moles of methyl esters in the biodiesel phase were divided by three to get the moles of soybean oil reacted.

[0100] To calculate the soybean oil moles entered in the reaction at each MRT, 77.27% of the total product sample volume (biodiesel phase+glycerol phase) was assumed to be originally soybean oil and the rest to be methanol. This assumption was based on the syringes' flow rate volume ratio of soybean oil-to-methanol, which was 3.4:1 or 77.27%:22.72%. The conversion of soybean oil in the transesterification reaction was calculated by dividing the reacted soybean oil by the soybean oil which entered the reaction.

Example 2

[0101] This example concerns biodiesel production using a microreaction process, and one embodiment of a microreactor having an adjustable μ-channel thickness (100 μm or 200 μm) as previously described. To show that biodiesel production is feasible in the microreaction process, two sets of soybean oil transesterification procedures were performed in the microreactor. A first production run used a microreactor having a 100 μm μ-channel thickness (spacers) and the other run was with a 200 μm μ-channel thickness (spacers). This was done to assess the effect of μ-channel thickness on biodiesel production. Both production runs were conducted at the same operating conditions: 7.2:1 methanol/soybean oil molar ratio; 1.0 wt % (with respect to oil) NaOH catalyst;

room temperature (25° C.); atmospheric pressure; and substantially the same mean residence times (MRT).

[0102] A 10-milliliter syringe was filled with a stock solution of dried sodium hydroxide dissolved in methanol. Another 60-milliliter syringe was filled with 34 milliliters of soybean oil. The syringe pump delivered the two solutions from both syringes to the microreactor at a constant volumetric flow rate ratio. The ratio of the flow rates of soybean oil to methanol was 3.4:1 which corresponds to a 1:7.2 molar ratio.

[0103] The reaction products flowed from the microreactor in two phases: a biodiesel phase and a glycerol phase. Both phases were collected in a single container. Part of the biodiesel phase was diluted and injected into the GC to obtain peak records of the methyl esters. Using the methyl esters standards, the recorded chromatographic values were converted into methyl esters concentrations at different MRT.

[0104] For production runs using the microreactor with a 100 μm thickness, six volumetric flow rates (0.0559, 0.02915, 0.01363, 0.00760, 0.004328, 0.002314 milliliter/min) were used. These volumetric flow rates corresponded to MRTs of 0.41, 0.79, 1.69, 3, 5.3, and 10 min. Each experiment corresponds to one MRT.

[0105] FIG. **16** shows that soybean oil conversion increases with MRT. Soybean oil conversion ranges from 12.33% at 0.41 MRT to 91.1% at 10 minutes MRT. Remaining unconverted reactant is not pure soybean oil but it instead contains some intermediate reactants, such as diglycerides and monoglycerides. However, the remaining percentage was considered to be pure soybean oil due to lack of an analytical method useful for measuring the concentrations of these intermediates. Therefore, the conversions of soybean oil in reality may be higher than stated.

[0106] FIG. **17** provides the total methyl ester concentration as a function of MRT. The methyl esters concentration ranges from 0.355 mol/l at 0.41 minute MRT to 2.56 moles/l at 10 minutes MRT.

[0107] FIG. **18** shows individual methyl ester concentrations at different MRTs. The differences in the concentration of each methyl ester at a given MRT depend on the original composition of fatty acids in the soybean oil.

[0108] For production runs using the microreactor having a 200 μm thickness, six volumetric flow rates (0.107, 0.0559, 0.02915, 0.01363, 0.00760 and 0.004328 milliliter/min) were used. These volumetric flow rates corresponded to MRTs of 0.43, 0.82, 1.58, 3.37, 6.05 and 10.63 min. Each production run corresponds to one MRT.

[0109] FIG. **19** shows that soybean oil conversion increases with the MRT. For the disclosed working embodiments, the soybean oil conversion ranged from 4.75% at 0.43 MRT to 86.36% at 10.63 minutes MRT.

[0110] FIG. **20** shows that the total methyl esters concentration is a function of MRT. The methyl esters concentration ranges from 0.136 mol/l at 0.43 minute MRT to 2.45 moles/l at 10.63 minutes MRT.

