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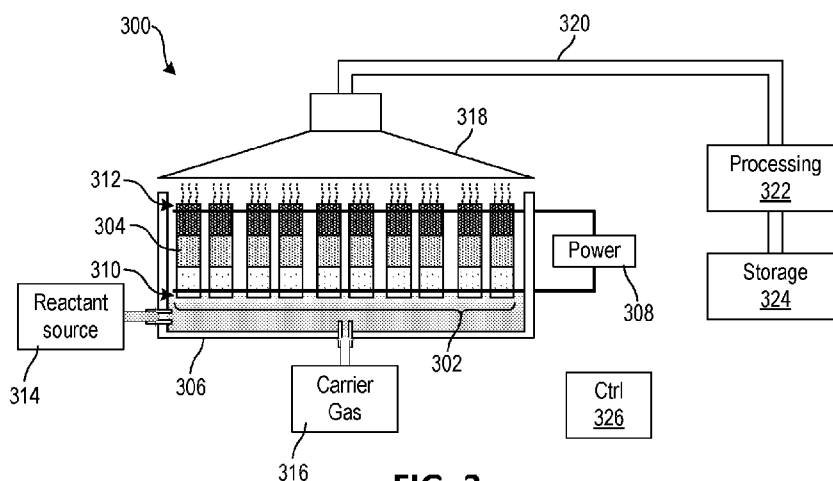


FIG. 3

(57) Abstract: An organic polymer can be converted to one or more lower molecular weight products by subjecting to one or more heating cycles in a porous reactor. The reactant can be provided to an inlet end of the reactor, and the products can be provided from an outlet end of the reactor. A first reactor portion at the inlet end of the reactor can have a pore size or porosity greater than that of a second reactor portion at an outlet end of the reactor. In some embodiments, the different pore sizes or porosities of the reactor portions can modulate mass transport and/or heat transfer behavior of intermediates to select for particular products at the outlet end with high yield.



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**THERMOCHEMICAL CONVERSION METHODS, AND
REACTOR SYSTEMS FOR THERMOCHEMICAL CONVERSION**
CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of and priority under 35 U.S.C. § 119(e) to and
5 is a non-provisional of U.S. Provisional Application No. 63/508,181, filed June 14, 2023, entitled
“Systems, Devices, and Methods for Converting Plastics and Natural Macromolecules into Useful
Chemicals,” which is hereby incorporated by reference herein in its entirety.

FIELD

The present disclosure relates generally to chemical processing, and more particularly, to
10 conversion of plastics and other macromolecules (e.g., biomass) into useful chemicals, such as but
not limited to fuel (e.g., jet fuel, gasoline, diesel fuel, etc.).

BACKGROUND

Despite promotion as an ecological solution, plastic recycling faces significant challenges.
Current mechanical recycling methods are limited, yielding low-quality products. While existing
15 thermochemical methods have the capability to yield higher-value products, they suffer from poor
product selectivity and low system durability due to coking, catalyst degradation, and side
reactions. The limited product yield and selectivity is due in part to the inability of existing
methods to control the reaction progress and pathways. In particular, conventional plastic
pyrolysis techniques often exhibit broadening of molecular weight distribution of the
20 intermediates and the final product due to the poorly controlled reaction progress, which
fundamentally prevents achievement of high selectivity. The utilization of natural
macromolecules (e.g., lignin) as a feedstock in conventional thermochemical processes faces
similar hurdles. Embodiments of the disclosed subject matter may address one or more of the
above-noted problems and disadvantages, among other things.

SUMMARY

Embodiments of the disclosed subject matter system provide thermochemical conversion
of a reactant with enhanced and/or controllable selectivity for one or more products. In some
embodiments, the reaction progress and/or pathway for conversion of the reactants can be
controlled using a reactor with different pore sizes or porosities, for example, to tailor for
30 particular intermediates and eventual products based on size as the chemicals move through the
reactor. Alternatively or additionally, in some embodiments, the heat transfer to the reactants can
be improved, for example, by coating surfaces of the reactor with the reactant, and/or residence
time within the reactor controlled, for example, by using vibration applied to the reactor to enhance
extraction of products therefrom before undesirable reactions of the products can occur. In some

embodiments, the reactant is an organic polymer (e.g., plastic, biomass, etc.), and the one or more products comprise C₈-C₁₈ hydrocarbons.

5 In one or more embodiments, a method can comprise converting a reactant to one or more products by subjecting to one or more heating cycles in a porous reactor. The reactant can be provided to an inlet end of the reactor, and the one or more products can be provided from an outlet end of the reactor. A first reactor portion at the inlet end of the reactor can have a first pore size or porosity. A second reactor portion at the outlet end of the reactor can have a second pore size or porosity. The inlet and outlet ends can be separated from each other along an axial direction of the reactor. The second pore size or porosity can be less than the first pore size or porosity. The
10 reactant can be a polymer comprising carbon. At least some of the one or more products can have a molecular weight less than a molecular weight of the reactant.

In one or more embodiments, a system can comprise one or more porous reactors. Each reactor can have first and second reactor portions. The first reactor portion can be at an inlet end of the respective reactor and can have a first pore size or porosity. The second reactor portion can
15 be at an outlet end of the respective reactor and can have a second pore size or porosity. The inlet and outlet ends can be separated from each other along an axial direction of the respective reactor. The second pore size or porosity can be less than the first pore size or porosity. Each porous reactor can be configured to convert a reactant supplied to the inlet end into one or more products at the outlet end by subjecting to one or more heating cycles.

20 In one or more embodiments, a method can comprise loading a reactant onto one or more surfaces of a reactor, and subjecting the reactor to heating at a first temperature such that the loaded reactant forms a reactant coating on the one or more surfaces. The method can further comprise, after the subjecting to heating at the first temperature, converting at least part of the reactant coating to one or more products by subjecting to one or more heating cycles. The one or
25 more heating cycles can comprise a peak temperature greater than the first temperature. The reactant can be a thermoset plastic or biomass. At least some of the one or more products can have a molecular weight less than a molecular weight of the reactant.

In one or more embodiments, a system can comprise a reactor having one or more surfaces coated with a reactant. The reactant can be a thermoset plastic or biomass. The reactor can be
30 configured to convert the reactant coating into one or more products by subjecting to one or more heating cycles.

Any of the various innovations of this disclosure can be used in combination or separately. This summary is provided to introduce a selection of concepts in a simplified form that are further described below in the detailed description. This summary is not intended to identify key features

or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter. The foregoing and other objects, features, and advantages of the disclosed technology will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments will hereinafter be described with reference to the accompanying drawings, which have not necessarily been drawn to scale. Where applicable, some elements may be simplified or otherwise not illustrated in order to assist in the illustration and description of underlying features. Throughout the figures, like reference numerals denote like elements.

FIG. 1A is a simplified schematic diagram of a polymer conversion system employing a porous reactor having two portions with different pore sizes, according to one or more embodiments of the disclosed subject matter.

FIG. 1B is a simplified schematic diagram of a polymer conversion system employing a porous reactor with gradually narrowing pores, according to one or more embodiments of the disclosed subject matter.

FIG. 1C is a simplified schematic diagram of a polymer conversion system employing a porous reactor having two portions with different porosity, according to one or more embodiments of the disclosed subject matter.

FIG. 1D is a simplified schematic diagram of a polymer conversion system employing porous reactors portions with different pore sizes or porosities, according to one or more embodiments of the disclosed subject matter.

FIG. 2A is a simplified schematic diagram of a polymer conversion system employing a porous reacting having sequential Joule heating portions heated via a common electrical current, according to one or more embodiments of the disclosed subject matter.

FIG. 2B is a graph depicting aspects of a non-continuous or discontinuous heating profile than can be employed in a polymer conversion system, according to one or more embodiments of the disclosed subject matter.

FIG. 2C is a graph of an exemplary pulse heating profile that can be employed in a polymer conversion system, according to one or more embodiments of the disclosed subject matter.

FIG. 2D is a simplified schematic diagram of a polymer conversion system employing a porous reacting having sequential Joule heating portions heated via respective electrical currents, according to one or more embodiments of the disclosed subject matter.

FIG. 2E is a simplified schematic diagram of a polymer conversion system employing a porous reactor having sequential portions heated by respective heating modules, according to one or more embodiments of the disclosed subject matter.

5 FIG. 3 illustrates a continuous-type integrated electrified polymer conversion system, according to one or more embodiments of the disclosed subject matter.

FIG. 4 is a process flow diagram of a generalized method for conversion a polymer reactant into one or more products using a porous reactor, according to one or more embodiments of the disclosed subject matter.

10 FIG. 5A is a simplified schematic diagram illustrating aspects for pre-processing a reactor to coat surfaces thereof with reactant, according to one or more embodiments of the disclosed subject matter.

FIG. 5B is a simplified schematic diagram of a conversion system employing Joule heating of a reactant-coated reactor, according to one or more embodiments of the disclosed subject matter.

15 FIG. 5C is a simplified schematic diagram of a conversion system employing a heating module to heat a reactant-coated reactor, according to one or more embodiments of the disclosed subject matter.

20 FIG. 5D is a simplified schematic diagram of a conversion system employing a vibration module to assist release of product from a reactant-coated reactor, according to one or more embodiments of the disclosed subject matter.

FIG. 6 is a process flow diagram of a generalized method for conversion of a reactant into one or more products using a reactant-coated reactor, according to one or more embodiments of the disclosed subject matter.

25 FIG. 7 depicts a generalized example of a computing environment in which the disclosed technologies may be implemented

FIG. 8A is a simplified cross-sectional view of a three-zone pyrolysis reactor fabricated with graded internal pore sizes.

FIG. 8B is a simplified cross-sectional view of a fabricated single zone pyrolysis reactor having only large pore size.

30 FIG. 8C is a simplified cross-sectional view of a fabricated single zone pyrolysis reactor having only small pore size.

FIG. 9A show schematic representations of cross-sections of the different zones of the pyrolysis reactor of FIG. 8A.

FIG. 9B illustrates the core temperature of the different zones of the fabricated pyrolysis reactor of FIG. 8A during multiple heating cycles, measured using femto-second laser-inscribed single crystal sapphire fiber Bragg grating.

FIG. 9C illustrates the temperature distribution across the cross-section of the different stages of the fabricated pyrolysis reactor of FIG. 8A at peak temperature of a heating cycle.

FIG. 10A is a graph of product composition and polydispersity index for the different pyrolysis reactors of FIGS. 8A-8C.

FIGS. 10B-10D illustrate the yield of different hydrocarbon compositions for the different pyrolysis reactors of FIGS. 8B, 8C, and 8A, respectively.

FIG. 11A is a graph comparing adiabatic flame temperatures of products generated using the fabricated pyrolysis reactor of FIG. 8A and of common aviation fuels (jet fuels A1-C6).

FIG. 11B is a graph comparing radical indices of products generated using the fabricated pyrolysis reactor of FIG. 8A and a common aviation fuel (jet fuel A).

DETAILED DESCRIPTION

General Considerations

For purposes of this description, certain aspects, advantages, and novel features of the embodiments of this disclosure are described herein. The disclosed methods and systems should not be construed as being limiting in any way. Instead, the present disclosure is directed toward all novel and nonobvious features and aspects of the various disclosed embodiments, alone and in various combinations and sub-combinations with one another. The methods and systems are not limited to any specific aspect or feature or combination thereof, nor do the disclosed embodiments require that any one or more specific advantages be present, or problems be solved. The technologies from any embodiment or example can be combined with the technologies described in any one or more of the other embodiments or examples. In view of the many possible embodiments to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated embodiments are exemplary only and should not be taken as limiting the scope of the disclosed technology.

Although the operations of some of the disclosed methods are described in a particular, sequential order for convenient presentation, it should be understood that this manner of description encompasses rearrangement, unless a particular ordering is required by specific language set forth below. For example, operations described sequentially may in some cases be rearranged or performed concurrently. Moreover, for the sake of simplicity, the attached figures may not show the various ways in which the disclosed methods can be used in conjunction with other methods. Additionally, the description sometimes uses terms like “provide” or “achieve” to

describe the disclosed methods. These terms are high-level abstractions of the actual operations that are performed. The actual operations that correspond to these terms may vary depending on the particular implementation and are readily discernible by one skilled in the art.

The disclosure of numerical ranges should be understood as referring to each discrete point within the range, inclusive of endpoints, unless otherwise noted. Unless otherwise indicated, all numbers expressing quantities of components, molecular weights, percentages, temperatures, times, and so forth, as used in the specification or claims are to be understood as being modified by the term “about.” Accordingly, unless otherwise implicitly or explicitly indicated, or unless the context is properly understood by a person skilled in the art to have a more definitive construction, the numerical parameters set forth are approximations that may depend on the desired properties sought and/or limits of detection under standard test conditions/methods, as known to those skilled in the art. When directly and explicitly distinguishing embodiments from discussed prior art, the embodiment numbers are not approximates unless the word “about,” “substantially,” or “approximately” is recited. Whenever “substantially,” “approximately,” “about,” or similar language is explicitly used in combination with a specific value, variations up to and including 10% of that value are intended, unless explicitly stated otherwise.

Directions and other relative references may be used to facilitate discussion of the drawings and principles herein but are not intended to be limiting. For example, certain terms may be used such as “inner,” “outer,” “upper,” “lower,” “top,” “bottom,” “interior,” “exterior,” “left,” “right,” “front,” “back,” “rear,” and the like. Such terms are used, where applicable, to provide some clarity of description when dealing with relative relationships, particularly with respect to the illustrated embodiments. Such terms are not, however, intended to imply absolute relationships, positions, and/or orientations. For example, with respect to an object, an “upper” part can become a “lower” part simply by turning the object over. Nevertheless, it is still the same part, and the object remains the same.

As used herein, “comprising” means “including,” and the singular forms “a” or “an” or “the” include plural references unless the context clearly dictates otherwise. The term “or” refers to a single element of stated alternative elements or a combination of two or more elements unless the context clearly indicates otherwise.

