



(51) International Patent Classification:

C10B 53/02 (2006.01) C10B 49/14 (2006.01)
C10L 1/02 (2006.01)

(21) International Application Number:

PCT/US2016/041063

(22) International Filing Date:

6 July 2016 (06.07.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/188,841 6 July 2015 (06.07.2015) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: MOLTEN SALT PYROLYSIS FOR BIO-OIL AND CHEMICALS

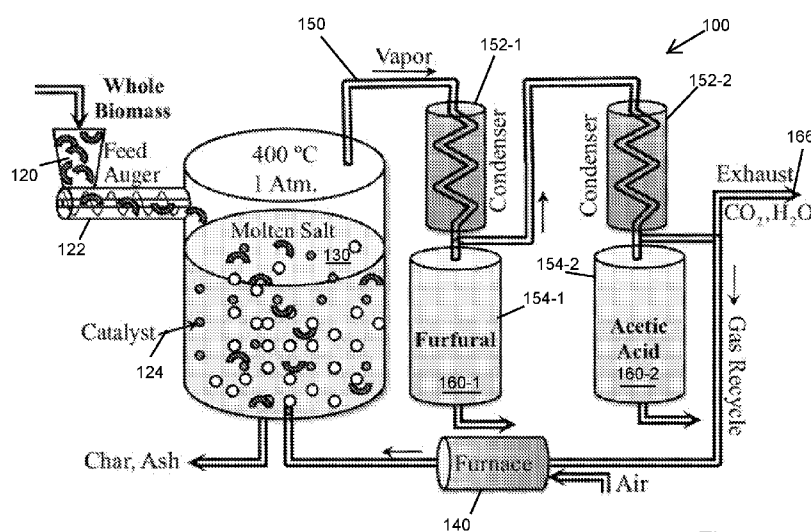


Fig. 1

(57) Abstract: A bio-oil reactor leverages chemically recalcitrant lignocellulosic biomass using a moderate temperature molten-salt based process to unlock hydrocarbon content having the potential to substantially supplement demand for petroleum based fuels and chemicals. Bio-oil is a precursor to production of other chemicals and hydrocarbons, and can be refined as an effective replacement to conventional petroleum products and fossil fuels. A disclosed approach employs Molten-Salt Pyrolysis (MSP), for the efficient and economical production of such precursor chemicals directly from whole biomass under moderate conditions (~400 °C, 1 atm.). Lignocellulosic biomass, freely available in renewable wood and plant products, undergoes a moderate temperature heating process in a eutectic molten salt mixture to generate a condensable vapor of the precursor or platform chemicals.

MOLTEN SALT PYROLYSIS FOR BIO-OIL AND CHEMICALS

BACKGROUND:

Fossil fuels, such as crude oil, natural gas and coal were formed in a process
5 spanning millions of years, yet are being consumed at a rate that guarantees their
depletion in decades. Further, their rapid usage is causing a “green house effect”
and climate change. Hydrocarbons based in prehistoric plants and animals formed
the reserves that are continually sought for combustible fuels. Vast supplies of
renewable hydrocarbons still exist in abundant forests in the form of lignocellulose,
10 yet can be difficult to access due to the recalcitrance of its molecular structure.

Lignocellulosic biomass, in the form of agricultural waste, trees, grasses, and
other plant based mediums, is the most abundant, potentially carbon neutral,
renewable resource available in the world, with more than one billion tons/y
potentially available in the U.S. This could yield ~85 billion gallons of
15 fuels/chemicals, enough to supplant 30% of U.S. petroleum consumption.
Developing new technologies that can utilize this huge renewable resource
effectively and economically could have dramatic implications in the wake of
expiring fossil fuels.

20 SUMMARY:

A method of producing bio-oil and platform chemicals leverages chemically
recalcitrant lignocellulosic biomass using a moderate temperature molten-salt based
process to unlock hydrocarbon content having the potential to substantially
supplement demand for petroleum based fuels and chemicals. Bio-oil hence
25 produced is a precursor to production of other chemicals and hydrocarbons, and can
be refined as an effective replacement to conventional petroleum products and fossil
fuels. A disclosed approach employs Molten-Salt Pyrolysis (MSP), for the efficient
and economical production of such precursor chemicals directly from whole

biomass under moderate conditions (~400 °C, 1 atm.). Lignocellulosic biomass, freely available in renewable wood and plant products, undergoes a moderate temperature heating process in a eutectic molten salt mixture with or without a catalyst to generate a condensable vapor of the bio-oil precursor or platform chemicals. Condensation of the vapor results in a high yield bio-oil having either a broad distribution of products or relatively pure precursor chemicals such as furfural and acetic acid, depending on the molten-salt and catalysts employed and other reaction conditions. Moderate temperatures avoid excessive gasification into non-condensable gases associated with partial combustion or gasification, and avoid non-selective introduction of extraneous chemicals, as in the higher temperature conventional pyrolysis process, that require extensive upgrading or refinement to generate useable yields.

Configurations herein are based, in part, on the observation that current fossil fuel reserves are finite, and subject to inevitable depletion as demand continues. Unfortunately, conventional approaches to petroleum resource management suffers from the shortcoming that alternatives to fossil fuel production are too slow for largescale application or require high temperatures that increase combustion and/or venting of harmful gases. Accordingly, configurations herein substantially overcome the shortcomings of conventional petroleum chemical production by leveraging extensive hydrocarbon resources remaining locked up in renewable vegetation resources. A bio-oil generation process employs common wood and plant feedstock for lignocellulosic biomass input to a moderate temperature MSP for generating high yield and high purity bio-oil that is more easily refineable as a replacement to conventional petroleum based chemicals.