[0111] FIG. **21** shows individual methyl ester concentrations at different MRTs. The differences in the concentration of each methyl ester at a given MRT depend on the original composition of fatty acids in soybean oil. t-test statistic of the mean difference for the experimental data obtained for soybean oil conversion in both thicknesses (100 and 200 μm) establish that the two sets of experimental data are statistically different.

[0112] A survey of the work of other researchers, as reported by Noureddini & Zhu, (1997), shows that the conversion of soybean oil to methyl esters in a batch reactor is a reaction process with changing mechanisms. These mechanisms are reflected in a sigmoidal conversion curve for the soybean oil conversion as shown in FIG. **22**, which illustrates transesterification reaction mechanisms in a batch reactor using a stirrer operating at 300 rpm and 50° C. using a 6:1 molar ratio (methanol:soybean oil).

[0113] The transesterification reaction process in the batch reactor clearly exhibits three different rates: a) an initial mass-transfer-controlled region (slow rate) followed by b) a kinetically controlled region (fast rate) and c) a final slow region when equilibrium is approached. In a batch reactor, soybean oil and methanol are not miscible and form two liquid phases upon their initial introduction into the reactor. The reaction process is diffusion-controlled. Slowly diffusing reactants in two different phases results in a slow reaction rate. Mechanical mixing increases the contact between the reactants, resulting in an increase in the mass transfer rate. The duration of the slow rate region decreases as the mixing intensity increases. The mixing effect is most significant during the slow rate region of the reaction. As a single phase is established, increased mixing intensity becomes insignificant and the reaction rate primarily is influenced by the reaction temperature.

[0114] One benefit of using a microreactor for producing biodiesel is the mass transfer intensification. Eliminating the mass transfer-controlled regime in the transesterification reaction process is one of the main reasons for applying microreactor technology to biodiesel production. Setting the thickness of soybean oil and methanol layers in a microreactor to a few tens of micrometers (100 μm and 200 μm in disclosed working embodiments) allows diffusion to play a major role in the mass transfer-controlled region. Because there is a short diffusion distance, the time required for a reactant molecule to diffuse through the interface to react with other molecular species is reduced to seconds and in some cases to milliseconds. The conversion rate therefore is significantly enhanced and the transesterification reaction process appears to be more efficient. The diffusion-controlled region is no longer a rate-determining step.

[0115] FIGS. **23** and **24** compare the soybean oil conversions obtained in a microreactor (100 μm and 200 μm; 25° C.) and the conversions obtained in a batch reactor (30° C., 50° C. and 70° C.) as reported by Noureddini & Zhu, 1997. Noureddini, H. (University of Nebraska); Zhu, D. Kinetics of transesterification of soybean oil, JAOCS, Journal of the American Oil Chemists' Society, V. 74, n 11, November, 1997, p 1457-1463. In the batch reactor, 90% conversion is achieved after 90 minutes at 70° C. This conversion decreases to 80% and 65% as the reaction temperature decreases to 50° C. and 30° C., respectively. In working embodiments of microreactors having 100 and 200 μm thicknesses, 91% and 86% conversions, respectively, were obtained in a 10 minute period at 25° C. This confirms that the microreactor-based process produces biodiesel much more efficiently than a batch process. For industrial applications, changing the production technology and reducing process times and temperatures would result in substantial cost reduction, increased production capacity and lower maintenance.

[0116] Improvement in the overall process performance is achieved when the microreactor (μ-channel) thickness is reduced from 200 μm to 100 μm. Reducing the diffusion distance improves mass transfer and reduces diffusion time for reactant molecules to react with each other. FIGS. **25** and

26 show these process improvements. The soybean oil conversion increases from 86% to 91% and total methyl esters concentrations increase from 2.45 to 2.59 moles/l.

[0117] FIG. 27 shows the increase in concentrations for each methyl ester between 100 μm and 200 μm. Again, this emphasizes the advantage of the microreaction process in processes requiring mechanical mixing to improve mass transfer. The microreactor process is faster than processes performed in conventional reactors if mass transfer is an important step in the chemical process rate.