Although there are alternatives for various components, parameters, operating conditions, etc. set forth herein, that does not mean that those alternatives are necessarily equivalent and/or perform equally well. Nor does it mean that the alternatives are listed in a preferred order, unless stated otherwise. Unless stated otherwise, any of the groups defined below can be substituted or unsubstituted.

Unless explained otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one skilled in the art to which this disclosure belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described below.

- 5 The materials, methods, and examples are illustrative only and not intended to be limiting. Features of the presently disclosed subject matter will be apparent from the following detailed description and the appended claims.

Overview of Terms

10 The following is provided to facilitate the description of various aspects of the disclosed subject matter and to guide those skilled in the art in the practice of the disclosed subject matter.

Heating Cycle: Application of a high temperature (e.g., at least 300 °C, for example, at least 500 °C) to a reactor for a short duration time period, after which heating ceases to allow the reactor and material therein to rapidly cool (e.g., via passive cooling, or active cooling via a cooling modality). In some embodiments, the duration of the heating cycle includes a duration of the heating period (first time period) and the duration of immediately following non-heating or cooling period (second time period). In some embodiments, the duration of the heating period may be no more than 10% of a duration of the heating cycle. In some embodiments, the duration of the heating cycle is less than or equal to 5 s (e.g., ≤ 2 s), the duration of the first time period is less than 500 ms (e.g., 10-200 ms), and the duration of the second time period is less than or equal to 4.5 s (e.g., ≤ 1 s). In some embodiments, heating to a peak temperature immediately prior to the heating period may be at a ramp rate of at least 10^2 °C/s (e.g., about 10^2 - 10^5 °C/s), and/or cooling from the peak temperature immediately after the heating period may be at a ramp rate of at least 10^2 °C/s (e.g., about 10^2 - 10^5 °C/s). In some embodiments, the heating cycle may be similar to that described in U.S. Publication No. 2023/0144856, published May 11, 2023, and entitled “High-temperature shock heating for thermochemical reactions,” and International Publication No. WO 2023/059622, published April 13, 2023 and entitled “Polymer processing systems and methods employing pulsed heating,” both of which are incorporated by reference herein.

Peak temperature: A maximum temperature of one or more heating elements when energized (e.g., by application of a current pulse) and/or experienced by materials within the reactor (e.g., reactant and/or intermediate products) during the heating period of the heating cycle. In some embodiments, the peak temperature is greater than a melting temperature of a reactant being processed, for example, at least about 300 °C (e.g., at least 500 °C). In some embodiments, the temperature at a material being processed (e.g., reactant and/or reactor) can match or substantially match (e.g., within 10%) the temperature of the heating element.

Reactant: A starting material to be subjected to heating in a reactor to convert the material into one or more products having a lower molecular weight than the starting material. In some embodiments, the reactant comprises a synthetic organic polymer (e.g., plastic, rubber, etc.), a natural organic polymer (e.g., rubber or a biomass, such as plant, algae, and/or sawdust, or components thereof, such as cellulose, hemicellulose, lipids, carbohydrates, and/or proteins),
5 supramolecule (e.g., hydrogen-bonded acetic acid dimer), biomass, or any combination of the foregoing.

Pore size: A cross-sectional dimension (e.g., diameter) of pores (e.g., voids or openings) in a reactor, or portion thereof. In some embodiments, the size of the pores can be measured via
10 imaging of a cross-section of the material, for example, via optical microscopy, electron microscopy (e.g., scanning electron microscopy), or X-ray micro-computed-tomography (micro-CT) imaging (e.g., American Society for Testing and Materials (ASTM) F2450-18, *Standard Guide for Assessing Microstructure of Polymeric Scaffolds for Use in Tissue-Engineered Medical Products*, ASTM International, West Conshohocken, PA, 2018, which is incorporated herein by
15 reference). Alternatively or additionally, in some embodiments, the pore sizes of the reactor can be characterized by performing one or more porometry or porosimetry tests on the reactor (or portion thereof). For example, the pore sizes can be characterized by capillary flow porometry, bubble point testing (e.g., ASTM F316-03(2019) *Standard Test Methods for Pore Size Characteristics of Membrane Filters by Bubble Point and Mean Flow Pore Test*, ASTM
20 International, West Conshohocken, PA, 2019, which is incorporated herein by reference), or mercury intrusion porosimetry (e.g., UOP578-11, *Automated Pore Volume and Pore Size Distribution of Porous Substances by Mercury Porosimetry*, ASTM International, West Conshohocken, PA, 2011, or U.S. Pharmacopeial Convention for Micromeritics and Particulate Systems Instruments <267>, *Porosimetry by Mercury Intrusion*, U.S. Pharmacopeial Convention,
25 Rockville, MD, 2012, both of which are incorporated herein by reference). In some embodiments, the pore size is a mean value for pores in the cross-section. In some embodiments, the pore size of a reactor portion is less than or equal to 2 mm, for example, in a range of 100 nm to 2 mm, inclusive.

Porosity: A measure of void spaces within a reactor, or portion thereof. In some
30 embodiments, the porosity can be measured using liquid displacement, gas pycnometry, SEM imaging, mercury intrusion porosimetry, or any other method known in the art. Alternatively or additionally, porosity can be determined based on a size (e.g., diameter) and packing density of constituent structures (e.g., fibers) forming the reactor portion.

Fluidity: The ability of the reactant to flow when heated above its glass transition or melting temperature, for example, reactants having a Melt Flow Index (MFI). In some embodiments, the reactants with fluidity are thermoplastics. Alternatively, in some embodiments, reactants without fluidity are substantially incapable of flowing regardless of heating, for example, thermoset plastics or biomass.

Introduction

Embodiments of the disclosed subject matter provide systems and methods for thermochemical conversion (e.g., pyrolysis) of reactants with enhanced and/or controllable selectivity for one or more products, for example, for polymers in a particular size range (e.g., C₈-C₁₈ hydrocarbons). In some embodiments, the reaction progress and/or pathway for conversion of the reactants can be controlled using a reactor with different pore sizes or porosities, for example, to tailor for particular intermediates and eventual products based on size. For example, for reactants with fluidity, a porous reactor can be used to subject the reactant to one or more heating cycles (e.g., in an oxygen-free environment) so as to convert the reactant to the one or more products. The porous reactor can have portions with different pore sizes or porosities. For each successive reactor portion (e.g., downstream zone), the pore size or porosity thereof can be decreased as compared to previous reactor portions (e.g., upstream zones). In some embodiments, the decreasing pore sizes or porosities as chemicals move through the reactor can modulate mass transport and/or heat transfer behavior of intermediates to select for particular products with high yield (e.g., $\geq 60\%$).

In some embodiments, the heat transfer to the reactants can be improved and/or release of products enhanced to limit residence time within the reactor. For example, for reactants without fluidity, one or more surfaces of a reactor can be coated with the reactant, and the coated reactor can be used to subject the reactant to one or more heating cycles so as to convert the reactant to one or more products. In some embodiments, vibration can be applied to the reactor to assist in release and/or removal of the one or more products from the reactor for use and/or further processing before undesirable reactions of the products can occur.

In some embodiments, the reactor and materials therein (e.g., reactant, intermediates, etc.) can be subjected to one or more heating pulses of short duration (e.g., < 1 s, for example, in a range of 10-500 ms) that break bonds between molecular fragments, while a rest period (e.g., non-heating or cooling period) between consecutive heating pulses can suppress pathways (e.g., random scission, dehydrogenation, and aromatization side reactions that have longer reaction timescales) toward undesired side products (e.g., aromatics, coke, soot, etc.). Embodiments of the disclosed subject matter employing pulsed heating can thus operate in the far-from-equilibrium

regime, as opposed to the near-equilibrium reactions offered by constant heating. In some embodiments, the pulsed heating can heat the reactor to induce a spatial temperature profile therein (e.g., a temperature gradient), for example, due to the different pore sizes and/or porosities of reactor portions. Thus, in some embodiments, the heating can generate a spatial temperature profile that varies along an axial direction of the reactor (e.g., a direction in which the reactant, intermediates, and/or products flow) and a temporal temperature profile (e.g., with periods of heating at a high temperature separated by periods without heating), which temperature profiles may further enhance product selectivity and/or yield.

In some embodiments, the thermochemical conversion of reactant can offer high product yields (e.g., greater than 50%, e.g., at least 60%) without requiring a catalyst (e.g., substantially catalyst-free). Rather, the reactor configurations in combination with the pulsed heating approach disclosed herein can offer high selectivity by controlling the reaction kinetics while also creating periodic high temperatures (e.g., ≥ 300 °C for ≤ 0.5 s) to enable rapid bond activation and thus a high reaction rate.

Embodiments of the disclosed subject matter can be applied to process a wide range of synthetic polymers (e.g., plastic), rubber, natural macromolecules, supramolecules, and biomass, for example, to produce value-added feedstock chemicals (e.g., fuels) and/or other desirable products. For example, the reactant can comprise a plastic having a carbon-carbon backbone (e.g., C-C bond connecting monomer fragments), such as but not limited to rubber, polypropylene (PP), polystyrene (PS), polyvinyl alcohol (PVA), polyvinyl acetate (PVAc), polyethylene (PE), poly(methyl methacrylate) (PMMA), acrylonitrile butadiene styrene (ABS), and/or polyvinyl chloride (PVC). Alternatively or additionally, the reactant can comprise a plastic having a carbon-noncarbon backbone (e.g., C-X bond connecting monomer fragments, such as C-O or C-N), such as but not limited to polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyurethane (PU), nylon, unsaturated polyester (UPE), polycarbonate (PC), epoxy, and/or polyether. Alternatively or additionally, the reactant can comprise a biomass derived from, produced by, and/or existing in a naturally-occurring plant (e.g., wood, grass, bamboo, etc.), insect, crustacean, algae, or other organism, such as but not limited to lignin, cellulose, hemicellulose, rosin, chitin, chitosan, lipid, carbohydrate, and/or protein.

Conversion Reactors and Systems for Reactants with Fluidity

FIG. 1A illustrates a generalized thermochemical reaction system according to one or more embodiments of the disclosed subject matter, for example, for use in converting a reactant with fluidity into one or more desired products. In the illustrated example, the reaction system has a porous reactor 100 formed by a first reactor portion 102 (e.g., upstream portion adjacent to inlet

end 124 of the reactor) and a second reactor portion 106 (e.g., downstream portion adjacent to outlet end 126 of the reactor). The first and second reactor portions can be arranged sequentially (e.g., adjacent to and/or in direct contact with each other) each other along an axial direction 122 of the reactor 100 (e.g., parallel to a direction in which reactant proceeds through the reactor). A reactant source 110 (e.g., a reservoir) arranged at the inlet end 124 (e.g., adjacent to and/or in direct contact with the first reactor portion 102) can provide a continuous or batch supply of reactant for processing by the reactor. Although illustrated separately, in some embodiments, the first reactor portion 102, the second reactor portion 106, and/or the reactant source 110 can be formed as different portions of a single integrated structure (e.g., a 3D printed structure).

The reaction system can also include a control system 114, for example, for regulating heating 116, 118 applied to reactor portions 102, 106, respectively. In some embodiments, the control system 114 can heat the reactor portions to a high temperature (e.g., ≥ 300 °C) for a short duration (e.g., ≤ 500 ms) followed by a longer duration period without heating to allow the reactor portions to cool to a lower temperature (e.g., at least 50 °C less). In some embodiments, the same heating can be applied to each reactor portion 102, 106. Alternatively or additionally, the heating applied to the reactor portions 102, 106 can result in a spatial temperature gradient along the axial direction 122, for example, such that a peak temperature in the first reactor portion 102 is greater than a peak temperature in the second reactor portion 106.

In the illustrated example, the first reactor portion 102 has pores 104 (e.g., channels) extending along the axial direction 122, and the second reactor portion 106 has pores 108 (e.g., channels) extending along the axial direction 122. In some embodiments, the size of pores 104 of the first reactor portion 102 are greater than the size of pores 108 of the second reactor portion 106, such that the pore size is reduced as the reactant (or intermediates) proceed through the reactor from the inlet end 124 to the outlet end 126. For example, the residence time of the reactant (or intermediates) in a particular reactor portion (stage or zone) can be defined at least in part by a size of the pores to enter a subsequent stage and/or exit a current stage.

One or more carrier gases can optionally be provided (e.g., to reactant source 110 and/or inlet end 124 of the reactor). For example, the carrier gas can comprise hydrogen (H_2), nitrogen (N_2), or a noble gas (e.g., argon (Ar) or helium (He)). In some embodiments, the carrier gas can be supplied to a flowpath in the reactor separate from the reactants, for example, to act as a sweep gas to carry resulting products emanating at 120 from the outlet end 126. In some embodiments, the reactor 100 is not pressurized during operation, such that the thermochemical reactions proceeding therein occur at or near atmospheric pressure (e.g., ~ 1 bar). Alternatively, in some

embodiments, the reactor 100 can be disposed in a pressure chamber or other enclosure, for example, to allow the reactions to occur at an elevated pressure (e.g., 20 MPa or ~200 bar).

In operation, reactant from the reactant source 110 is conveyed (e.g., via carrier gas 112, gravity, capillary forces, and/or diffusion) into the pores 104 of the first reactor portion 102 heated by heating 116 to a first elevated temperature (e.g., ≥ 500 °C), which drives pyrolysis of the reactant therein into intermediates. Smaller-sized intermediates are able to progress downstream into the second reactor portion 106, while larger-sized intermediates are prevented from progressing by the smaller pores 108 of the second reactor portion 106. Rather, the larger-sized intermediates are retained in the first reactor portion 102 for further pyrolysis during the same or subsequent heating cycle. Meanwhile, the smaller-sized intermediates in the second reactor portion 106 can be subjected to a second elevated temperature via heating 118 during the same or subsequent heating cycle, for further pyrolysis to one or more desired products. In some embodiments, the second elevated temperature is less than the first elevated temperature, which can minimize, or at least reduce, reaction of the intermediates in the second reactor portion 106 to undesired products (e.g., low-value lighter hydrocarbons).