Configurations below, for example, depict a biomass processing platform that involves catalytic pyrolysis of whole biomass in a molten-salt (e.g., KCl-LiCl-ZnCl₂) at moderate temperatures (~400 °C) that directly provides a high yield (>20%) and selectivity (>90%) of platform chemicals, including furfural and acetic acid. Lignocellulosic biomass has the potential to supplant up to a third of petroleum feedstock, a tenth of which is used for chemicals, often commanding a 50% higher market value than fuels, which have been the focus of conventional

biomass conversion processes. These include: 1) the low-temperature (<150°C) solution-phase routes that are selective, but require extensive pretreatment, are sluggish, and produce significant waste; and 2) high-temperature (>500 °C) pyrolysis routes, that are fast but not selective, requiring many upgrading steps to improve purity due to the varied selectivity of the yield. The disclosed approach is an intermediate temperature (350-450 °C) molten-salt pyrolysis (MSP) route that combines these two approaches by using a molten-salt as a solvent phase for efficiently and selectively producing fuels and commodity chemicals directly from whole biomass. The inexpensive molten-salts provide a highly reactive and nonvolatile ionic medium with excellent heat transfer characteristics that allows biomass: 1) dissolution, 2) deconstruction, 3) catalytic dehydration & reconstruction into chemicals, and 4) overhead recovery of product vapors, all in a single containment.

Pyrolysis is generally defined as a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. It typically refers to an irreversible change of chemical composition and physical phase, producing a complex and corrosive conventional bio-oil that can be difficult to refine further, along with significant gases such as carbon monoxide, carbon dioxide, and hydrogen. Configurations herein therefore depict use of MSP for a lower temperature pyrolysis reaction for generating a condensable vapor from which the novel bio-oil is extracted such that gasification of non-condensable products has not yet occurred to a significant extent, as is the case with higher temperate pyrolysis.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following description of particular embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

Fig 1 is a diagram of a bio-oil or chemicals generation apparatus as disclosed herein;

Fig. 2 is a transition diagram of some of the compounds formed in an example configuration in the apparatus of Fig. 1;

5 Fig. 3 is an apparatus of a particular configuration for condensation of furfural and acetic acid from the molten-salt pyrolysis process; and

Fig. 4 shows the effect on liquid yield from vapor condensation of varying the eutectic salt composition, temperature of operation, and biomass feed particle size in various arrangements of the apparatus of Fig. 1.

10

DETAILED DESCRIPTION

Depicted below is an example of operation of a configuration including a containment and condensers for evaporating and collecting the bio-oil. The containment, such as a closed vessel, couples to a cooled condenser or other vessel
15 to undergo cooling for causing the collected vapors to condense. A variety of suitable containment, condensing, and related couplings and/or interconnections may be envisioned in alternate configurations.

The configurations below disclose a method of producing bio-oil from biomass by combining a plurality of salts to form a eutectic salt mixture having a
20 melting point lower than any of the salts individually, and adding a particulated biomass to form a mixture with the eutectic salt. A heat source or furnace heats the mixture in a containment sealed from ambient oxygen above the melting point to generate a molten salt mixture including the particulated biomass and resulting in a vapor. An exhaust conduit, pipe or outflow collects the vapor including bio-oil
25 components, and condenses the vapor for recovering the bio-oil components to generate bio-oil suitable for chemicals or for refining into fuels. In the disclosed configurations, the liquid yield of bio-oil is between 40-60% of the added biomass, substantially higher than conventional pyrolysis approaches. Further, temperatures below 450°C, and typically between 300°-400°C, produce the bio-oil rich vapor,
30 well below that of conventional pyrolysis and refining techniques. The reactor or containment also recovers and reuses the molten salt, since the molten salt remains

unconsumed by the evaporative process. This is permitted because pyrolysis of the bio-mass occurs in MSP at a temperature between the low-temperature solvent based processes that are slow and high temperature pyrolysis processes resulting in gasification of non-condensable gases including H₂ and CO₂.

5 It should be emphasized that the term "Bio-oil" is a generally accepted industry term for products resulting from pyrolysis. Bio-oil is therefore a term often used for the liquids resulting from conventional pyrolysis, which is a mixture of dozens if not hundreds of organic chemicals, hence the name that reminds one of crude oil. Like crude oil, substantial processing is often employed to refine it into
10 fuels and chemicals.

The liquid products resulting from MSP often include much fewer chemicals, e.g., the example cited frequently has only a couple - furfural and acetic acid, and are easier to separate. Such MSP-produced bio-oil as disclosed herein defines the liquid fuels and chemicals resulting from this MSP process. The claimed MSP bio-oil is
15 distinguishable from conventional pyrolysis oil in that the yield is higher and the number of chemicals in it is much smaller, so that it is easier to process as well.

Fig 1 is a diagram of a bio-oil or chemical generation apparatus as disclosed herein. Referring to Fig. 1, the apparatus 100 for performing molten salt pyrolysis (MSP) as disclosed herein includes a single containment vessel 110 receptive to the
20 biomass 120 delivered via a feed auger 122 or other suitable introduction mechanism. Also in the containment vessel 110 is the molten salt mixture 130 and an optional catalyst 124, discussed further below. A furnace 140 or other heat source heats the molten salt mixture (mixture) 130 to result in a vapor 150 drawn into one or more condensers 152-1..152-2 (152 generally). The condensers 152 cool
25 the vapor 150 to cause condensation of the bio-oil 160-1..160-2 (160 generally). Depending on the conditions in the MSP process and temperature of each condenser 152, the extracted condensate may comprise a high purity of condensed substances, such as furfural 160-1 and acetic acid 160-2. Varying the temperature, composition of the molten-salt and catalysts, and arrangement of the bio-oil condensers 154
30 allows collection of varying substances and purity, also discussed further below. Uncondensed gases 166 are exhausted or reused to heat the containment 110,

however the exhausted gases such as recycled CO₂ are expected to result in a net reduction in gaseous by-products and certainly less harmful than corresponding fossil fuel production.