[0118] Derived mathematical models and production data of soybean oil conversion using the microreactor having 100 μm thickness were used to estimate the reaction rate constants (k_1). Finite Element Method Laboratory (FEMLAB) Software was used to solve the mathematical model numerically. The reactions rate constants (k_1 to k_6) were estimated by fitting the experimentally obtained conversions to the predicted model conversions. The published values of the reaction rate constants obtained in a batch reactor for soybean oil transesterification reactions, as reported by Noureddini & Zhu, 1997, were first used to estimate reaction rate constants in the microreactor. Rate constants obtained in the batch reactor were most probably impacted and determined under the influence of mass transfer caused by a mechanical stirrer. The mass transfer influence is particularly swaying in two-phase systems. Conventional stirring techniques have definite limitations as to the characteristic minimum droplet size of the dispersed phase in the two-phase system. Stirring typically produces a wide range of droplet distribution, thus causing a wide range of pathlength diffusion and characteristic diffusion times. More importantly, in any stirring process a mixing regime is reached when additional increases in stirring intensity does not significantly change the droplet size distribution of the dispersed phase. Under these conditions most investigators who use conventional batch reactors conclude that mass transfer influence is eliminated from the process and that the observed process kinetics can be credited completely to chemical reaction kinetics. For all practical purposes, this approach is sufficiently correct as any industrial size process typically operates with mixing power input several orders of magnitude smaller than those achieved under laboratory conditions.

[0119] However, in microchannel reactors, the characteristic diffusion length may be reduced to a size that is often much smaller than the characteristic droplet size attained in a conventional mixing. For certain working embodiments of the present invention, the characteristic diffusion length is approximately 100 μm, which is the thickness of the film obtained in the microreactor. Furthermore, this diffusion length is maintained approximately uniformly throughout the reactor, and it is achieved without mixing or power consumption. These conditions are much more favorable to the chemical reaction process and the reaction rate process therefore likely will increase. Regardless of the fact that the rate constants obtained in the batch reactor were determined under the influence of mass transfer caused by a mechanical stirrer, their equilibrium constants were much less influenced by mass transfer contribution. Therefore, these equilibrium constants are preserved by increasing the rate constants simultaneously at all MRTs until a good fitting was achieved.

[0120] The best estimated reaction rate constant (k_1) values for the microreactor with 100 μm are shown in Table 8.

TABLE 8

	Microreactor Rate Constants					
	k_1	k_2	k_3	k_4	k_5	k_6
Values (m^3 milliliter second)	4.37e−6	9.62e−6	1.88e−5	1.074e−4	2.117e−5	9.0e−7

[0121] For the microreactors with 100 and 200 μm thicknesses, FIGS. 28 and 29, respectively, show good correlation of production and model results for soybean oil conversions at different MRTs using the estimated reaction rate constants (k_1) values. The microreactor type used for certain working embodiments may be used to predict soybean oil conversion and biodiesel concentration under a variety of operating conditions.

[0122] The present disclosure clearly establishes that microreactors can be used to produce biodiesel, such as by transesterification of soybean oil. Reducing microreactor (μ-channel) thickness from 200 μm to 100 μm improved the overall process performance. In the microreactor with a 100 μm thickness (spacers), a 91% soybean oil conversion (2.59 moles/l biodiesel concentration) was achieved. In the microreactor with a 200 μm thickness, an 86% conversion (2.45 moles/l biodiesel concentration) was achieved.

Example 3

[0123] This examples concerns determining microreactor residence time based on the oil phase since it had higher flow rate than methanol. Residence time was calculated according to the following equation:

$$\text{Residence time (min)} = \frac{\textit{microreactor chanal} \text{ volume (cm}^3)}{\text{60 ml syringe flow rate through } \textit{mircoreactor} \text{ (cm}^3\text{/min)}}$$

[0124] A. 100 Micron Microreactor Thickness Residence Time

[0125] The microreactor channel area includes a rectangular area and a triangle area. The channel volume therefore has been calculated according to the following definition:

Microreactor channel volume=channel area (rectangular+triangle)*thickness of oil phase (B_a)

where the rectangular area was 2.3×1.05=2.415 cm^2, the triangular area was 0.5×1.05×0.6=0.315 cm^2, and the microreactor channel volume was (2.415+0.315)×(84.4/10000)=0.023 cm^3. Table 9 provides the residence time for a 100 μm microreactor thickness.