In some embodiments, the thermochemical conversion of reactant via the porous reactor to one or more products at 120 can be performed without use of any catalyst. However, although embodiments of the disclosed subject matter do not require a catalyst, any known or later developed catalyst can optionally be used for a particular thermochemical reaction conducted by the reaction system. For example, a catalyst can be incorporated on or embedded within the reactor (e.g., one or more of the reactor portions 102, 106). In some embodiments, the catalyst can be a single element or multi-elemental (e.g., binary, ternary, high-entropy, etc.) and/or the catalyst can comprise a metal (e.g., Ru, Fe, Ni, etc.) or alloys thereof. Exemplary catalysts can include, but are not limited to, Zeolite Socony Mobil-5 (ZSM-5), Co/Ni pillared montmorillonites, iron oxide impregnated HY zeolite, mesoporous HZSM-5, $\text{Al}_2\text{O}_3/\text{ZSM-5}$ tandem, Ru/SiO_2 , $\text{m-SiO}_2/\text{Pt}/\text{SiO}_2$, Ru/C , $\alpha\text{-Ni}/\text{SiO}_2$, single-site formally cationic Zr-alkyl/hydride, $\text{p-Ru}/\text{SBA}$, $\text{L-ZrO}_2/\text{m-SiO}_2$, $\text{m-SiO}_2/\text{Pt}/\text{SiO}_2$, $\text{Pt}/\text{WO}_3/\text{ZrO}_2+\text{HY}$, $\text{Pt}/\text{WO}_3/\text{ZrO}_2$, $\text{Pt}/\text{W}/\text{beta}$, bifunctional zeolite, Pt-impregnated USY, zeolite beta, ruthenium nanoparticles on zeolite FAU or zeolite BEA, $\text{Ni}/\text{HZSM-5}$, MoS_x -H beta, Ir PINCER complex, $\text{Re}_2\text{O}_7/\text{g-Al}_2\text{O}_3$, Ru/TiO_2 , or any combination of the foregoing. In some embodiments, the catalysts can comprise nanoparticles formed *in situ* within the reactor 100 (e.g., one or more of the reactor portions 102, 106), for example, by using a high-temperature shock synthesis method, such as that described in U.S. Pat. Application Publication No. 2019/0161840, which is incorporated by reference herein.

In the illustrated example of FIG. 1B, the size of pores 104, 108 in the respective reactor portions 102, 106 is substantially constant along the axial direction 122. However, in some embodiments, the pore sizes within reactor can change along the axial direction, for example, to provide pores that narrow as the flow moves through the reactor. For example, FIG. 1B illustrates a porous reactor 130 with pores 132 that gradually narrow from the inlet end 136 to the outlet end 138. Thus, a first reactor portion 134a of the reactor 130 adjacent to the inlet end 136 exhibits the largest pore size while a downstream second reactor portion 134b adjacent to the outlet end 138 exhibits the smallest pore size. Similar to the example of FIG. 1A, the reactant from the reactant source 140 is conveyed (e.g., via carrier gas 112, gravity, capillary forces, and/or diffusion) into the larger-sized end of pores 132 in the first reactor portion 134a, while heating 142 can drive pyrolysis of the reactant therein into intermediates. The intermediates are able to progress downstream within the pores 132 until the narrowed pore size prevents, or at least restricts, further movement downstream, thereby controlling residence time within the heated reactor for selection of particular products.

In the illustrated examples of FIGS. 1A-1B, the pores within the porous reactor (or portion thereof) are configured as continuous channels extending along the axial direction 122. However, embodiments of the disclosed subject matter are not limited to such a configuration. Indeed, in some embodiments, the pores of the reactor (or portions thereof) may form tortuous paths (e.g., due to randomly arranged or interwoven constituent fibers) rather than axially-extending continuous channels. In such configurations, the different portions of the reactor may be characterized by porosity in place of, or in addition to, pore size. For example, FIG. 1C illustrates a porous reactor 150 formed by a first reactor portion 152 (e.g., upstream portion adjacent to inlet end 162 of the reactor) and a second reactor portion 156 (e.g., downstream portion adjacent to outlet end 164 of the reactor). The first reactor portion 152 can have a porosity 154 that is greater than a porosity 158 of the second reactor portion 156, such that porosity is reduced as the reactant (or intermediates) proceed through the reactor from the inlet end 162 to the outlet end 164.

The residence time of the reactant (or intermediates) in a particular reactor portion (stage or zone) can be defined at least in part by the porosity of the subsequent stage. Thus, similar to the example of FIG. 1A, the reactant from the reactant source 160 can be conveyed (e.g., via carrier gas, gravity, capillary forces, and/or diffusion) into the more porous first reactor portion 152, which is heated by heating 166 to a first elevated temperature (e.g., ≥ 500 °C) to drive pyrolysis of the reactant therein into intermediates. Smaller-sized intermediates are able to progress downstream into the second reactor portion 156, while larger-sized intermediates are prevented, or at least restricted, from progressing due to the lower porosity in the second reactor

portion 156. Meanwhile, the smaller-sized intermediates in the second reactor portion 156 can be subjected to a second elevated temperature via heating 168 during the same or subsequent heating cycle, for further pyrolysis to one or more desired products.

In the illustrated examples of FIGS. 1A-1C, the pore size or porosity extends through the entire reactor portion. However, in some embodiments, the pore size or porosity may be provided at only an entry to or exit from a particular reactor portion (e.g., a boundary between successive reactor portions and/or adjacent to an outlet end of the reactor). For example, FIG. 1D illustrates a porous reactor 170 formed by a first stage 172 and a second stage 175. In the illustrated example, the first stage 172 includes first reactor portion 173 and a second reactor portion 174 adjacent to the second stage 175. Similar to the above-described examples, the second reactor portion 174 can have a pore size and/or porosity that prevents, or at least restricts, downstream movement of reactant and/or larger-sized intermediates therethrough while allowing smaller-sized intermediates to proceed downstream. In the illustrated example, the second stage 175 includes a third reactor portion 177 and a fourth reactor portion 176 adjacent to an outlet end 184 of the reactor 170. The fourth reactor portion 176 can have a pore size and/or porosity smaller than that of the second reactor portion 174, for example, to allow only products less than a particular size to exit the reactor. In some embodiments, one or both of the first reactor portion 173 of the first stage 172 and the third reactor portion 177 of the second stage 175 can have a plurality of large size pores (e.g., greater than that of the second reactor portion 174) or simply have a single chamber.

Similar to the previously described examples, the residence time of the reactant (or intermediates) in a particular stage can be defined at least in part by the pore size or porosity of the reactor portion at the end of the respective stage. Thus, the reactant from the reactant source 180 adjacent the inlet end 182 can be conveyed (e.g., via carrier gas, gravity, capillary forces, and/or diffusion) into first reactor portion 173 of the first stage 172, which is heated by heating 186 to a first elevated temperature (e.g., ≥ 500 °C) to drive pyrolysis of the reactant therein into intermediates. Smaller-sized intermediates are able to progress downstream through the second reactor portion 174 into the third reactor portion 177 of the second stage 175, while larger-sized intermediates are prevented, or at least restricted, from progressing due to the lower pore size or porosity in the second reactor portion 174. Meanwhile, the smaller-sized intermediates in the third reactor portion 177 can be subjected to a second elevated temperature via heating 188 during the same or subsequent heating cycle, for further pyrolysis. Products of the desired size can exit the reactor via the fourth reactor portion 176 of the second stage 175, while intermediates that have

not yet attained the desired size are retained within the third reactor portion 177 by the fourth reactor portion 176 for further pyrolysis.

Although the examples of FIGS. 1A, 1C, and 1D illustrate porous reactors with only two reactor portions or stages, any number of reactor portions and/or stages are also possible according to one or more contemplated embodiments. Moreover, in some embodiments, the reactor itself can provide the elevated temperature via self heating in response to a current flow therethrough (e.g., Joule heating) or a separate heating module can be used to heat the reactor to the elevated temperature.

Referring to FIG. 2A, a thermochemical reaction system employing a reactor 200 with more than two reactor portions or stages 202 is shown. In the illustrated example, the reactor 200 includes reactor portions 202-1 through 202- n , where n is an integer greater than 2. Similar to the above-described examples, the pore size and/or porosity of a downstream reactor portion can be less than that of an adjacent upstream reactor portion, such that the pore size and/or porosity of the reactor 200 decreases (e.g., in a step-wise manner) as flow moves along the axial direction 214 from an inlet end 210 (e.g., adjacent reservoir 204) to an outlet end 212. For example, in some embodiments, the number (n) of reactor portions is three, the first reactor portion 202-1 can have a pore size that is at least two times a pore size of the second reactor portion 202-2, and the second reactor portion 202-2 can have a pore size that is at least two times a pore size of the third reactor portion 202-3. For example, the pore size of the first reactor portion 202-1 can be in a range of 500 μm to 2 mm (e.g., ≤ 1 mm), the pore size of the second reactor portion 202-2 can be in a range of 200 nm to 1 mm (e.g., ≤ 500 μm), and the pore size of the third reactor portion 202-3 can be in range of 100 nm to 300 μm (e.g., ≤ 200 nm).

In the illustrated example of FIG. 2A, the reactor 200 is configured as a Joule heating element, with an electrical power supply 206 connected to the opposite axial ends 210, 212 for applying a voltage thereto. Due to their different pore sizes and/or porosities, the reactor portions have different electrical resistivities, with the first reactor portion 202-1 having the highest resistance and the last reactor portion 202- n having the lowest resistance. Since the same current 216 from the power supply 206 flows through each of the reactor portions 202-1 through 202- n , the reactor portions experience different levels of Joule heating, with the high-resistance first reactor portion 200-1 experiencing the highest temperature and the last reactor portion 202- n experiencing the lowest temperature, thereby forming a temperature gradient (e.g., stepwise gradient) along the axial direction 214.

The reactor portions 202-1 through 202- n can be constructed of any material that has sufficient electrical resistivity (e.g., to achieve peak temperature for a given power input of at least

300 °C), high temperature resistance (e.g., a melting temperature greater than planned peak temperature), and low heat capacity (e.g., to enable rapid, sub-second heating (R_H) and cooling (R_C) rates in a range of 10^2 °C/s to 10^5 °C/s). In some embodiments, one, some, or all portions of the reactor 200 can be formed of pure carbon or a carbon-containing material, such as silicon carbide (SiC). For example, in some embodiments, the reactor is composed only of carbon fibers, carbon felt, carbon cloth, carbon nanotube fibers, carbon nanofibers, carbon foam, graphene, or combinations thereof. Alternatively, in some embodiments, one, some, or all portions of the reactor 200 can be formed of carbon, metal, ceramic, or any combination thereof.

In some embodiments, a control system 208 can be operatively coupled to the power supply 206 to control operation thereof, for example, to periodically apply current 216 to provide discontinuous heating (also referred to herein as pulsed heating or programmable heating and quenching (PHQ)) of the reactor 200. Alternatively, the control system 208 and the power supply 206 can be combined together as a single unit (e.g., a programmable or programmed power supply). In operation, the reactant from reservoir 204 be provided to the inlet end 210 of the reactor 200, where it is subjected to multiple heating cycles (e.g., each with its own peak temperature and minimum temperature) in either a continuous mode of operation (e.g., reactant flow from the inlet end 210, through the interior of the reactor 200, to the outlet end 212 remains substantially constant or at least active during the multiple heating cycles) or batch mode of operation (e.g., reactant flow into the inlet end 210 and/or product flow from outlet end 212 is paused after one or more of the multiple heating cycles, for example, to replenish reactant in reservoir 204). In some embodiments, the residence time (e.g., the time period during which the reactant, resulting intermediates, and/or resulting products are in thermal contact with the reactor) for the reactant can be on the order of tens of seconds or minutes (or even greater), while the period of each heating cycle may be on the order of seconds (e.g., 5 seconds or less, such as ~ 1 second).

Referring to FIG. 2B, an exemplary heating profile or waveform 230 for PHQ is shown. During each heating cycle, the material within a respective reactor portion (e.g., reactant and/or intermediate) is subjected to a peak temperature, T_H , (e.g., at least 300 °C, such as 500 °C or greater) for a first part 232 of the heating cycle and a lower quenching temperature, T_L , (e.g., at least 50 °C less than the peak temperature) for a second part 234 of the heating cycle. In some embodiments, the second part 234 of the heating cycle is achieved by cessation of heating (e.g., by not applying a voltage or current 216 to the reactor 200), such that the reactor 200 rapidly cools from the peak temperature T_H to the lower quenching temperature T_L , for example, at a cooling rate of at least 10^2 °C/s. In some embodiments, the duration, t_1 , of the first part 232 for peak temperature is less than the remainder of the heating cycle, for example, no more than 10% of the

cycle period, τ (e.g., a first part of 15-150 ms in duration for a total cycle duration of 2 s). Conversely, the duration, t_2 , of the second part 234 for the quenching temperature can constitute the majority of the heating cycle period, τ (e.g., a second part of less than or equal to 1 s in duration). The systems and methods for providing Joule heating of the reactor can be similar to those disclosed in International Publication No. WO 2020/236767, published November 26, 2020, and entitled “High temperature sintering systems and methods,” and International Publication No. WO 2022/204494, published September 29, 2022, and entitled “High temperature sintering furnace systems and methods,” both of which are incorporated herein by reference.

Although shown in idealized form in FIG. 2B, temperatures experienced in practical implementations of the disclosed thermochemical reaction system may deviate slightly from the idealized form. For example, FIG. 2C illustrates an example of a pulsed heating profile 236 for Joule heating of the reactor 200. While the waveform 238 of the applied electrical power follows the desired rectangular pulse configuration, with a first part 240 defining the peak temperature and a second part 242 defining the quench temperature, the actual temperatures 244 generated by the reactor can deviate slightly therefrom, for example, by having a longer cooling rate due to slower cooling effect. Nevertheless, the reactor is constructed such that the temperature of the reactants can be rapidly changed between a peak temperature and a minimum temperature in each heating cycle in the second or sub-second regime. In some embodiments, active or passive cooling techniques can be employed to enhance the cooling rate (e.g., to more closely follow the idealized form of the rectangular pulse).