Fig. 2 is a transition diagram of some of the compounds in an example configuration in the apparatus of Fig. 1. Referring to Figs. 1 and 2, in the disclosed approach, leveraging the lignocellulose encapsulated in woody plants 200 for harvesting and deconstruction includes some of the chemical transformations shown in Fig. 2.

A particular difficulty in exploiting the vast lignocellulosic resource is that it is structurally and chemically recalcitrant, comprising of a matrix of cross-linked polysaccharide network of: 1) cellulose 202 (C₆ sugars) and 2) hemicellulose 204 (C₅ sugars), with 3) lignin 206 (aromatic). This recalcitrance is a result of: a) cellulose crystallinity, because of the hydrogen bonding between OH groups on the glucose with O atoms on the same or a neighboring chain, b) presence of biologically and chemically resistant lignin, and c) the cross-linking between polysaccharides (cellulose and hemicellulose) and lignin. To access the carbohydrates for production of bio-based fuels and chemicals, one must first deconstruct this matrix and disrupt the hydrogen-bonding network, either via rapid heating as in pyrolysis, or by the use of a strong derivatizing or non-derivatizing solvent as in solution-phase routes. For instance, in a conventional Kraft process, an NaOH and Na₂S solution (white liquor) is used to separate cellulose from lignin.

In the disclosed approach, the bio-oil is defined by organic compounds resulting from a lignocellulose solution and deconstruction of the biomass. The biomass is easily obtainable from renewable forestry and vegetation sources, and may be in the form of wood chips, shavings, or sawdust, or any suitable plant material. The expected biomass, therefore, is a lignocellulosic biomass defined by a matrix of cross-linked polysaccharide network of the cellulose 202 (C₆ sugars), a hemicellulose 204 (C₅ sugars) and lignin 206.

The MSP process as disclosed herein facilitates deconstruction of the lignocellulosic matrix plus cellulose dissolution via a molten-salt medium, teeming with ions, that is readily able to disrupt the hydrogen-bonding network with its

strong intermolecular forces. Further, via a choice of molten salt anions (e.g. Cl^-) and cations (e.g. Zn^{2+}), multi-step catalysis can be accomplished in situ. In fact, additional catalysts such as acids, bases, metals, and oxides may be readily dispersed within the molten salt for further enhancing selectivity and yield. Furthermore, by using significantly higher temperatures ($\sim 400^\circ\text{C}$) than allowed by conventional solvents or even ionic liquids (ILs) ($< 200^\circ\text{C}$), the MSP process is able to effectively combine the solvation and the lower temperature pyrolysis to accrue the advantages of both routes.

The vapor therefore includes non-volatile components resulting from heating below a temperature defining conventional pyrolysis, which would result in significant gasification of non-condensable substances as well as in a complex bio-oil. The MSP is, thus, is a transformative improvement over competing biomass routes. A particular configuration, shown in Figs. 1 and 2, results in a high yield and purity of furfural and acetic acid. Potential reaction pathways for the wood and woody plants 200 to furfural 210, acetic acid 212, char 214, and other gases are depicted in Fig. 2.

Fig. 3 is an apparatus of a particular configuration for condensation of furfural and acetic acid from the bio-oil. Referring to Figs. 1 and 3, in a production scale, the apparatus 100 defines a continuously operating arrangement 100' for reusing the molten salt 130 and handling particulate accumulations such as char. The arrangement 100' includes a reactor 300 containing the molten salt 130, and a carrier gas 311 to provide a continuous flow and inert environment 312 in the reactor devoid of oxygen and other gases that hinder purity and yield. A carrier gas flow 314 at a regulator 316 controlled pressure ensures a continuous flow 340 of low pressure vapor at the reactor 300 (i.e. containment) outflow 325. A cyclone 330 removes particulate matter from the vapor flow 340 before passing to the collection condensers 154 where the vapor 150 is condensed by a cooling medium 170 surrounding the respective condensers. It should be noted that any suitable condensing device for containing and routing the vapor 150 to a region of lower temperature where the bio-oil components in the vapor are permitted to condense may be employed.

In the example of Fig. 3, the arrangement 100' introduces an inert gas 311 into the sealed containment or reactor 300 for displacing the vapor 150 to a lower temperature containment (condenser 154) for condensing and to ensure an inert atmosphere. The vaporization of the bio-mass occurs at a temperature between solvent based processes and high temperature pyrolysis that would result in gasification of non-condensable gases including H₂ and CO₂. This further results in condensing furfural in a purity of at least 75% and a yield of at least 21% at a temperature substantially around 120° C (condenser 154-1), and in condensing acetic acid in a purity of at least 75% and a yield of at least 25% at a temperature substantially around 105° C (condenser 154-2).