TABLE 9

Pump Flow Position	60 milliliter syringe flow Rate (Q_4, milliliter/min)	Microreactor Channel Volume (cm^3)	Residence Time (min)
20	0.0559	0.023	0.41
22	0.02915	0.023	0.79
24	0.01363	0.023	1.69
26	0.00760	0.023	3

TABLE 9-continued

Pump Flow Position	60 milliliter syringe flow Rate (Q_4, milliliter/min)	Microreactor Channel Volume (cm^3)	Residence Time (min)
28	0.004328	0.023	5.3
30	0.002314	0.023	10

Table 10 provides the residence time for a 200 μm microreactor thickness, where the microreactor channel volume was (2.415+0.315)×(168.75/10000)=0.046 cm^3.

TABLE 10

Pump Flow Position	60 milliliter syringe flow Rate (Q_4, milliliter/min)	Microreactor Channel Volume (cm^3)	Residence Time (min)
18	0.107	0.046	0.43
20	0.0559	0.046	0.82
22	0.02915	0.046	1.58
24	0.01363	0.046	3.37
26	0.00760	0.046	6.05
28	0.004328	0.046	10.63

Example 4

[0126] This example concerns determining the amount of soybean conversion using one embodiment of a microreactor process according to the present invention. Methyl ester ratio factors were determined using the following formula:

$$\text{Ratio factor} = \frac{\text{methyl standard concentration}}{GC\ \text{methyl standard area}}$$

Table 11 provides standard methyl ester relative response factors (RRFs)

TABLE 11

Methyl Ester Name	Methyl Standard Concentration	GC Methyl Standard Area	RRFs
Methyl palmitate	0.000833	2278422	3.656e−10
Methyl stearate	0.000833	2290152	3.637e−10
Methyl oleate	0.000833	2225547	3.743e−10

TABLE 11-continued

Methyl Ester Name	Methyl Standard Concentration	GC Methyl Standard Area	RRFs
Methyl linoleate	0.000833	2272309	3.666e−10
Methyl linolenate	0.000833	2304266	3.615e−10

[0127] Performing this calculation first involved analyzing a 5 μl sample of the biodiesel phase in the experimental sample. The total methyl esters at biodiesel phase of the sample were then calculated. Finally, the amount of soybean oil reacted and entered in the transesterification reaction were calculated. The 5 μl taken from biodiesel phase was diluted using 4,000 μl of hexane. One μl of the diluted solution was injected into a GC. The resulting GC areas for each of the methyl esters were multiplied by the corresponding Relative Response Factors (RRFs) to determine the concentration of each methyl ester in 1 μl. The concentration of each methyl ester was multiplied by 4,000 μl of hexane to determine the concentration in a 5 μl biodiesel sample. The moles of each methyl ester were calculated in 5 μl followed by calculating the moles of each methyl ester in the biodiesel phase of the sample.

[0128] The reacted soy bean oil was calculated by dividing the total moles of methyl esters in the biodiesel phase by three. The soybean oil moles entered in the reaction was calculated by assuming 77.27% of the total products sample volume (biodiesel phase+glycerol phase) was originally soybean oil and the rest was methanol. This assumption was based on the syringe flow rate volume ratio of soybean oil to methanol, which is 3.4:1 or 77.27%:22.72%. The percent conversion of soybean oil in the transesterification reaction was calculated by dividing the amount of soybean oil reacted by the soybean oil entering the reaction. Table 12 provides the areas of methyl esters sample analysis, 100 μm thickness, with a 1-minute mean residence time.