In the illustrated example of FIG. 2A, the same current flows through each reactor portion (e.g., along the axial direction 214), with the different pore characteristics (e.g., pore size and/or porosity) of the reactor portions generating a spatial temperature gradient within the reactor during each heating cycle. Alternatively, in some embodiments, one, some, or each of the reactor portions can be separately Joule heated (e.g., by flowing current along the axial direction or crossing the axial direction) to allow for independent control of the temperature in the different reactor portions. For example, FIG. 2D shows a thermochemical reaction system employing a reactor 250 with serially-arranged reactor portions 252-1, 252-2,... 252- n having different pore sizes and/or porosities, such that the pore size and/or porosity of the reactor 250 decreases (e.g., in a step-wise manner) as flow moves along the axial direction from an inlet end 260 (e.g., adjacent reservoir 254) to an outlet end 262. Separate power supplies 256-1, 256-2,... 256- n (or independently controllable outputs of a common power supply) are electrically connected to reactor portions 252-1, 252-2,... 252- n , respectively, for supplying independent electrical currents 266-1, 266-2,... 262- n thereto. Control system 258 can be operatively coupled to the power supplies for controlling

operation thereof, for example, to periodically apply the respective currents to the reactor portions to provide temporal heating in a manner similar to that described above.

Although Joule heating of the reactor has been used to provide temporal heating (e.g., PHQ) in FIGS. 2A and 2D, embodiments of the disclosed subject matter are not limited thereto.

5 Rather, in some embodiments, one or more separate heating modalities can be used to heat the reactor, or portions thereof, with or without Joule heating of the reactor. For example, FIG. 2E shows a thermochemical reaction system employing a reactor 270 with serially-arranged reactor portions 272-1, 272-2,... 272-*n* having different pore sizes and/or porosities, such that the pore size and/or porosity of the reactor 270 decreases (e.g., in a step-wise manner) as flow moves along
10 the axial direction from an inlet end 2800 (e.g., adjacent reservoir 274) to an outlet end 282. Separate heating modules 276-1, 276-2,... 276-*n* (or independently controllable outputs of a single heating module) are in thermal communication with reactor portions 272-1, 272-2,... 272-*n*, respectively, for providing heating 286-1, 286-2,... 286-*n* thereto. Control system 278 can be operatively coupled to the heating modules for controlling operation thereof, for example, to
15 periodically apply heating to the reactor portions to provide temporal heating in a manner similar to that described above. In some embodiments, each heating module can comprise a Joule heating system, a microwave heating system, a laser heating system, an electron beam heating system, a spark discharge heating system, a plasma heating system, and/or any other heating system capable of providing the peak temperature, heating rate, and/or cooling rate to the reactor portion.

20 In some embodiments, multiple reactors can be arrayed together, for example, to increase a scale of production and/or to operate in a continuous or semi-continuous manner. For example, FIG. 3 illustrates a thermochemical conversion system 300 having an array 302 of porous reactors 304 (e.g., 3-stage reactors) arranged in parallel within a housing 306 for converting reactants (e.g., plastic) provided from a reactant source 314 (e.g., shredder) in a continuous manner. In the
25 illustrated configuration, ten column reactors 304 are connected in parallel to electrical power supply 308. However, other numbers of reactors and/or different connections are also possible according to one or more contemplated embodiments.

In some embodiments, reactant (e.g., polyolefin plastics) can be provided to an inlet end 310 of the array 302 within housing 306, where the reactant can melt. Propelled by a carrier gas
30 from gas supply 316, the reactant melt can enter the individual reactors 304, where the pulsed heating generated by passing a current through the reactor 304 via power supply 308 can convert the reactant to desired products at high selectivity and yield, in a manner similar to that described above. The products exiting the reactors 304 at an outlet end 312 thereof can be collected by a capture hood 318, conveyed via conduit 320 to a post-processing unit 322 (e.g., cooling unit to

condense, or at least reduce the temperature of, the collected products), and then stored at 324 for later use or transport. In the illustrated example, control system 326 may be in communication with the different components of system 300 and be configured to control operation thereof.

Conversion Methods for Reactants with Fluidity

5 FIG. 4 illustrates a method 400 for thermochemical conversion of a reactant (e.g., organic polymer) with fluidity to one or more products using a porous reactor. The method 400 can initiate at process block 402, where the porous reactor for thermochemical reaction system can be provided. In some embodiments, the provided reactor has a pore characteristic (e.g., pore size and/or porosity) that varies along a direction of flow of reactants, for example, to provide size
10 selection for products and/or control residence time within the reactor. For example, the provided reactor can have a structure similar to any of the porous reactors and/or reactor systems described with respect to FIGS. 1A-3, or elsewhere herein. In some embodiments, the provision of process block 402 can include 3D printing. Alternatively or additionally, the provision of process block 402 can include assembling together different porous substrates or structures, e.g., felt, cloth,
15 foam, etc.

 The method 400 can proceed to decision block 404, where it is determined if a catalyst is desired. While a catalyst is not required for effective thermochemical conversion, provision of a catalyst may further increase product yield or selectivity in some embodiments. If a catalyst is desired, the method 400 can proceed to process block 406, where the reactor is provided with an
20 appropriate catalyst. In some embodiments, the catalyst can be provided on and/or within the reactor (e.g., an internal volume thereof, such as surfaces of the pores and/or constituent fibers forming the reactor). For example, the catalyst can be a metal catalyst (e.g., Ru, Fe, Ni, alloys thereof), a multi-elemental catalyst (e.g., binary, ternary, high-entropy, etc.), any other known or later developed catalyst, or combinations thereof. When the catalyst is loaded in the reactor, the
25 loading can be in the range of 0.5-40 wt% inclusive, for example, about 2 wt%. In some embodiments, the loading of the catalyst in the reactor comprises forming catalyst nanoparticles by a high-temperature shock synthesis method, such as that described in U.S. Publication No. 2019/0161840, published December 7, 2021, and entitled "Thermal shock synthesis of multielement nanoparticles," which is incorporated by reference herein.

30 After provision of the catalyst at process block 406, or if no catalyst was desired at decision block 404, the method 400 can proceed to process block 408, where the reactor (and reactants and/or intermediates therein) can be subjected to a single heating cycle. The heating of process block 408 is generally non-continuous and includes at least a first part 410, where a peak temperature (e.g., at least 300 °C, such as ≥ 500 °C) is applied to the reactor for a duration t_1 , and

a second part 412, where heating is not applied to the reactor for a duration t_2 (e.g., such that a temperature of the reactor and/or reactant is at least 50 °C less than the peak temperature, for example, at least 70-100 °C less). In some embodiments, the second part 412 can include using one or more passive or active cooling modalities (e.g., directed air or liquid flow, heat exchanger, thermoelectric cooler, heat pump, etc.) in addition to cessation of heating. In some embodiments, the duration t_1 of the first part 410 is less than a remainder of the heating cycle in process block 408, for example, no more than 10% of the heating cycle duration (e.g., ≤ 150 ms for a total cycle duration ≤ 2 s). In some embodiments, the duration t_2 of the second part 412 constitutes a majority of the heating cycle in process block 408, for example, at least 90% of the heating cycle duration.

In some embodiments, the heating cycle of process block 408 can generate both a spatial temperature profile that varies along the flow direction (e.g., axial direction) of the reactor and a temporal temperature profile with periods of heating separated by periods without heating.

In some embodiments, process block 408 can also include flowing a carrier gas through, or at least proximal to, the porous reactor. In some embodiments, the carrier gas can be used to flow the reactant into the reactor, to move reactant and/or intermediates within the reactor, and/or convey products from the reactor. For example, the carrier gas can include hydrogen (H_2), nitrogen (N_2), a noble gas (e.g., helium, argon, etc.), or any combination thereof. Alternatively or additionally, in some embodiments, movement of reactant, intermediates, and/or products within and/or from the reactor can be gravity, capillary forces, and/or diffusion.

The peak temperature generated in the first part 410 (e.g., heating period) can be effective to initiate (e.g., enable bond activation) one or more thermochemical reactions of the reactant within the reactor. The provision of second part 412 (e.g., non-heating or cooling period) within the heating cycle of process block 408 can help tune selectivity for particular reaction products or alter reaction equilibrium. For example, in some embodiments, the heating cycle of process block 408 can provide high yield (e.g., $\geq 60\%$) and selectivity for C_8 - C_{12} hydrocarbon products resulting from thermochemical conversion of thermoplastic reactants (e.g., polyolefins).

The method 400 can proceed to decision block 414, where it is determined if additional heating cycles should be applied. In some embodiments, heating cycles can be repeated in a substantially continuous manner, for example, as long as reactant is provided as input to the reactor. However, even in batch operations, the heating can be repeated at least once, and preferably multiple times, in order to subject reactant within the reactor to multiple heating cycles. If additional heating cycles are desired, the method 400 can return to process block 408 for repetition.

Otherwise, the method 400 can proceed to process block 416, where products generated by the thermochemical reactions in the reactor are removed for storage or use. Such products can include, but are not limited to C₈-C₁₈ hydrocarbons, which can be used for fuels (e.g., gasoline, diesel fuel, and/or aviation fuel). In some embodiments, the yield for C₈-C₁₈ hydrocarbons can be at least 30%, for example, at least 60%. In some embodiments, a weight-average molecular weight of the products from the reactor can be less than or equal to 500 g/mol, and/or a polydispersity index for the products can be less than or equal to 1.5. In some embodiments, the removal for process block 416 can involve flowing a carrier or sweep gas to carry products exiting the reactor to an appropriate outlet. Although shown separately from process block 408, in some embodiments, process block 416 occurs concurrently with process block 408, such that heating occurs while products flow out of the reactor. Alternatively, in some embodiments employing batch processing, the removing of process block 416 can occur after the heating in process block 408 is completed.

Although illustrated separately, it is contemplated that various process blocks may occur simultaneously or iteratively. Furthermore, certain process blocks illustrated as occurring after others may indeed occur before. Although some of blocks 402-416 of method 400 have been described as being performed once, in some embodiments, multiple repetitions of a particular process block may be employed before proceeding to the next decision block or process block. In addition, although blocks 402-416 of method 400 have been separately illustrated and described, in some embodiments, blocks may be combined and performed together (simultaneously or sequentially). Moreover, although FIG. 4 illustrates a particular order for blocks 402-416, embodiments of the disclosed subject matter are not limited thereto. Indeed, in certain embodiments, the blocks may occur in a different order than illustrated or simultaneously with other blocks. In some embodiments, method 400 may comprise only some of blocks 402-416 of FIG. 4.

Conversion Reactors and Systems for Reactants without Fluidity

FIGS. 5A-5D illustrate certain aspects of thermochemical reaction systems according to one or more embodiments of the disclosed subject matter, for example, for use in converting a reactant without fluidity into one or more desired products. Such fluidity-lacking reactants can include, but are not limited to, thermoset plastics and biomass (e.g., lignin). Due to its lack of fluidity, the reactant may be incapable of making good thermal contact with the reactor if simply disposed on or within the reactor, which could in turn lead to slow heat transfer and progression of undesired secondary reactions. Thus, in some embodiments, the reactant can be integrated with

the reactor prior to initiating pulsed heating (e.g., PHQ), in order to improve thermal contact and heat transfer efficiency.

In some embodiments, the reactant can be coated on surfaces of the reactor (e.g., by coating constituent fibers thereof). For example, FIG. 5A shows aspects of forming a coated reactor 522.

5 At an initial loading stage 500, a solution 506 comprising the reactant can be dispensed on the porous reactor 502, which can comprise a plurality of fibers 504 (e.g., carbon fibers in a felt). For example, the solution 506 can be formed by dissolved reactant particles (e.g., powder) in an appropriate solvent (e.g., organic or aqueous solvent, depending on the type of reactant, for example, ammonia for lignin). Once the solution has infiltrated the porous reactor, the reactor can
10 be dried (e.g., by air drying, freeze-drying, or any other form of drying) to form a reactant-loaded reactor 512, where reactant particles 514 are interspersed within and loosely attached to the porous matrix formed by fibers 504 of the reactor. At a second stage 510, the loaded reactor 512 can be subjected to relatively low-temperature heating to form a thin layer of reactant coating 524 over surfaces of the reactor (e.g., constituent fibers), thereby producing the coated reactor 522 ready
15 for processing at the third stage 520. In some embodiments, the heating during the coating stage 510 can be at a temperature about or greater than a glass transition temperature of the reactant (e.g., ~150 °C for lignin) and/or the boiling point of the solvent from solution 506. In the illustrated example, a separate heating module 508 is used to heat the loaded reactor 512 to form the reactant coating 524. Alternatively or additionally, the heating can be provided via Joule heating of the
20 loaded reactor 512, e.g., by passing an electrical current therethrough.

In some embodiments, after the coated reactor is formed, it can then be subjected to PHQ, for example, as described above with respect to FIGS. 2B-2C, in order to thermochemically convert the reactant therein into one or more products (e.g., bio-oil). For example, FIG. 5B illustrates a conversion system 530 using a coated reactor 532. An electrical power source 536 is
25 electrically connected to the coated reactor 532, and a pulsed electrical current can be applied from the power source 536 (e.g., at the direction of control system 534) to the coated reactor 532 to cause Joule heating thereof. Alternatively or additionally, a separate heating module 546 (e.g., at the direction of control system 544) can be used to heat coated reactor 532, for example, as shown for system 540 in FIG. 5C. Application of the peak temperature (e.g., ≥ 300 °C, such as
30 ~400 °C) for a limited duration (e.g., ≤ 500 ms, such as ~55 ms) can convert the reactant into one or more products 538 (e.g., bio-oil), which can then be collected from the reactor via a carrier gas flow 526.