Operating Condition	Value
P (MPa)	0.1
T (°C)	400
N ₂ sweep rate (L min ⁻¹)	2-10
Salt mass (kg)	0.10
Biomass feed rate* (hr ⁻¹)	0.5-2.0
<u>Salt composition</u>	
ZnCl ₂ (mol%)	50
LiCl (mol%)	25
KCl (mol%)	25
<u>Condenser Temperatures</u>	
Furfural condenser (°C)	120
Acetic Acid condenser (°C)	105
Water condenser (°C)	0

* Normalized by total salt mass

TABLE I

In further detail, an example reactor operating according to the parameters in TABLE I is a 316 stainless steel, bolted enclosure, equipped with a high-shear impeller, electric heating blanket 318, and sapphire window 319 for visual access of the process. The less corrosive nature of the bio-oil from MSP permits the use of more conventional vessels and containments. A further advantage to the moderate

temperature, eutectic salt mixture is the conventional containment materials utilized. An auger type biomass feeder 322 delivers ground biomass 320 (1-5 mm diameter) to the reactor 300 and feed rate varied to determine an optimum for stable operation. The inert carrier gas 311 is (N₂) and may be used to strip away volatiles and

5 particulate char. Downstream of the reactor 300, the cyclone 330 removes particular matter larger than 2.5 μ m, and three temperature-controlled condensers at appropriate temperatures for fractional collection of furfural (B.P. = 162 °C), acetic acid (118 °C), and water, respectively. An electrostatic precipitator or HEPA filter 342 may be used for removal of finer particles. An exhaust valve or filter 346 may

10 be used to segregate liquid and gaseous exhaust. Product gas will be continuously analyzed using a dedicated on-line mass spectrometer 344 (1-100 amu).

As indicated above, eutectic salt mixtures have a melting point lower than any of the individual salts. The most favorable results were generated using chloride based molten salts. The selection criterion of molten salts was based on their melting

15 point, pyrolysis performance, and cost. It should be apparent that low melting point, high performance in bio-oil production and lower costs are preferable. Conventional single chloride salts usually have very high melting points; for example potassium chloride melts at 770 °C, sodium chloride at 801 °C, and lithium chloride at 605 °C. In contrast to a single salt, the melting point of mixed salts is usually much lower,

20 especially at some compositions corresponding to eutectic points. Phase diagrams may assist in finding a suitable composition of a eutectic that will melt at a given temperature. TABLE II lists example types of molten salts and eutectic characteristics employed in various configurations. A large variety of other eutectic salt mixtures may be employed.

25

CHLORIDE SALTS USED IN PYROLYSIS OF BIOMASS.

Molten Salts	Molar Ratio	Melting Point (°C)
ZnCl ₂ -KCl-LiCl	40:20:40 ^a	240
AlCl ₃ -KCl	67:33	128
AlCl ₃ -NaCl	55:45	133
CuCl-KCl	65:35	150

ZnCl ₂ -KCl-NaCl	52.9:33.7:13.4	204
ZnCl ₂ -KCl-NaCl	60:20:20	203
KCl-LiCl-NaCl	36:55:9	346
KCl-LiCl-NaCl	24:43:33	357
KCl-MgCl ₂ -NaCl	28.75:43.75:27.5	383
ZnCl ₂	-	283
ZnCl ₂ -KCl	70:30	262
ZnCl ₂ -NaCl	70:30	255
ZnCl ₂ - SnCl ₂	70:30	/

a. These mole percentages are based on the molecular weight of the metal cation.

TABLE II

5

TABLE III depicts the effect of molten salts on the bio-oil composition both qualitatively and quantitatively. Referring to TABLE III and Fig. 3, various bio-oil 160 samples are depicted. Gas chromatography–mass spectrometry (GC-MS) is an effective analytical method to determine the composition of the samples that were produced. Three samples of vapor 150 collected without molten salts comprising the reactor contents yield scattered results of multiple components in the extracted vapor. In contrast, a yield from a MSP generated vapor 150 depicts highly selective and pure furfural and acetic acid.

15 GC/MS results (area %) with (MSP) and without (No.1-3) molten salts.

Content	No. 1	No. 2	No. 3	MSP
Water	28.63	24.51	14.28	49.89
Acetic acid	25.06	25.81	19.82	25.86
Furfural	11.63	14.11	6.90	21.62
2-propanone,1-hydroxy-	11.20	11.50	10.36	-
Acetic acid, methyl ester	2.98	2.73	1.96	-
Propanic acid	2.02	2.28	1.15	-

1-hydroxy-2-butanone	0.97	1.81	1.87	-
2-cyclopenten-1-one,2-hydroxy-	-	1.46	2.6	-
Phenol,2-methoxy-4-methyl	2.50	1.23	3.66	-
Ethanone,1-(2-furanyl)-	1.47	1.18	2.34	-
Undefined organic products	10.88	9.78	66.68	-

TABLE III

Another contributing factor is the particle size of the shredded and/or particularized biomass fed through the auger. Four groups of sawdust biomass, each having a different particle size range, were processed through the reactor 310. The mass of sawdust in each run was 5 g and the reaction was conducted at carrier gas flow rate of 165 CC/min and at a temperature of 350 °C. TABLE IV shows the effect of particle size of biomass on bio-oil yield without molten salts. Theoretically, the finer the particle size that biomass has, the higher the bio-oil yield should be. Since the woody composition exhibits low thermal conductivity, fine particle size biomass has the ability of transferring heat to its inner core faster than the larger particle size biomass, which favors the formation of bio-oil. Moreover, smaller particles show better mass transfer.

15

Effect of particle size on yield of bio-oil without molten salt.

Particle size (μm)	Yield (%)
<106	18.6
106-212	19.1
300-450	14
600-850	13.8

TABLE IV

5 In contrast, Fig. 4 shows the improvement of addition of molten salts on the bio-oil yield. Compared with Table 3, 32.6% liquid yield was obtained with CuCl-KCl molten salts for the particle size between 106-212 μm , while only 19.1% was attained without molten salts at the same temperature. This improvement was even more significant for the particle size lower than 106 μm , i.e., 41% with molten salts and 18.6% without salts. In the presence of CuCl-KCl molten salts, biomass of

10 particle size between 106-212 μm exhibited lower yield of bio-oil than that of particle size < 106 μm . This finding not only proved that fine particle should produce high yield of bio-oil, but also illustrated that the advantage of molten salts. Thus, biomass particles would be evenly distributed within a molten salt solvent

15 which could suppress the possible agglomeration of fine particles in the absence of molten salts. The ternary molten salts, ZnCl_2 -KCl-LiCl also had the same function and gave higher yield below 450 °C.