TABLE 12

Methyl Ester Type	Retention Time (min)	Residence Time (min)	GC Area
methyl palmitate	9	10	325323
methyl stearate	16.3	10	136429
methyl oleate	17.6	10	695992
methyl linoleate	20.5	10	1619204
methyl linolenate	25.3	10	216570

TABLE 13

Summary of Experimental Results and Analysis for Microreactor with 100 μm Thickness

Mean Residence	Experimental Sample Volume (milliliter)/ Biodiesel Phase	GC Areas of Methyl esters in 1 μm Injected Sample					Hexane Dilution	
Time (min)	Volume (milliliter)	Methyl Palmitate	Methyl Stearate	Methyl oleate	Methyl linoleate	Methyl linolenate	Amount (μm)	Conversion (%)
0.41	7.7/6.3	191215	69582	365751	854369	120111	1000	12.33
0.79	8.5/7.4	484809	201420	1045391	2425050	255002	1000	36.98
1.69	5.6/5.2	203395	81272	454879	1032176	132451	4000	66.56

TABLE 13-continued

Summary of Experimental Results and Analysis for Microreactor with 100 μm Thickness

Mean Residence Time (min)	Experimental Sample Volume (milliliter)/ Biodiesel Phase Volume (milliliter)	GC Areas of Methyl esters in 1 μm Injected Sample Methyl Palmitate	Methyl Stearate	Methyl oleate	Methyl linoleate	Methyl linolenate	Hexane Dilution Amount (μm)	Conversion (%)
3	6.8/6.3	253044	100467	570985	1319497	178556	4000	84.48
5.3	5/4.3	239830	87929	546143	1269683	169773	4000	74.96
10	4.7/3.8	325323	136429	695992	1619204	216570	4000	91.1

TABLE 14

Summary of Experimental Results and Analysis for Microreactor with 200 μm Thickness

Mean Residence Time (min)	Experimental Sample Volume (milliliter)/ Biodiesel Phase Volume (milliliter)	GC Areas of Methyl esters in 1 μm Injected Sample Methyl Palmitate	Methyl Stearate	Methyl Oleate	Methyl Linoleate	Methyl Linolenate	Hexane Dilution Amount (μm)	Conversion (%)
0.43	5.6/4.6	74967	23600	140556	331087	43463	1000	4.75
0.82	6.2/4.9	305350	122218	598454	1387648	195037	1000	19.41
1.58	5.5/4.6	247056	102669	541407	1260741	171289	3000	54.85
3.37	5.7/4.8	249555	104971	545144	1274116	163123	4000	74.07
6.05	5.2/4.4	276830	114604	601475	1404626	191850	4000	82.47
10.63	5.8/4.8	300559	123772	651132	1506251	190634	4000	86.36

[0129] The present invention has been described with reference to particular embodiments. A person of ordinary skill in the art will appreciate that the invention is not limited to those features exemplified.

1. A method for producing biodiesel, comprising:
providing a microreactor;
flowing a first fluid comprising an alcohol and a second fluid comprising an oil to the microreactor; and
using the microreactor to produce biodiesel.

2-5. (canceled)

6. The method according to claim **1** where the alcohol is methanol, ethanol, propanol, butanol, amyl alcohol or combinations thereof.

7. (canceled)

8. The method according to claim **1** where the oil is derived from soy, inedible tallow and grease, corn, edible tallow and lard, cotton, rapeseed, sunflower, canola, peanut, safflower, and combinations thereof.

9. The method according to claim **1** further comprising using a catalyst to produce the biodiesel, where the catalyst is a metal oxide, metal hydroxide, metal carbonate, alcoholic metal oxide, alcoholic metal hydroxide, alcoholic metal carbonate, an alkoxide, a mineral acid, an enzyme, or combinations thereof.

10-11. (canceled)

12. The method according to claim **9** where the catalyst is sodium hydroxide, potassium hydroxide, sodium alkoxide, potassium alkoxide, or combinations thereof.

13-14. (canceled)

15. The method according to claim **1** further comprising blending biodiesel produced by the method in an amount greater than zero weight percent petroleum product to less than 100 weight percent with petroleum-based products.

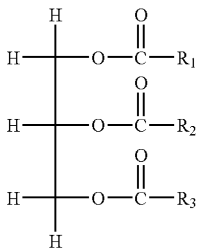
16. (canceled)

17. The method according to claim **1** comprising a transesterification process.

18. The method according to claim **1** performed at supercritical conditions.

19. The method according to claim **18** where the alcohol is supercritical.

20. The method according to claim **1** where the oil is a triglyceride having a formula



where R_1, R_2 and R_3 independently are fatty acids.