In some embodiments, the viscosity and/or size of the one or more products (e.g., sticky and/or heavy bio-oils) may make removal from the reactor difficult. In addition to the application

of peak temperature via the PHQ technique, vibration can optionally be applied during part or all of the heating cycle to help release the products from the reactor by promoting mass transport and/or convection therein. For example, FIG. 5D illustrates a conversion system 550 similar to system 530 of FIG. 5B, but employing a vibration device 556 (e.g., mechanical shaker, vibration transducer, acoustic transducer, ultrasonic transducer, etc.). In some embodiments, the vibration device 556 can apply vibrations (e.g., ≥ 20 Hz, such as ≥ 20 kHz) to the coated reactor 532 in order to increase the convection within the porous network of the reactor and promote release of products. The detachment of products from the reactor provided by the vibration application can help reduce the chance of potential repolymerization and secondary cracking. Moreover, when combined with an appropriately designed pulse temperature, the vibration could help maximize, or at least increase, the product yield by suppressing the formation of char and gas.

Conversion Methods for Reactants without Fluidity

FIG. 6 illustrates a method 600 for thermochemical conversion of a reactant (e.g., thermoset plastic or biomass) without fluidity to one or more products (e.g., bio-oil) using a porous reactor. The method 600 can initiate at decision block 602, where it is determined if the reactant should be integrated with the reactor by coating or by another technique. If coating with the reactant is desired, the method 600 can proceed to process block 604, where the reactor can be provided. In some embodiments, the reactor comprises a network of randomly arranged or interwoven fibers (e.g., carbon fibers in a felt or cloth). Alternatively, in some embodiments, the provision of process block 604 can include 3D printing the reactor.

The method 600 can proceed to process block 606, where the reactant can be provided in solution, for example, by dissolving in an appropriate solvent (e.g., aqueous or organic solvent). In some embodiments, the reactant can comprise a thermoset plastic. Alternatively or additionally, in some embodiments, the reactant can be a biomass comprising and/or derived from a plant (e.g., wood or grass), algae, or other creature, such as but not limited to sawdust, cellulose, hemicellulose, lipid, carbohydrate, and/or protein. In some embodiments, the reactant is a lignin, such as but not limited to soda lignin, Kraft lignin, hydrolyzed lignin, organosolv lignin, liginosulfonates, or other special engineered lignin and derivatives. The solution can be provided on the reactor (e.g., dispensed onto the reactor, reactor immersed in solution, etc.) at process block 606, and the reactor subsequently dried (e.g., air drying and/or freeze-drying) at process block 608 to form the reactant-loaded reactor. The reactant-loaded reactor can then be subjected to preheating at process block 610, for example, to form the reactant within the reactor as a coating on the reactor surfaces. In some embodiments, the preheating can be performed at a temperature

greater than or about equal to a glass transition temperature of the reactant (e.g., ~150 °C) and/or a boiling point of the solvent.

Alternatively, if coating the reactor surfaces with the reactant is not possible or desired at decision block 602, the method 600 can proceed to process block 612, where the constituent material of the reactor (e.g., carbon) can be integrally formed with the reactant particles (e.g., thermoset plastic or biomass) to form a composite reactor. For example, the providing of process block 612 can include 3D printing of carbon and reactant particles to form the composite reactor. Alternatively or additionally, carbon and reactant particles can be mixed together and cast. Other techniques for forming a composite reactor with the reactant particles are also possible according to one or more contemplated embodiments.

After provision of the composite reactor at process block 612, or after forming the coated reactor at process block 610, the method 600 can proceed to process block 614, where the reactor (and reactant therein) can be subjected to a single heating cycle. The heating of process block 614 is generally non-continuous and includes at least a first part 616, where a peak temperature (e.g., at least 300 °C, such as ~400 °C) is applied to the reactor for a duration t_1 , and a second part 618, where heating is not applied to the reactor for a duration t_2 (e.g., such that a temperature of the reactor and/or reactant is at least 50 °C less than the peak temperature). In some embodiments, the second part 618 can include using one or more passive or active cooling modalities (e.g., directed air or liquid flow, heat exchanger, thermoelectric cooler, heat pump, etc.) in addition to cessation of heating. In some embodiments, the duration t_1 of the first part 616 is less than a remainder of the heating cycle in process block 614, for example, no more than 10% of the heating cycle duration (e.g., ≤ 500 ms for a total cycle duration ≤ 2 s). In some embodiments, the duration t_2 of the second part 618 constitutes a majority of the heating cycle in process block 614, for example, at least 90% of the heating cycle duration.

In some embodiments, vibration can optionally be applied at process block 620 during process block 614, for example, during one or both of the first part 616 and the second part 618. In some embodiments, the vibration has a frequency of at least 20 Hz (e.g., ≥ 20 kHz). In some embodiments, the vibration is applied via one or more mechanical connections between a vibration source and the reactor (e.g., via electrical connections to the reactor used to provide Joule heating thereof). Alternatively or additionally, the vibration can be applied via directed vibration waves (e.g., focused acoustic or ultrasound).

In some embodiments, process block 614 can also include flowing a carrier gas through, or at least proximal to, the porous reactor. In some embodiments, the carrier gas can be used to

convey products from the reactor. For example, the carrier gas can include hydrogen (H₂), nitrogen (N₂), a noble gas (e.g., helium, argon, etc.), or any combination thereof.

The peak temperature generated in first part 616 (e.g., heating period) can be effective to initiate (e.g., enable bond activation) one or more thermochemical reactions of the reactant within the reactor. The provision of second part 618 (e.g., non-heating or cooling period) within the heating cycle of process block 614 can help tune selectivity for particular reaction products or alter reaction equilibrium. For example, in some embodiments, the heating cycle of process block 614 can provide high yield (e.g., $\geq 50\%$) and selectivity for bio-oil products resulting from thermochemical conversion of biomass reactants (e.g., lignin).

The method 600 can proceed to decision block 622, where it is determined if additional heating cycles should be applied. In some embodiments, heating cycles can be repeated in a substantially continuous manner, for example, as long as reactant is provided as input to the reactor. However, even in batch operations, the heating can be repeated at least once, and preferably multiple times, in order to subject reactant within the reactor to multiple heating cycles. If additional heating cycles are desired, the method 600 can return to process block 614 for repetition.

Otherwise, the method 600 can proceed to process block 624, where products generated by the thermochemical reactions in the reactor can be removed for storage, use, or further processing. For example, such products can include, but are not limited to bio-oils (e.g., phenols), which can be subjected to separation, purification, and hydrogenation to form components for fuels (e.g., gasoline, diesel fuel, and/or aviation fuel). Process block 624 can also include collecting gas phase product and/or char generated by the process, for example, for further use as fuel or as soil fertilizer. Although shown separately from process block 614, in some embodiments, process block 624 occurs concurrently with process block 614, such that heating occurs while products flow out of the reactor. Alternatively, in some embodiments employing batch processing, the removing of process block 624 can occur after the heating in process block 408 is completed.

Although illustrated separately, it is contemplated that various process blocks may occur simultaneously or iteratively. Furthermore, certain process blocks illustrated as occurring after others may indeed occur before. Although some of blocks 602-624 of method 600 have been described as being performed once, in some embodiments, multiple repetitions of a particular process block may be employed before proceeding to the next decision block or process block. In addition, although blocks 602-624 of method 600 have been separately illustrated and described, in some embodiments, blocks may be combined and performed together (simultaneously or

sequentially). Moreover, although FIG. 6 illustrates a particular order for blocks 602-624, embodiments of the disclosed subject matter are not limited thereto. Indeed, in certain embodiments, the blocks may occur in a different order than illustrated or simultaneously with other blocks. In some embodiments, method 600 may comprise only some of blocks 602-624 of FIG. 6.

Computer Implementation Examples

FIG. 7 depicts a generalized example of a suitable computing environment 731 in which the described innovations may be implemented, such as but not limited to aspects of control system 114, control system 208, control system 258, control system 278, control system 326, method 400, control system 534, control system 544, and/or method 600. The computing environment 731 is not intended to suggest any limitation as to scope of use or functionality, as the innovations may be implemented in diverse general-purpose or special-purpose computing systems. For example, the computing environment 731 can be any of a variety of computing devices (e.g., desktop computer, laptop computer, server computer, tablet computer, etc.).

With reference to FIG. 7, the computing environment 731 includes one or more processing units 735, 737 and memory 739, 741. In FIG. 7, this basic configuration 751 is included within a dashed line. The processing units 735, 737 execute computer-executable instructions. A processing unit can be a central processing unit (CPU), processor in an application-specific integrated circuit (ASIC), or any other type of processor (e.g., hardware processors, graphics processing units (GPUs), virtual processors, etc.). In a multi-processing system, multiple processing units execute computer-executable instructions to increase processing power. For example, FIG. 7 shows a central processing unit 735 as well as a graphics processing unit or co-processing unit 737. The tangible memory 739, 741 may be volatile memory (e.g., registers, cache, RAM), non-volatile memory (e.g., ROM, EEPROM, flash memory, etc.), or some combination of the two, accessible by the processing unit(s). The memory 739, 741 stores software 733 implementing one or more innovations described herein, in the form of computer-executable instructions suitable for execution by the processing unit(s).

A computing system may have additional features. For example, the computing environment 731 includes storage 761, one or more input devices 771, one or more output devices 781, and one or more communication connections 791. An interconnection mechanism (not shown) such as a bus, controller, or network interconnects the components of the computing environment 731. Typically, operating system software (not shown) provides an operating environment for other software executing in the computing environment 731, and coordinates activities of the components of the computing environment 731.

The tangible storage 761 may be removable or non-removable, and includes magnetic disks, magnetic tapes or cassettes, CD-ROMs, DVDs, or any other medium which can be used to store information in a non-transitory way, and which can be accessed within the computing environment 731. The storage 761 can store instructions for the software 733 implementing one or more innovations described herein.

The input device(s) 771 may be a touch input device such as a keyboard, mouse, pen, or trackball, a voice input device, a scanning device, or another device that provides input to the computing environment 731. The output device(s) 781 may be a display, printer, speaker, CD-writer, or another device that provides output from computing environment 731.

The communication connection(s) 791 enable communication over a communication medium to another computing entity. The communication medium conveys information such as computer-executable instructions, audio or video input or output, or other data in a modulated data signal. A modulated data signal is a signal that has one or more of its characteristics set or changed in such a manner as to encode information in the signal. By way of example, and not limitation, communication media can use an electrical, optical, radio-frequency (RF), or another carrier.

Any of the disclosed methods can be implemented as computer-executable instructions stored on one or more computer-readable storage media (e.g., one or more optical media discs, volatile memory components (such as DRAM or SRAM), or non-volatile memory components (such as flash memory or hard drives)) and executed on a computer (e.g., any commercially available computer, including smart phones or other mobile devices that include computing hardware). The term computer-readable storage media does not include communication connections, such as signals and carrier waves. Any of the computer-executable instructions for implementing the disclosed techniques as well as any data created and used during implementation of the disclosed embodiments can be stored on one or more computer-readable storage media. The computer-executable instructions can be part of, for example, a dedicated software application or a software application that is accessed or downloaded via a web browser or other software application (such as a remote computing application). Such software can be executed, for example, on a single local computer (e.g., any suitable commercially available computer) or in a network environment (e.g., via the Internet, a wide-area network, a local-area network, a client-server network (such as a cloud computing network), or any other such network) using one or more network computers.

For clarity, only certain selected aspects of the software-based implementations are described. Other details that are well known in the art are omitted. For example, it should be understood that the disclosed technology is not limited to any specific computer language or

program. For instance, aspects of the disclosed technology can be implemented by software written in C++, JavaTM, Python®, and/or any other suitable computer language. Likewise, the disclosed technology is not limited to any particular computer or type of hardware. Certain details of suitable computers and hardware are well known and need not be set forth in detail in this disclosure.

It should also be well understood that any functionality described herein can be performed, at least in part, by one or more hardware logic components, instead of software. For example, and without limitation, illustrative types of hardware logic components that can be used include Field-programmable Gate Arrays (FPGAs), Program-specific Integrated Circuits (ASICs), Program-specific Standard Products (ASSPs), System-on-a-chip systems (SOCs), Complex Programmable Logic Devices (CPLDs), etc.

Furthermore, any of the software-based embodiments (comprising, for example, computer-executable instructions for causing a computer to perform any of the disclosed methods) can be uploaded, downloaded, or remotely accessed through a suitable communication means. Such suitable communication means include, for example, the Internet, the World Wide Web, an intranet, software applications, cable (including fiber optic cable), magnetic communications, electromagnetic communications (including RF, microwave, and infrared communications), electronic communications, or other such communication means. In any of the above-described examples and embodiments, provision of a request (e.g., data request), indication (e.g., data signal), instruction (e.g., control signal), or any other communication between systems, components, devices, etc. can be by generation and transmission of an appropriate electrical signal by wired or wireless connections.

Examples and Experimental Results

CONVERSION EXAMPLES – REACTANTS WITH FLUIDITY

Plastics or natural molecules that have fluidity can be converted to useful chemicals, such as liquid fuel (e.g., C₈-C₁₈ hydrocarbons), optionally without use of any catalysts and with high selectivity, competitive energy efficiency, and excellent scalability. In particular, a Joule-heated carbon column reactor was fabricated with three graded porous zones along the pathway of reactants, which flow through and experience a pore-modulated molecular weight rectification process. The graded pores can help control reaction progress via modulating the mass transport and heat transfer behaviors of the intermediates. Unlike conventional pyrolysis processes where the molecular weight distribution broadens as the molecular weight decreases, the fabricated reactor and process

led to products with even narrower molecular weight distribution upon pyrolysis than the original feedstock, which can achieve a high yield for value-added chemicals.

As shown in FIGS. 8A and 9A, a porous reactor 800 was formed of carbon and featuring three portions or zones 802-1, 802-2, and 802-3. The three zones had different pore sizes from each other, with the pore size between the zones decreasing along an axial direction (e.g., in a same direction in which reactants flow) from inlet end 804 at a bottom of the reactor 800 to outlet end 806 at the top of the reactor 800. The first zone 802-1, in which reactants initially enter the reactor 800, had the largest pore size of 1.0 mm. The second zone 802-2, which is downstream from the first zone 802-1, had an intermediate pore size of 500 μm . The third zone 802-3, which is downstream from the second zone 802-2 and from which products can exit the reactor 800, had the smallest pore size of 200 nm.