Referring to Figs. 1 and 4, Fig. 4 shows the effect of varying the eutectic salt composition and particle size in various arrangements of the apparatus of Fig. 1.

20 Referring to Figs. 1 and 4, various compositions and yields are as follows. An example biomass feed scenario includes a feed of 5 g sawdust at a flow rate of 165 CC/min. The mass ratio of feed to molten salt was 1:10. The % yield 410 plotted according to temperature 420 yields the following:

25 Diamond 401 : CuCl (65% mol), KCl (35% mol), particle size: <106 μm ;
 Square 402: CuCl (65% mol), KCl (35% mol), particle size: 106-212 μm ;

Triangle 402 : ZnCl₂ (40% mol), KCl (20% mol), LiCl (20% mol), particle size: <106 μm.

Circle 402 : ZnCl₂ (40% mol), KCl (20% mol), LiCl (20% mol), particle size: 106-212 μm.)

- 5 Mole percentages in ZnCl₂- KCl- LiCl were based on the molecular weight of the metal cation.

- As discussed above, MSP product yield and selectivity can benefit from addition of additional catalysts 124, such as Bronsted acids, Lewis acids, or Bronsted bases to the molten salt 130. For example, phosphomolybdic acid
- 10 generally improves liquid yield at all temperatures. It has been found that the stronger Lewis acids (e.g., AlCl₃ and CuCl₂) are less effective than ZnCl₂, providing a lower yield, and a significantly wider product distribution.. For Bronsted acids, we can use the Keggin-type heteropolyacids containing W, Mo, and Si, with a focus on silicotungsten and phosphotungstic acids, given their superior thermal stability.¹⁰⁰
- 15 These represent a clear trend in Brønsted acidity (W > Mo > Si for the polyatom, and P > Si = Ge for the central atom) permitting trends in acid strength to be examined. A tandem Lewis acid (e.g., ZnCl₂) and Bronsted acid functionality can also have beneficial effects. For Bronsted bases, KOH, NaOH, and LiOH may be employed. Again, these follow a clear trend in strength (LiOH > NaOH > KOH).
- 20 Table V shows the effect of addition of a catalyst on the bio-oil yield with different molten salts. In Table V, yield 1 represent bio-oil yields obtained without catalyst, while yield 2 represented bio-oil yields obtained with phosphomolybdic acid catalyst, just as an example of a catalyst that might be employed. In most cases shown, ternary molten salt provided higher bio-oil yield than binary molten salt. The
- 25 groups containing ZnCl₂ gave higher yield than those without ZnCl₂. In ZnCl₂ containing salts, the one with LiCl showed higher yield than the ones with Na.

Effect of combination of different molten salts (yield 1) and
addition of catalyst (yield 2) on bio-oil yield.

Molten salt	Yield 1	Yield 2
Cu-K	36.80%	48%
Zn-K-Li	51.50%	60.40%
Zn-Na-K	47.80%	51.60%
Zn-Na-K ¹	46.70%	54.60%
K-Li-Na	36.20%	43.00%
K-Li-Na ¹	39.50%	46.00%

(Condition: Feed: 5 g sawdust; Flow rate: 165 CC/min; Mass ratio of feed to molten salt: 1:10; Particle size: 106-212 μm ; Temperature: 400 °C. Cu-K: CuCl (65% mol), KCl (35% mol); 2 g phosphomolybdic acid was used as catalyst; Zn-K-Li: ZnCl₂ (40% mol), KCl (20% mol), LiCl (20% mol), molar ratio based on the molecular weight of the metal cation; 1 g phosphomolybdic acid; Zn-Na-K: ZnCl₂ (52.9% mol), NaCl (13.4% mol), KCl (33.7% mol); 1 g phosphomolybdic acid; Zn-Na-K¹: ZnCl₂ (60% mol), NaCl (20% mol), KCl (20% mol); 1 g phosphomolybdic acid; K-Li-Na: KCl (36% mol), LiCl (55% mol), NaCl (9% mol); 1 g phosphomolybdic acid; K-Li-Na¹: KCl (24% mol), LiCl (43% mol), NaCl (33% mol); 1 g phosphomolybdic acid.)

TABLE V

In summary, the composition of bio-oil derived from pyrolysis of sawdust can be very complicated which could contain hundreds of substances. Moreover, as the pyrolysis temperature increases, the composition of bio-oil became more complicated. Introduction of molten salt to the pyrolysis system narrowsthe product distribution significantly.

20

While the system and methods defined herein have been particularly shown and described with references to embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

25

CLAIMS

What is claimed is:

1. A method of producing bio-oil and chemicals from biomass, comprising:
combining a plurality of salts to form a eutectic salt mixture having a melting
5 point lower than any of the salts individually;
adding a particulated biomass to form a mixture with the eutectic salt;
heating the mixture in a containment sealed from ambient oxygen to a
temperature above the melting point to generate a molten salt mixture including the
particulated biomass and resulting in a product vapor;
10 collecting the product vapor, the vapor including bio-oil components and
chemicals, and
condensing the vapor for recovering the bio-oil components to generate bio-oil
for refining.
- 15 2. The method of claim 1 wherein the bio-oil is defined by a plurality of organic
compounds resulting from a solution and deconstruction of the lignocellulose biomass.
3. The method of claim 2 wherein the biomass is a lignocellulosic biomass defined
by a matrix of cross-linked polysaccharide network of cellulose (C₆ sugars) a
20 hemicellulose (C₅ sugars) and lignin.
4. The method of claim 1 wherein the vapor further includes non-volatile
components resulting from heating below a temperature defining conventional
pyrolysis.
25
5. The method of claim 1 wherein a liquid yield of bio-oil is between 40-60% of
the added biomass.