21. The method according to claim **20** where the fatty acids have carbon chain lengths ranging from at least as few as 10 carbon atoms to at least as many as 20 carbon atoms.

22. (canceled)

23. The method according to claim **20** where the fatty acids are selected from lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid.

24. The method according to claim **20** where the fatty acid includes at least one site of unsaturation other than a carbon-carbon double bond.

25. The method according to claim **1** further comprising providing at least a 3:1 molar ratio of alcohol-to-triglycerides.

26. The method according to claim **1** where a temperature at which a transesterification reaction is conducted is within a range of from about 25° C. to less than about 350° C.

27. (canceled)

28. The method according to claim **1** further comprising providing plural microreactors.

29. The method according to claim **1** where oil and alcohol fluid layers have fluid layer thicknesses in the microreactor of from about 10 μm to about 500 μm.

30. The method according to claim **1** where surface-to-volume ratio of microreactor microchannels is from about 10,000 m^2/m^3 to about 50,000 m^2/m^3.

31. (canceled)

32. The method according to claim **1** where the microreactor includes at least one manifold for distributing fluid flow to individual microchannels.

33. (canceled)

34. The method according to claim **1** where the oil is soybean oil, the alcohol is methanol or ethanol, and the method further comprises using a metal hydroxide catalyst.

35. The method according to claim **34** where metal hydroxide catalyst is used in an amount of about 1.0 weight % of the soybean oil used for transesterification.

36. The method according to claim **1** where oil and alcohol fluids are pumped to the microreactor using a pump volume flow rate ratio of oil:alcohol of about 3.4.

37. The method according to claim **1** where oil and alcohol fluids are used at a molar ratio of oil-to-alcohol of about 1:7.2.

38. The method according to claim **1** further comprising separating two phases produced by the reaction using a distillation process, a centrifugation process, or combinations thereof.

39-40. (canceled)

41. The method according to claim **1** comprising using a microreactor microchannel having a 100 μm thickness, soybean oil, and a transesterification processing temperature at or about ambient, and where conversion of soybean oil to biodiesel ranges from about 12% at about 0.4 MRT to about 91% at 10 minutes MRT.

42. The method according to claim **1** comprising using a microreactor microchannel having a 100 μm thickness, soybean oil, and a transesterification processing temperature at or about ambient, and where total methyl ester concentration ranges from about 0.3 mol/l at about 0.4 minute MRT to about 2.5 moles/l at about 10 minutes MRT.

43. The method according to claim **1** comprising using a microreactor microchannel having a 200 μm thickness, soybean oil, and a transesterification processing temperature at or about ambient.

44. The method according to claim **43** where conversion of soybean oil to biodiesel ranges from about 4% at about an 0.4 MRT to about 86% at about 10 minutes MRT.

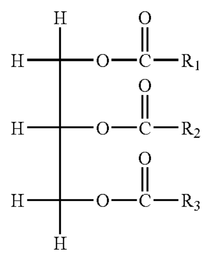
45-64. (canceled)

65. A method for producing biodiesel comprising:

providing a microreactor;

flowing a first fluid to the microreactor comprising a lower aliphatic alcohol;

flowing a second fluid comprising an oil to the microreactor, the oil comprising a triglyceride having a formula



where R_1, R2 and R_3 independently are fatty acids having hydrocarbon chain lengths ranging from at least as few as 10 carbon atoms to at least as many as 20 carbon atoms;

providing a reaction catalyst selected from the group consisting of metal oxides, metal hydroxides, metal carbonates, alcoholic metal oxides, alcoholic metal hydroxides, alcoholic metal carbonates, alkoxides, mineral acids, enzymes, or combinations thereof;

using the microreactor to produce biodiesel; and

blending biodiesel produced by the method with petroleum-based products in an amount greater than zero weight percent petroleum product to less than 100 weight percent petroleum product.

66. The method according to claim **65** performed at supercritical conditions.

67. The method according to claim **65** where the alcohol is supercritical.

68. The method according to claim **65** further comprising providing plural microreactors.

69. The method according to claim **65** further comprising using a cosolvent.

70. The method according to claim **69** where the cosolvent is carbon dioxide.

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