In the fabricated example, each of the zones had substantially the same cross-sectional area in a plane perpendicular to the axial direction. The provision of different pore sizes between the zones thus imbued the zones with different electrical resistances, with the first zone 802-1 having the largest electrical resistance and the third zone 802-3 having the smallest electrical resistance. Flowing a common electrical current (e.g., by applying a voltage between the inlet end 804 and the outlet end 806) to effect Joule heating of the reactor 800 generates a temperature gradient due to the graded porous structure, with the reactor 800 having a higher temperature in the first zone 802-1, an intermediate temperature in the second zone 802-2, and a lower temperature in the third zone 802-3. When reactant enters from the inlet end 804, the reactant quickly decomposes and converts to smaller species, which travel upward along the axial direction through the different zones of the reactor 800 due to capillary forces and/or diffusion.

Without being bound by any particular theory, it is hypothesized that the larger pores at lower positions (e.g., first and second zones 802-1, 802-2) retain larger polymers for a longer residence time as they move more slowly, while smaller pores (e.g., second and third zones 802-2, 802-3) facilitate the entrance of smaller polymeric or oligomeric species due to their better mobility and smaller kinetic diameters. As larger species have longer residence times, further thermal cracking reduces their molecular weight until they are able to enter smaller pores with lower temperatures, which slow down the pyrolytic process to the same level of the smaller species at the same vertical position. Without being bound by any particular theory, it is hypothesized that this mechanism can effectively rectify the broadening of molecular weight distribution during the pyrolysis of plastics, which is lacking in conventional reactors.

Scanning electron microscopy (SEM) was used to confirm the graded porous structure along the axial direction. As shown in FIG. 9A, the three graded porous zones exhibit

characteristic pore sizes from bottom to top, varying from 1.0 mm to 500 μ m to 200 nm. To conduct the thermochemical conversion reaction, a voltage was applied to the reactor, generating electric current that flows along the axial direction and generates heat based on the Joule heating mechanism. Since the material density is unevenly distributed among the three porous zones (i.e., 80% in Zone 1, 84% in Zone 2, and 100% in Zone 3, therefore $R_{\text{Zone 1}} > R_{\text{Zone 2}} > R_{\text{Zone 3}}$, $P_{\text{Zone 1}} > P_{\text{Zone 2}} > P_{\text{Zone 3}}$), the same current leads to three different temperatures vertically, with the bottom zone being hotter and the top zone being colder.

In addition to the spatial temperature gradient, a temporal temperature gradient (e.g., by applying pulsed Joule heating) can further reduce parasitic secondary reactions and enhance selectivity for desired products. Thus, a pulsed temperature profile was applied to the reactor using a programmed heating cycle of 110 ms power on (heating or first period) and 990 ms power off (cooling or second period), which heating cycle can be repeated periodically. The current input to the reactor was selected to control the temperature of Zone 1 to about 620 $^{\circ}$ C to drive the pyrolytic reaction of low density polyethylene as a model reactant. However, other temperatures may be selected for Zone 1 and/or other portions of the reactor depending on the reactant and/or products desired.

The temperature distribution was characterized during Joule heating of the 3D printed reactor using a suite of tools. In particular, dual-wavelength pyrometry was used to measure the surface temperature changes across different zones, which revealed temperature changes between 630 $^{\circ}$ C and 360 $^{\circ}$ C in Zone 1, 525 $^{\circ}$ C and 350 $^{\circ}$ C in Zone 2, and 440 $^{\circ}$ C and 330 $^{\circ}$ C in Zone 3 over each 1100 ms heating cycle. Interestingly, the efficient heat dissipation of carbon allowed surface temperatures of all three zones to reach the same temperature (e.g., $\sim$ 380 $^{\circ}$ C) at the end of each heating cycle. To investigate internal temperature variations, a femtosecond laser-inscribed single crystal sapphire fiber Bragg gratings (SFBG) was plugged inside of the carbon media without interrupting its operation or altering thermal properties. The results showed that temperature changes between 630 $^{\circ}$ C and 530 $^{\circ}$ C in Zone 1, 530 $^{\circ}$ C to 470 $^{\circ}$ C in Zone 2, and 490 $^{\circ}$ C to 420 $^{\circ}$ C in Zone 3 occurred over each 1100 ms cycle, as shown in FIG. 9B. These results indicate that the core of the reactor exhibits higher temperature and smaller temperature change compared to those on the surface. Nevertheless, temperature fluctuations of 70-100 $^{\circ}$ C are expected to be beneficial for improving the product selectivity by suppressing secondary reactions.

The theoretical overall temperature distribution within the reactor was modeled and calculated based on the energy input of the pyrolysis experiments and the physical properties of the materials used. Along the cross-section of the reactor (in a plane perpendicular to the axial direction), the temperature exhibits a Gaussian distribution trend, with higher core temperatures

and lower surface temperatures. As shown in FIG. 9C, temperature simulations indicated that the core temperature in Zone 1 was 63 °C higher than the surface temperature, with a 57 °C difference in Zone 2, and a 29 °C difference in Zone 3. These results demonstrate the presence of a spatial temperature gradient (e.g., across the graded porous zones) as well as a temporal temperature gradient (e.g., during the entire pulsed Joule heating process within each heating cycle). These three factors – the graded pores, the spatial temperature gradient arising from the porous structure, and the temporal temperature gradient arising from the pulsed heating – together can contribute to controlling the reaction pathway and progress, thereby leading to the rectified molecular weight distribution and enhanced product selectivity. However, one, some, or all of these factors may be employed in certain embodiments to provide improved product yield as compared to conventional methods.

Reactors with graded porous zones (e.g., reactor 800) and without graded porous zones (e.g., comparative reactor shown in FIGS. 8B-8C) were fabricated using 3D printing. In particular, multiwalled carbon nanotubes (MWCNTs) were selected as a readily available candidate for 3D printing of the reactor 800 without further optimization of material properties (e.g., conductivity, heat capacity, cost effectiveness, etc.). However, a wide variety of other materials (e.g., carbon materials, metal materials, ceramic materials, or any combination thereof) can also be used according to one or more contemplated embodiments. For example, the 3D printing process employed to fabricate the disclosed reactors, such as reactor 800, can begin with preparation of a polylactic acid/dichloromethane (PLA/DCM) solution by mixing 42 g of PLA into 200 ml of DCM solvent, followed by blending and heating at 70 °C until the PLA is fully dissolved. Subsequently, 18 g of functionalized MWCNTs were evenly dispersed in the PLA/DCM solution by continuous stirring. The solution was then heated at 70 °C to evaporate the DCM, yielding a dry membrane composed of 30 wt% MWCNT/PLA. This membrane was then chopped into small pieces and extruded to create a filament with a diameter of 1.75 ± 0.01 mm for subsequent 3D printing. Prior to printing, the build plate was prepped at 30 °C and coated with glue. Once the general structure for the reactor (or portion thereof) has been formed on the build plate via the printed filament, the 3D-printed MWCNT/PLA nanocomposites can be carbonized, for example, by subjecting to a temperature of 600 °C under nitrogen, to produce fully carbonized reactors (or portions thereof).

Other configurations for reactors were also fabricated using the 3D-printing process. For example, one reactor had a diameter of 10 mm and a length of 115 mm. The reaction zone contained three segments, each with a length of 30 mm. Segments 1 and 2 have pores of 1.5 mm and 1 mm diameter, respectively, resulting in porosities of 20% and 16%. A 25 mm long material

reservoir was located at a bottom end of the reactor. In another example, the reactor had a larger size, with a diameter of 46 mm and a length of 100 mm. The pores in segments 1 and 2 have diameters of 4 mm and 3 mm, respectively, resulting in porosities of 24% and 16%. A 10 mm long material reservoir was located at a bottom end of the reactor.

5 Compared to the disclosed reactors with graded porous structures (e.g., reactor 800 of FIGS. 8A and 9A), porous reactors with uniform pore size and no spatial temperature gradient were expected to lack a rectifying effect to the molecular weight distribution during plastic pyrolysis. LDPE was used as a model feedstock and the performance of reactors (e.g., product distribution) was characterized using Gas Chromatography-Mass Spectrometry (GC-MS) and
10 High-Temperature Gel Permeation Chromatography (HT-GPC), with a focus on gaseous products and non-condensable hydrocarbons, C₈-C₁₈ hydrocarbons, and waxy compounds. A porous carbon column 810 with uniform large pores of 1.0 mm was fabricated, as shown in FIG. 8B. In addition, a porous carbon column 812 with uniform small pores of 200 nm was fabricated, as shown in FIG. 8C. Because the column 810 only contained large pores, a lower cracking degree of plastics was
15 expected to result due to the short residence time of the reactant and intermediates, and the incomplete pyrolysis would yield a wide distribution of predominantly oligomeric hydrocarbons (>C₁₈). And as shown in FIG. 10A, the product stream from the large pore reactor 810 was dominated by waxy oligomers (C_{>23}) with a yield of 35.5% (55.4% yield to C_{>18} hydrocarbons), indicating a low degree of pyrolysis. Because the column 812 only contained small dense pores,
20 it was expected that the higher degree of cracking and a limited heat diffusion therein would produce low-value lighter hydrocarbons (e.g., gaseous species) and a higher proportion of carbonized products. And as shown in FIG. 10A, reactor 812 produced mostly gaseous products (main component are C₁ and C₂) with a total yield of 55.3%, suggesting high degree of pyrolysis. Moreover, the molecular weight distributions of the products generated from the large pore reactor
25 810 and the small pore reactor 812 are substantially broader than the original polymer, as reflected by the markedly increased polydispersity index (PDI, $PDI = M_w/M_n$), as shown in FIG. 10A.

In contrast to the non-graded porous reactors 810, 812, the graded porous reactor 800 was able to convert LDPE into fuel-range chemicals (C₈-C₁₈) with a record-high yield of 71.3%, as shown in FIG. 10A. The graded porous reactor 800 outperformed conventional non-catalytic
30 thermal pyrolysis and even catalytic pyrolysis processes. Moreover, a narrower molecular weight distribution was measured for the products from reactor 800 compared to that of the original feedstock, which has not been observed before in conventional pyrolysis processes. In addition, by comparing the PDI of the intermediates at each porous zone, it was found that, while the

molecular weight decreases as the reactant travels upward, the molecular weight distribution of all intermediate products remains comparable or smaller to the original polymer reactant.

To better understand the effect of the graded porous structure, the detailed product distribution as a function of carbon numbers was plotted in the C₈-C₁₈ range for each of the tested reactors. As shown in FIG. 10B, reactor 810 with uniform large pores led to low yield C₈-C₁₈ range chemicals, with each type of hydrocarbon having a yield of < 3.5%, likely due to the short residence time and therefore low degree of depolymerization. Meanwhile, as shown in FIG. 10C, the pyrolysis of LDPE in reactor 812 with uniform small pores primarily generated small molecules, with yields for C₈ to C₁₁ products decreasing from 8.90% to 1.52% and yield for C₁₂ to C₁₈ products lower than 1%. Using GC-FID, it was found that gaseous products dominate the product stream (55.3% total yield) from reactor 812, with 15.8% methane (C₁) and 22.8% of ethylene, ethane, and acetylene combined (C₂).

In contrast to the product outputs from non-graded porous reactors 810, 812, reactor 800 with graded porous structure demonstrated a Gaussian-like distribution of the C₈-C₁₈ range hydrocarbons, increasing from 5.18% to 9.98% from C₈ to C₁₂ then decreasing to 1.2% for C₁₈, as shown in FIG. 10D. For the reactor 800, the primary products were centered around C₁₂, which is a desired product distribution for gasoline and many types of aviation fuels. As a result, the total C₈-C₁₈ yield of reactor 800 from LDPE pyrolysis is substantially higher than non-graded porous reactors 810, 812, which mimic conventional reactors with uniform porous structures (71.3% vs. 19.6% and 24.0%, respectively). A detailed product analysis during the operation of reactor 800 revealed that 85% of the reaction completes within 1 minute and > 98% within 2 minutes for the LDPE feed in a batch reaction mode, suggesting fast reaction rates.

Taking advantage of the tunability of Joule heating (e.g., rapid quenching following the removal of power input to the circuit and heater), the temporal and spatial product evolution during the first minute of LDPE pyrolysis reaction was further studied. In particular, the products in the three zones of reactor 800 were sampled at time points of 20 s and 60 s, and the morphology, the molecular weight, and distribution of the intermediate species among the three zones were characterized. Distinct morphological variations across the different zones inside the reactor 800 were observed using SEM. Within the reservoir (adjacent to the first zone 802-1 of reactor 800), the melted LDPE forms a coating over the surface of the carbon media upon cooling down the reactor quickly after 20 s. Similarly, the first zone 802-1 also contained thin layers of polymer coating. In contrast, polymer coatings were not observed in the second zone 802-2. Instead, small particles having a size of ~1 μm (likely composed of oligomers) were found in the second zone 802-2 after 20 s. In the third zone 802-3, neither polymer coating nor particles were observed,

indicating that the intermediate species in this region are highly volatile and not condensable in the temperature range of 490 °C to 420 °C.

The molecular weight (M_n) and distribution (polydispersity index (PDI)) of original LDPE feedstock and the samples from all three zones at 20 s and 60 s were compared using HT-GPC.

5 The LDPE feedstock had a M_n of 27,570 and a PDI of 1.38. After reacting for 20 s in the first zone 802-1 of reactor 800, the M_n decreased slightly to 21,453, while PDI slightly increased to 1.79. However, upon reacting in the second zone 802-2, the intermediate species exhibited an M_n of 1,551 with a decreased PDI of 1.63, indicating rectification of the product molecular weight distribution. Further, the intermediates sampled in third zone 802-3 show an even smaller M_n of
10 423 (corresponding to $\sim C_{30}$ hydrocarbons) and markedly reduced PDI of 1.24, even lower than the original feedstock. After 60 s of reaction, the results are even more pronounced, with M_n of 9,790 and PDI of 1.98 in the first zone 802-1, M_n of 640 and PDI of 1.26 in the second zone 802-2, and M_n of 426 and PDI of 1.21 in the third zone 802-3. Despite the increased reaction time, it is interesting to note that the PDI of the intermediate sampled in the third zone 802-3 continued
15 to enjoy a low PDI. Although the above-noted measurements did not account for gaseous species, their presence is expected to be in a low amount compared to the other products (e.g., < 10% at 20 s and 60 s) and thus should not significantly affect the above noted values of PDI and M_n .