6. The method of claim 5 wherein the temperature is below 450°C.
7. The method of claim 6 wherein the temperature is between 300-400°C.
- 5 8. The method of claim 1 further comprising recovering and reusing the molten salt, the molten salt being unconsumed by any evaporative process.
9. The method of claim 1 further comprising introducing an inert gas into the sealed containment for displacing the vapor to a lower temperature containment for
10 condensing and to ensure an inert atmosphere.
10. The method of claim 1 wherein vaporization of the bio-mass occurs at a temperature between low-temperature conventional solvent based processes and high temperature pyrolysis, the high temperature pyrolysis defined by gasification of non-
15 condensable gases including H₂ and CO₂.
11. The method of claim 5 further resulting in condensing furfural in a purity of at least 75% and a yield of at least 21%.
- 20 12. The method of claim 5 further resulting in condensing acetic acid in a purity of at least 75% and a yield of at least 25% at a temperature substantially around 105° C.
13. The method of claim 5 further resulting in a mixture of organic chemicals comprising the bio-oil.
25
14. The method of claim 1 wherein the plurality of salts are selected from the group consisting of:
ZnCl₂-KCl-LiCl,

AlCl₃-KCl,
AlCl₃-NaCl,
CuCl-KCl,
ZnCl₂-KCl-NaCl,
ZnCl₂-KCl-NaCl,
KCl-LiCl-NaCl,
KCl-LiCl-NaCl,
KCl-MgCl₂-NaCl,
ZnCl₂,
ZnCl₂-KCl,
ZnCl₂-NaCl and
ZnCl₂- SnCl₂.

15. The method of claim 1 wherein the bio-oil yield contains compounds selected from the group consisting of:

Acetic acid,
Furfural,
2-propanone,1-hydroxy-,
Acetic acid, methyl ester,
Propanic acid,
1-hydroxy-2-butanone,
2-cyclopenten-1-one,2-hydroxy-,
Phenol,2-methoxy-4-methyl and
Ethanone,1-(2-furanyl)-.

16. A biomass reactor device, comprising:
a containment vessel sealed from ambient oxygen and having a plurality of

combined salts to form a eutectic salt mixture having a melting point lower than any of the salts individually;

a feeder to add a particulated biomass to form a mixture with the eutectic salt;

a heat source to heat the mixture in the containment to an operating temperature

5 above the melting point of the eutectic salt mixture to generate a molten salt mixture including the particulated biomass and resulting in a vapor;

an outflow from the containment vessel to collect the vapor, the vapor including bio-oil components, and

at least one condenser coupled to the outflow to receive and condense the vapor
10 and recover the bio-oil components to generate bio-oil for refining.

17. The device of claim 16 wherein the bio-oil is defined by organic compounds resulting from a lignocellulose solution and deconstruction of the biomass, and the biomass is a lignocellulosic biomass defined by a matrix of cross-linked polysaccharide
15 network of cellulose (C₆ sugars) a hemicellulose (C₅ sugars) and lignin.

18. The device of claim 16 wherein the vapor includes non-volatile components resulting from heating below a temperature defining pyrolysis, the vaporization of the bio-mass occurring at a temperature between low temperature conventional solvent
20 based processes and high temperature pyrolysis that would result in substantial gasification of non-condensable gases including H₂ and CO₂.

19. The device of claim 16 wherein the liquid yield of bio-oil is between 40-60% of the added biomass and the operating temperature is between 300-450°C.

25

20. The device of claim 16 wherein the reactor is operative to recover and reusing the molten salt, the molten salt being unconsumed by the evaporative process, and further operative to introduce an inert gas into the sealed containment for displacing the

vapor to a lower temperature containment for condensing and to ensure an inert atmosphere.

21. The device of claim 16 further comprising:

5 a condensed bio-oil containing furfural in a purity of at least 75% and a yield of at least 21% at a temperature substantially around 120° C, and

a condensed bio-oil containing acetic acid in a purity of at least 75% and a yield of at least 25% at a temperature substantially around 105° C.