These results demonstrate that the graded pores of reactor 800, and the correspondingly regulated mass transport and heat transfer, contributes to the well-controlled reaction progress,
20 thereby achieving high selectivity and yield to the desired product distribution. Indeed, reactor 800 and associated process resulted in a record-high yield of 71.3% from LDPE to C_8 - C_{18} fuel-range chemicals, which is higher than the yields achieved by conventional pyrolysis approaches with or without using catalysts.

The disclosed reactors with graded pores offer promising scalability, owing to its
25 volumetric reaction mode as well as potential capability to accommodate intermittent renewable energy sources such as solar and wind. The scaling approach for electrified reactors may be different from combustion-based ones. In particular, since conventional reactors are powered by combustion heating, it is common to increase the size and volume of the reactor vessel. However, for electrified reactors, it may be more efficient and practical to increase the number of modules
30 and assemble them into arrays (e.g., operating in parallel) or other configurations. Although the above-noted fabricated examples relied on 3D printing to form the porous reactor, other configurations are also possible according to one or more contemplated embodiments. Indeed, any commercially available porous carbon materials (e.g., carbon felt, carbon cloth, carbon foam) or

other porous materials (e.g., formed of carbon, metal, ceramic, or combinations thereof) can be assembled into the graded porous structure with desired pore size and distribution (or porosity).

To provide an example of scalability, the disclosed graded porous reactors were used to convert 200 g of LDPE feedstock into C₈-C₁₈ fuel-range hydrocarbon chemicals with an average yield of 56% under non-optimized conditions. The combustion performance of the resulting product was evaluated. As shown in FIG. 11A, the product yielded by the graded porous reactor demonstrated a higher adiabatic flame temperature (2201 °C) than commercial jet fuels. Moreover, the laminar flame speed of the resulting product was comparable to that of Jet A and higher than other fuels, indicating high application potential. A comparison of the radical index between the resulting product and Jet A further suggested a higher combustion activity, as shown in FIG. 11B.

CONVERSION EXAMPLES – REACTANTS WITHOUT FLUIDITY

Kraft lignin, which is a major waste product from the pulp industry but has limited utilization, was selected as a model reactant. A porous carbon felt was used as the reactor, which served as both a Joule heating element and a network substrate to support the lignin. Lignin powder was dissolved in ammonia solution, and the solution was then dispensed onto carbon felt. Subsequently, the carbon felt was dried in air, and then further dried via freeze-drying, resulting in lignin-loaded carbon felt. The lignin-loaded carbon felt was connected to an electrical circuit and disposed within a sealed quartz tube (through which Ar-gas was flowed during the heating cycle) for subsequent processing. In particular, a relatively low and continuous current was applied to the carbon felt to cause Joule heating thereof, which generated a temperature of about 150 °C. Since this temperature was higher than the glass transition temperature of the lignin, the lignin transitioned from individual particles to a coating on the surfaces within the carbon felt (e.g., constituent fibers).

The current supplied to the resulting coated carbon felt was then altered to effect pulsed heating cycles for lignin decomposition, with the temperature and heating speed tuned for collection of bio-oil (mostly phenols, which can serve as precursors to produce, for example, jet fuel via separation, purification, and hydrogenation). In particular, experiments employed a pulse peak temperature of ~400 °C, a power on (heating) duration of 55 ms, and a power off (cooling) duration of 1045 ms, resulting in a bio-oil yield of about 52%. Gas phase product and char generated by the pulsed heating cycles could be collected for further usage as fuel or soil fertilizer.

In addition to the pulsed heating of the lignin-coated reactor, vibration was applied to the reactor to further promote mass transport therein. In particular, the carbon felt heater was vibrated under high frequency during the heating to decompose lignin. In the fabricated example, electrical

connections were made via copper wire at opposite ends of the carbon felt, and the copper wire at each end was wrapped around a respective rod (wooden rod) connected to a tunable-frequency vibration source. Vibration generated by the source was transmitted through the pair of rods to the coiled copper wire and thereby to the carbon felt via the copper wire. The vibration of the heater increased the convection within the porous carbon fiber networks, thus promoting the release of sticky and heavy bio-oil volatiles and reducing the chance of repolymerization and undesirable secondary cracking.

Additional Examples of the Disclosed Technology

In view of the above-described implementations of the disclosed subject matter, this application discloses the additional examples in the clauses enumerated below. It should be noted that one feature of a clause in isolation, or more than one feature of the clause taken in combination, and, optionally, in combination with one or more features of one or more further clauses are further examples also falling within the disclosure of this application.

Clause 1. A method comprising:

converting a reactant to one or more products by subjecting to one or more heating cycles in a porous reactor, the reactant being provided to an inlet end of the reactor, the one or more products being provided from an outlet end of the reactor, a first reactor portion at the inlet end of the reactor having a first pore size or porosity, a second reactor portion at the outlet end of the reactor having a second pore size or porosity, the inlet and outlet ends being separated from each other along an axial direction of the reactor,

wherein the second pore size or porosity is less than the first pore size or porosity, the reactant is a polymer comprising carbon, and

at least some of the one or more products have a molecular weight less than a molecular weight of the reactant.

Clause 2. The method of any clause or example herein, in particular, Clause 1, wherein the reactor comprises at least three reactor portions with different pore sizes or porosities.

Clause 3. The method of any clause or example herein, in particular, any one of Clauses 1-2, wherein each reactor portion is adjacent to and in direct contact with at least one other reactor portion along the axial direction.

Clause 4. The method of any clause or example herein, in particular, any one of Clauses 1-3, wherein a third reactor portion of the reactor is disposed between the first and second reactor portions along the axial direction, the third reactor portion having a third pore size or porosity that is less than the first pore size or porosity and greater than the second pore size or porosity.

Clause 5. The method of any clause or example herein, in particular, Clause 4, wherein:

the heating is such that one or more first intermediate products are generated in the first portion and conveyed along the axial direction to the third portion, and one or more second intermediate products are generated in the third portion and conveyed along the axial direction to the second portion;

at least some of the one or more first intermediate products have a first molecular weight less than the molecular weight of the reactant,

at least some of the one or more second intermediate products have a second molecular weight less than the first molecular weight, and

the molecular weight of the at least some of the one or more products is less than the second molecular weight.

Clause 6. The method any clause or example herein, in particular, any one of Clauses 4-5, wherein:

the first pore size is at least two times the third pore size;

the third pore size is at least two times the second pore size; or

both of the above.

Clause 7. The method of any clause or example herein, in particular, any one of Clauses 4-6, wherein:

the first pore size is in a range of 500 μm to 2 mm, inclusive;

the first pore size is less than or equal to about 1 mm;

the third pore size is in a range of 200 nm to 1 mm, inclusive;

the third pore size is less than or equal to about 500 μm ;

the second pore size is in a range of 100 nm to 300 μm , inclusive;

the second pore size is less than or equal to about 200 nm; or

any combination of the above.

Clause 8. The method of any clause or example herein, in particular, any one of Clauses 2-7, wherein:

for each reactor portion, the pore size or porosity therein is substantially constant; and

the pore size or porosity for each downstream reactor portion is less than that for an adjacent upstream reactor portion.

Clause 9. The method of any clause or example herein, in particular, any one of Clauses 1-7, wherein the pore size or porosity of the reactor gradually decreases from the first pore size or porosity at the inlet end to the second pore size or porosity at the outlet end.

Clause 10. The method of any clause or example herein, in particular, any one of Clauses 1-9, wherein the reactor is configured as a single Joule heating element, and each heating cycle comprises passing an electrical current through the reactor along the axial direction.

Clause 11. The method of any clause or example herein, in particular, Clause 10, wherein the passing the electrical current is such that a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

Clause 12. The method of any clause or example herein, in particular, any one of Clauses 1-9, wherein each reactor portion in the reactor is configured as a separate Joule heating element, and each heating cycle comprises passing a separate electrical current through the respective reactor portion.

Clause 13. The method of any clause or example herein, in particular, Clause 12, wherein the passing the separate electrical current is such that a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

Clause 14. The method of any clause or example herein, in particular, any one of Clauses 1-13, wherein:

the reactor comprises carbon, metal, ceramic, or any combination of the foregoing; or
the reactor is formed only of carbon.

Clause 15. The method of any clause or example herein, in particular, any one of Clauses 1-14, wherein the reactor comprises carbon nanotubes, carbon felt, carbon cloth, or carbon foam.

Clause 16. The method of any clause or example herein, in particular, any one of Clauses 1-15, wherein each heating cycle is such that a temperature gradient is formed within the reactor along the axial direction, with a peak temperature in the first reactor portion being greater than a peak temperature in the second reactor portion.

Clause 17. The method of any clause or example herein, in particular, any one of Clauses 1-16, wherein each heating cycle comprises:

actively heating the reactor during a first time period; and
cooling (e.g., not actively heating, passively cooling, and/or actively cooling) the reactor during a second time period following the first time period,
wherein a peak temperature in each reactor portion occurs during the first time period.

Clause 18. The method of any clause or example herein, in particular, Clause 17, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 19. The method of any clause or example herein, in particular, any one of Clauses 17-18, wherein the heating cycle duration is less than or equal to 2 s, the first time period is less than or equal to 150 ms, and/or the second time period is less than or equal to 1 s.

5 Clause 20. The method of any clause or example herein, in particular, any one of Clauses 17-19, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less (e.g., 70-100 °C less) than the corresponding peak temperature.

Clause 21. The method of any clause or example herein, in particular, any one of Clauses 1-20, wherein a peak temperature in the first reactor portion during the heating is at least 500 °C.

10 Clause 22. The method of any clause or example herein, in particular, any one of Clauses 1-21, wherein, during the converting, the reactant is flowed into and/or through the reactor via a carrier gas, gravity, capillary force, diffusion, or any combination of the foregoing.

Clause 23. The method of any clause or example herein, in particular, any one of Clauses 1-22, wherein the polymer has a carbon-carbon backbone, and the one or more products comprise
15 C₈-C₁₈ hydrocarbons.

Clause 24. The method of any clause or example herein, in particular, any one of Clauses 1-23, wherein the reactant comprises polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyvinyl alcohol, polyvinyl acetate, rubber, polymethyl methacrylate, or acrylonitrile butadiene styrene.

20 Clause 25. The method of any clause or example herein, in particular, any one of Clauses 1-24, wherein the reactant comprises polyethylene, and a yield for C₈-C₁₈ hydrocarbons in the one or more products is at least 60%, for example, at least 70%.

Clause 26. The method of any clause or example herein, in particular, any one of Clauses 1-22, wherein the polymer has a carbon-oxygen backbone or a carbon-hydrogen backbone.

25 Clause 27. The method of any clause or example herein, in particular, any one of Clauses 1-26, wherein the reactant comprises polyethylene terephthalate, polybutylene terephthalate, polyurethane, nylon, unsaturated polyester, polycarbonate, epoxy, or polyether.

Clause 28. The method of any clause or example herein, in particular, any one of Clauses 1-27, wherein the converting is performed without using a catalyst.

30 Clause 29. The method of any clause or example herein, in particular, any one of Clauses 1-28, wherein:

a yield for C₈-C₁₈ hydrocarbons in the one or more products is at least 30%;

a weight-average molecular weight of the one or more products is less than or equal to 500 g/mol;

a polydispersity index for the one or more products is less than or equal to 1.5; or

5 any combination of the above.

Clause 30. The method of any clause or example herein, in particular, any one of Clauses 1-29, wherein the heating comprises (i) a spatial temperature profile that varies along the axial direction, (ii) a temporal temperature profile with periods of heating separated by periods without heating, or both (i) and (ii).

10 Clause 31. The method of any clause or example herein, in particular, any one of Clauses 1-30, wherein the one or more products comprises one or more components for gasoline, diesel fuel, and/or aviation fuel.

Clause 32. The method of any clause or example herein, in particular, any one of Clauses 1-31, wherein the reactant comprises a thermoplastic.

15 Clause 33. A system comprising:

one or more porous reactors, each reactor having first and second reactor portions, the first reactor portion being at an inlet end of the respective reactor and having a first pore size or porosity, the second reactor portion being at an outlet end of the respective reactor and having a second pore size or porosity, the inlet and outlet ends being separated from each other along an axial direction of the respective reactor,

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wherein the second pore size or porosity is less than the first pore size or porosity, and each porous reactor is configured to convert a reactant supplied to the inlet end into one or more products at the outlet end by subjecting to one or more heating cycles.

Clause 34. The system of any clause or example herein, in particular, Clause 33, wherein each reactor comprises at least three reactor portions with different pore sizes or porosities.

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Clause 35. The system of any clause or example herein, in particular, any one of Clauses 33-34, wherein, for each reactor, each reactor portion is adjacent to and in direct contact with at least one other reactor portion along the axial direction.

Clause 36. The system of any clause or example herein, in particular, any one of Clauses 33-35, wherein, for each reactor, a third reactor portion thereof is disposed between the first and second reactor portions along the axial direction, the third reactor portion having a third pore size

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or porosity that is less than the first pore size or porosity and greater than the second pore size or porosity.

Clause 37. The system of any clause or example herein, in particular, Clause 36, wherein, for each reactor the first pore size is at least two times the third pore size, and/or the third pore size is at least two times the second pore size.