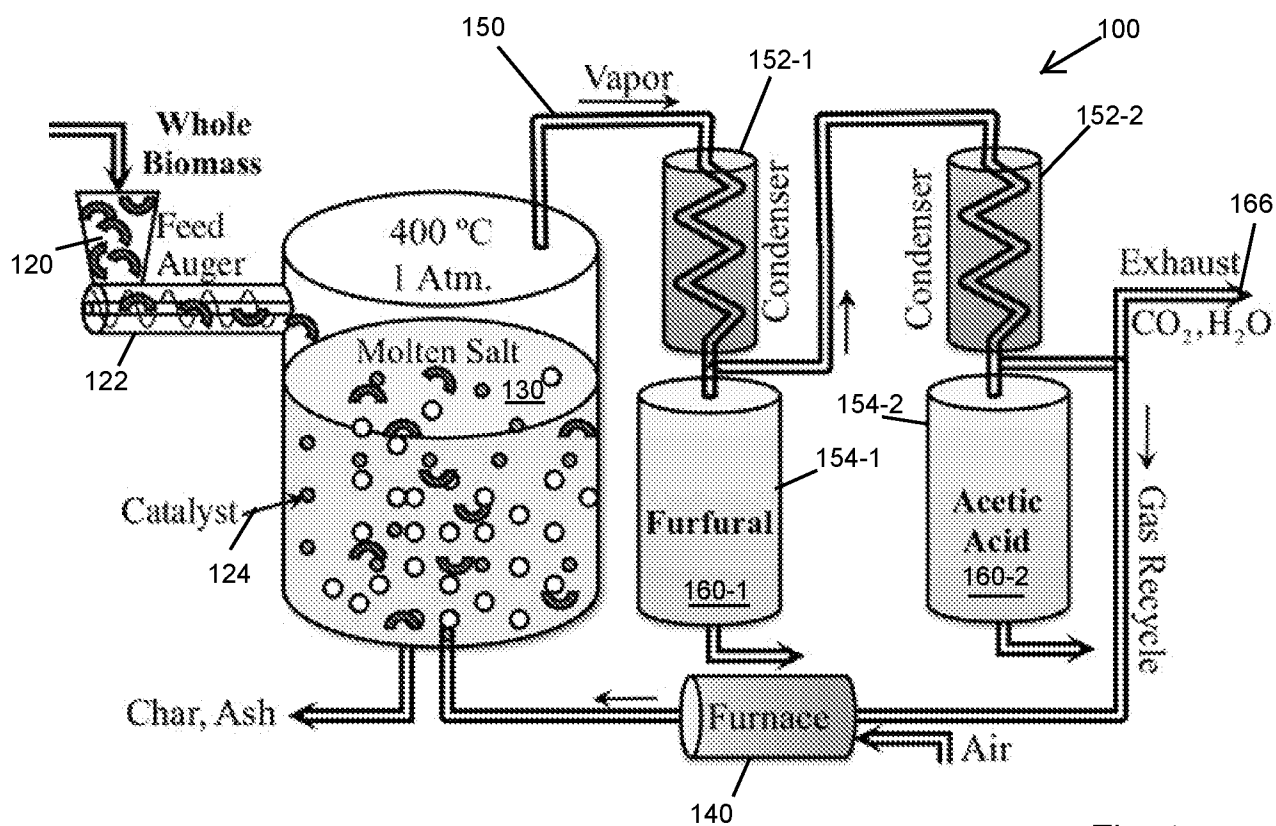


Fig. 1

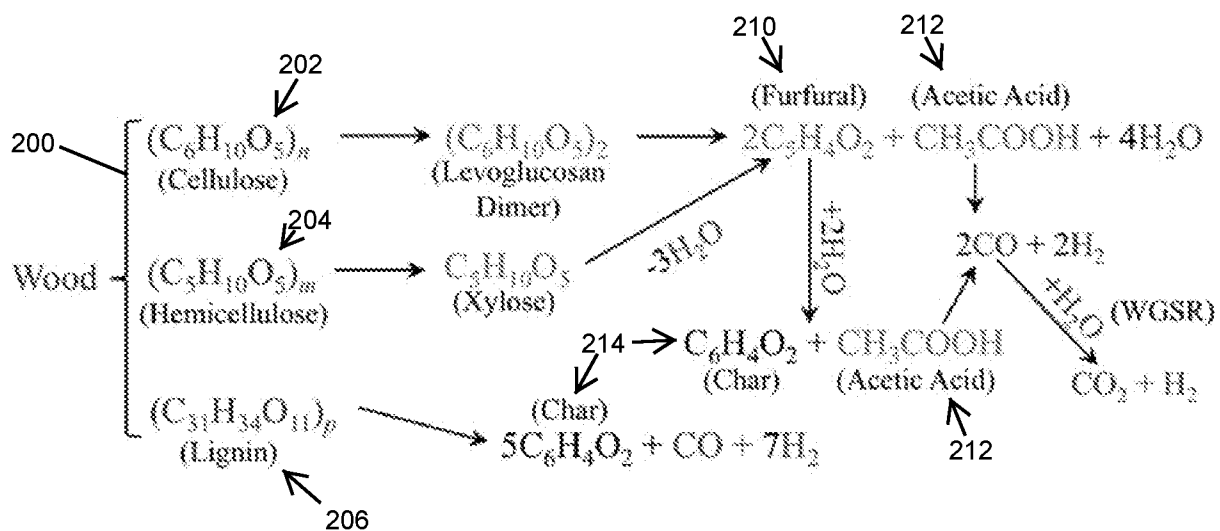


Fig. 2

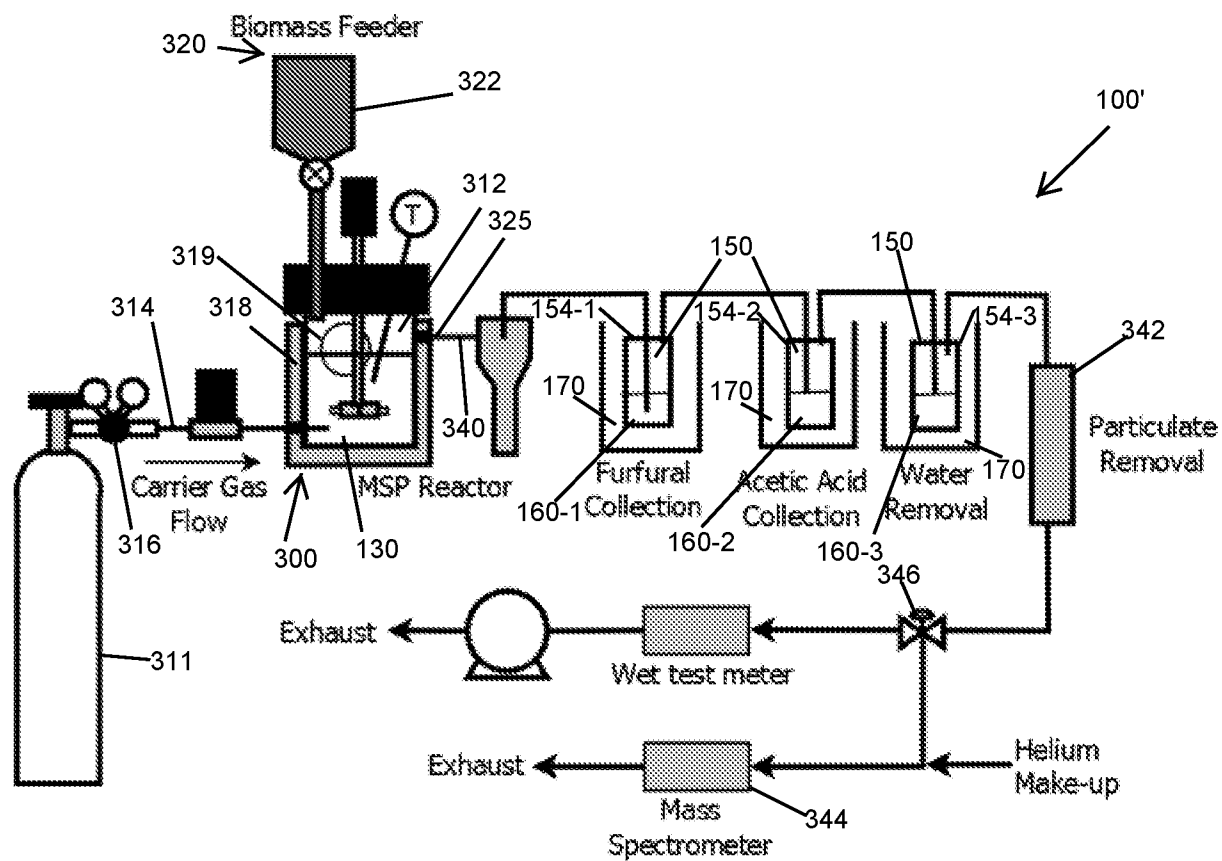


Fig. 3

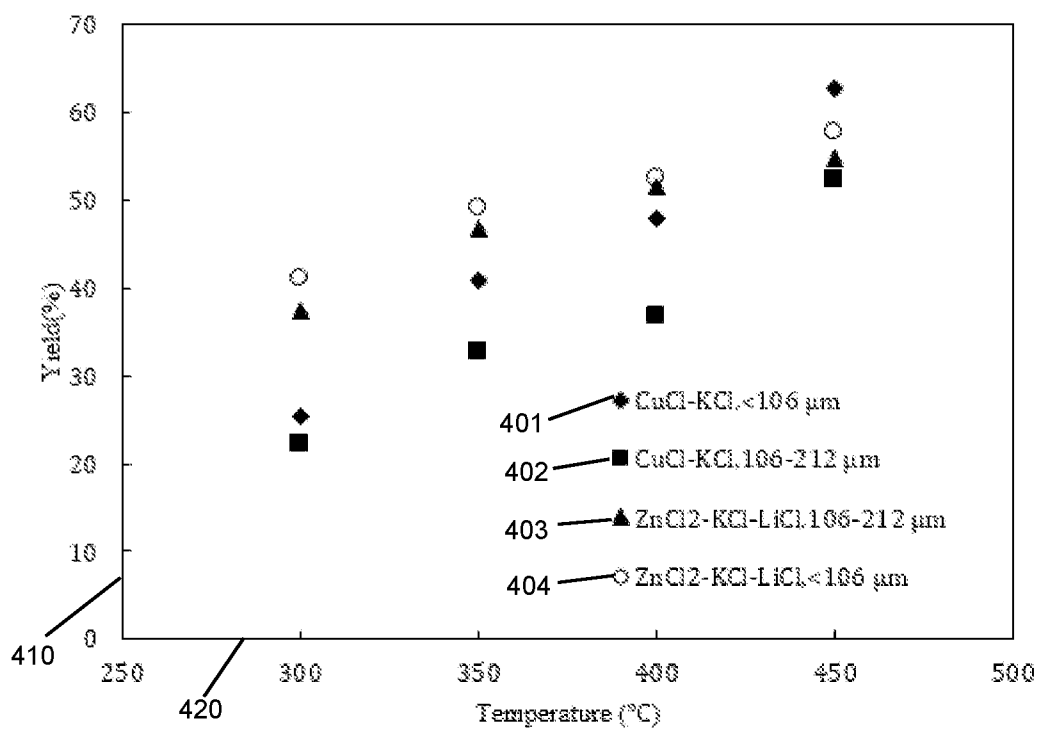


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/041063

A. CLASSIFICATION OF SUBJECT MATTER		
<i>C10B 53/02 (2006.01)</i> <i>C10L 1/02 (2006.01)</i> <i>C10B 49/14 (2006.01)</i>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C10B 53/02, C10L 1/02, C10B 49/14, F25J 1/00, 1/02, C10L 3/00, B01J 6/00, C10L 5/40, B01J 19/00, C10L 5/42, C01B 3/44		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
VINITI, RUPAT, EAPATIS, Espacenet, PAJ, USPTO, CIPO, DEPATISnet, Patentscope, PatSearch (RUPTO internal)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/016149 A1 (ACADEMIA SINICA et al.) 02.02.2012, claims, paragraphs [0003], [0012], [0031], [0033], [0047], [0082], [0084], tables, drawings	1-13, 15-21
Y		14
X	WO 2010/090863 A2 (RENTECH, INC. et al.) 12.08.2010, claim 13, paragraph [0055]	1-13, 15-21
A	WO 2010/122525 A1 (SARTORI SAVINO) 28.10.2010, claims, drawings	1-21
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
*	Special categories of cited documents:	
“A”	document defining the general state of the art which is not considered to be of particular relevance	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E”	earlier document but published on or after the international filing date	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O”	document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search		Date of mailing of the international search report
25 August 2016 (25.08.2016)		24 November 2016 (24.11.2016)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer E. Guseva Telephone No. (495)531-64-81