Clause 38. The system of any clause or example herein, in particular, any one of Clauses 36-37, wherein, for each reactor:

the first pore size is in a range of 500 μm to 2 mm, inclusive

the first pore size is less than or equal to 1 mm;

the third pore size is in a range of 200 nm to 1 mm, inclusive;

the third pore size is less than or equal to 500 μm ;

the second pore size is in a range of 100 nm to 300 μm , inclusive;

the second pore size is less than or equal to 200 nm; or

any combination of the above.

Clause 39. The system of any clause or example herein, in particular, any one of Clauses 33-38, wherein, for each reactor:

the pore size or porosity for each reactor portion is substantially constant; and

the pore size or porosity for each downstream reactor portion is less than that for an adjacent upstream reactor portion.

Clause 40. The system of any clause or example herein, in particular, any one of Clauses 33-38, wherein, for each reactor, the pore size or porosity thereof gradually decreases from the first pore size or porosity at the inlet end to the second pore size or porosity at the outlet end.

Clause 41. The system of any clause or example herein, in particular, any one of Clauses 33-40, wherein each reactor is configured as a single Joule heating element constructed to be heated by passing an electrical current therethrough along the axial direction.

Clause 42. The system of any clause or example herein, in particular, any one of Clauses 33-41, wherein, for each reactor, an electrical resistance of the first reactor portion is greater than an electrical resistance of the second reactor portion.

Clause 43. The system of any clause or example herein, in particular, any one of Clauses 41-42, further comprising:

one or more power supplies electrically coupled to the one or more reactors and configured to supply respective electrical currents to the one or more reactors; and

a controller operatively coupled to the one or more power supplies, the controller comprising one or more processors and one or more non-transitory computer-readable storage media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to:

- 5 supply the respective electrical currents via the one or more power supplies to the one or more reactors for each heating cycle, such that, for each reactor, a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

Clause 44. The system of any clause or example herein, in particular, Clause 43, wherein the computer-readable storage media stores instructions that, when executed by the one or more
10 processors, cause the one or more processors to, for each heating cycle:

 supply, via the one or more power supplies, the respective electrical current to actively heat each reactor during a first time period; and

 cease, via the one or more power supplies, supply of the respective electrical current so as to cool each reactor during a second time period following the first time period,

- 15 wherein the peak temperature in each reactor portion occurs during the first time period.

Clause 45. The system of any clause or example herein, in particular, Clause 44, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 46. The system of any clause or example herein, in particular, any one of Clauses 44-
20 45, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less (e.g., 70-100 °C less) than the corresponding peak temperature.

Clause 47. The system of any clause or example herein, in particular, any one of Clauses 33-
25 40, wherein, for each reactor, each reactor portion is configured as a separate Joule heating element constructed to be independently heated by passing a separate electrical current through the respective reactor portion.

Clause 48. The system of any clause or example herein, in particular, Clause 47, further comprising:

- 30 one or more power supplies electrically coupled to the one or more reactors and configured to supply respective electrical currents to the reactor portions; and

 a controller operatively coupled to the one or more power supplies, the controller comprising one or more processors and one or more non-transitory computer-readable storage

media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to:

supply the respective separate electrical currents via the one or more power supplies to the reactor portions for each heating cycle, such that, for each reactor, a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

Clause 49. The system of any clause or example herein, in particular, Clause 48, wherein the computer-readable storage media stores instructions that, when executed by the one or more processors, cause the one or more processors to, for each heating cycle:

supply, via the one or more power supplies, the respective electrical currents to actively heat each reactor portion during a first time period; and

cease, via the one or more power supplies, supply of the respective electrical currents so as to cool each reactor during a second time period following the first time period,

wherein the peak temperature in each reactor portion occurs during the first time period.

Clause 50. The system of any clause or example herein, in particular, Clause 49, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 51. The system of any clause or example herein, in particular, any one of Clauses 49-50, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less than the corresponding peak temperature.

Clause 52. The system of any clause or example herein, in particular, any one of Clauses 33-51, further comprising:

one or more heating modules separate from the one or more reactors and configured to heat the one or more reactors; and

a controller operatively coupled to the one or more heating modules, the controller comprising one or more processors and one or more non-transitory computer-readable storage media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to:

heat, via the one or more heating modules, the one or more reactors during each heating cycle, such that, for each reactor, a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

Clause 53. The system of any clause or example herein, in particular, Clause 52, wherein the one or more heating modules comprise a Joule heating system, a microwave heating system, a

laser heating system, an electron beam heating system, a spark discharge heating system, a plasma heating system, or any combination of the foregoing.

Clause 54. The system of any clause or example herein, in particular, any one of Clauses 52-53, wherein the computer-readable storage media stores instructions that, when executed by the one or more processors, cause the one or more processors to, for each heating cycle:

heat, via the one or more heating modules, the one or more reactors during a first time period; and

cease, via the one or more heating modules, heating so as to cool each reactor during a second time period following the first time period,

wherein the peak temperature in each reactor portion occurs during the first time period.

Clause 55. The system of any clause or example herein, in particular, Clause 54, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 56. The system of any clause or example herein, in particular, any one of Clauses 54-55, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less than the corresponding peak temperature.

Clause 57. The system of any clause or example herein, in particular, any one of Clauses 33-56, wherein:

each reactor comprises carbon, metal, ceramic, or any combination of the foregoing; or

each reactor is formed only of carbon.

Clause 58. The system of any clause or example herein, in particular, any one of Clauses 33-57, wherein the reactor comprises carbon nanotubes, carbon felt, carbon cloth, or carbon foam.

Clause 59. A method of operating the system of any clause or example herein, in particular, any one of Clauses 33-58, so as to convert the reactant into the one or more products, wherein at least some of the one or more products have a molecular weight less than a molecular weight of the reactant.

Clause 60. A method comprising:

loading a reactant onto one or more surfaces of a reactor;

subjecting the reactor to heating at a first temperature such that the loaded reactant forms a reactant coating on the one or more surfaces;

after the subjecting to heating at the first temperature, converting at least part of the reactant coating to one or more products by subjecting to one or more heating cycles, the one or more heating cycles comprising a peak temperature greater than the first temperature,

wherein the reactant is a thermoset plastic or biomass, and

5 at least some of the one or more products have a molecular weight less than a molecular weight of the reactant.

Clause 61. The method of any clause or example herein, in particular, Clause 60, wherein the biomass is lignin, and the one or more products comprises bio-oil.

Clause 62. The method of any clause or example herein, in particular, any one of Clauses 60-
10 61, wherein a yield for bio-oil in the one or more products is at least 45%.

Clause 63. The method of any clause or example herein, in particular, any one of Clauses 60-62, wherein the biomass comprises cellulose, hemicellulose, lipids, carbohydrates, proteins, or any combination thereof.

Clause 64. The method of any clause or example herein, in particular, any one of Clauses 60-
15 63, wherein the biomass comprises or is derived from algae, sawdust, or grass.

Clause 65. The method of any clause or example herein, in particular, any one of Clauses 60, wherein the loading comprises:

dissolving the reactant in a solvent to form a solution;

dispensing the solution onto the reactor; and

20 drying the reactor to remove the solvent.

Clause 66. The method of any clause or example herein, in particular, any one of Clauses 60-65, wherein the first temperature is greater than or equal to (i) a glass transition temperature of the reactant, (ii) a boiling temperature of the solvent, or both (i) and (ii).

Clause 67. The method of any clause or example herein, in particular, any one of Clauses 60-
25 66, wherein the first temperature is about 150 °C.

Clause 68. The method of any clause or example herein, in particular, any one of Clauses 60-67, wherein each heating cycle comprises:

actively heating the reactor during a first time period; and

30 cooling (e.g., not actively heating, passively cooling, and/or actively cooling) the reactor during a second time period following the first time period,

wherein a peak temperature in the reactor occurs during the first time period.

Clause 69. The method of any clause or example herein, in particular, Clause 68, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 70. The method of any clause or example herein, in particular, Clause 69, wherein:

- 5 the heating cycle duration is less than or equal to 5 s;
 the first time period is less than or equal to 500 ms;
 the second time period is less than or equal to 4.5 s; or
 any combination of the above.

10 Clause 71. The method of any clause or example herein, in particular, any one of Clauses 68-70, wherein a minimum temperature in the reactor occurs during the second time period.

Clause 72. The method of any clause or example herein, in particular, any one of Clauses 68-71, wherein the peak temperature in the reactor during each heating cycle is at least 300 °C.

Clause 73. The method of any clause or example herein, in particular, any one of Clauses 60-72, wherein the converting is performed without using a catalyst.

15 Clause 74. The method of any clause or example herein, in particular, any one of Clauses 60-73, further comprising, during each heating cycle, subjecting the reactor to vibration so as to release the one or more products from the reactor.

Clause 75. The method of any clause or example herein, in particular, Clause 74, wherein the vibration has a frequency of at least 20 Hz.

20 Clause 76. The method of any clause or example herein, in particular, any one of Clauses 60-75, further comprising subjecting the one or more products to hydrogenation to form one or more components for gasoline, diesel fuel, and/or aviation fuel.

25 Clause 77. The method of any clause or example herein, in particular, any one of Clauses 60-76, wherein the reactor is configured as a Joule heating element, and each heating cycle comprises passing an electrical current through the reactor.

Clause 78. The method of any clause or example herein, in particular, any one of Clauses 60-77, wherein the reactor is formed of carbon, metal, ceramic, or any combination of the foregoing.

Clause 79. The method of any clause or example herein, in particular, any one of Clauses 60-78, wherein the reactor comprises carbon nanotubes, carbon felt, carbon cloth, or carbon foam.

30 Clause 80. A system comprising:

a reactor having one or more surfaces coated with a reactant, the reactant being a thermoset plastic or biomass,

wherein the reactor is configured to convert the reactant coating into one or more products by subjecting to one or more heating cycles.

5 Clause 81. The system of any clause or example herein, in particular, Clause 80, wherein the biomass is lignin, and the one or more products comprises bio-oil.

Clause 82. The system of any clause or example herein, in particular, any one of Clauses 80-81, wherein the biomass comprises cellulose, hemicellulose, lipids, carbohydrates, proteins, or any combination thereof.

10 Clause 83. The system of any clause or example herein, in particular, any one of Clauses 80-82, wherein the biomass comprises or is derived from algae, sawdust, or grass.

Clause 84. The system of any clause or example herein, in particular, any one of Clauses 80-83, wherein the reactor, or a portion thereof, is configured as a Joule heating element constructed to be heated by passing an electrical current therethrough.

15 Clause 85. The system of any clause or example herein, in particular, Clause 84, further comprising:

 a power supply electrically coupled to the reactor and configured to supply the electrical current to the reactor; and

 a controller operatively coupled to the power supply, the controller comprising one or more
20 processors and one or more non-transitory computer-readable storage media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to supply the electrical current via the power supply to the reactor for each heating cycle.

Clause 86. The system of any clause or example herein, in particular, Clause 85, wherein the
25 computer-readable storage media stores instructions that, when executed by the one or more processors, cause, for each heating cycle:

 supply, via the power supply, the electrical current to actively heat the reactor during a first time period; and

 cease, via the power supply, supply of the electrical current so as to cool the reactor during
30 a second time period following the first time period,

 wherein a peak temperature in the reactor occurs during the first time period.

Clause 87. The system of any clause or example herein, in particular, Clause 86, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 88. The system of any clause or example herein, in particular, any one of Clauses 80-87, further comprising:

a heating module separate from the reactor and configured to heat the reactor; and

a controller operatively coupled to the heating module, the controller comprising one or more processors and one or more non-transitory computer-readable storage media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to heat, via the heating module, the reactor during each heating cycle.

Clause 89. The system of any clause or example herein, in particular, Clause 88, wherein the heating module comprises a Joule heating system, a microwave heating system, a laser heating system, an electron beam heating system, a spark discharge heating system, a plasma system, or any combination of the foregoing.

Clause 90. The system of any clause or example herein, in particular, any one of Clauses 88-89, wherein the computer-readable storage media stores instructions that, when executed by the one or more processors, cause the one or more processors to, for each heating cycle:

heat, via the heating module, the reactor during a first time period; and

cease, via the heating module, heating so as to cool the reactor during a second time period

following the first time period,

wherein a peak temperature in the reactor occurs during the first time period.

Clause 91. The system of any clause or example herein, in particular, Clause 90, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

Clause 92. The system of any clause or example herein, in particular, any one of Clauses 80-91, further comprising a vibration source coupled to the reactor and configured to apply vibration to the reactor during each heating cycle so as to release the one or more products from the reactor.

Clause 93. The system of any clause or example herein, in particular, Clause 92, wherein the vibration has a frequency of at least 20 Hz, for example, at least 20 kHz.

Clause 94. The system of any clause or example herein, in particular, any one of Clauses 80-93, further comprising:

a processing system constructed to subject the one or more products from the reactor to hydrogenation so as to form one or more components for gasoline, diesel fuel, and/or aviation fuel.

Clause 95. The system of any clause or example herein, in particular, any one of Clauses 80, wherein:

the reactor is formed only of carbon; or

the reactor comprises carbon, metal, ceramic, or any combination of the foregoing.

Clause 96. The system of any clause or example herein, in particular, any one of Clauses 80-95, wherein the reactor comprises carbon nanotubes, carbon felt, carbon cloth, or carbon foam.

Clause 97. A method of operating the system of any clause or example herein, in particular, any one of Clauses 80-96, so as to convert the reactant into the one or more products, wherein at least some of the one or more products have a molecular weight less than a molecular weight of the reactant.

Conclusion

Any of the features illustrated or described herein, for example, with respect to FIGS. 1A-11B or Clauses 1-97, can be combined with any other feature illustrated or described herein, for example, with respect to FIGS. 1A-11B or Clauses 1-97, to provide systems, devices, structures, methods, examples, or embodiments not otherwise illustrated or specifically described herein. All features described herein are independent of one another and, except where structurally impossible, can be used in combination with any other feature described herein. In view of the many possible embodiments to which the principles of the disclosed technology may be applied, it should be recognized that the illustrated embodiments are only examples and should not be taken as limiting the scope of the disclosed technology. Rather, the scope is defined by the following claims. We therefore claim all that comes within the scope and spirit of these claims.

CLAIMS

1. A method comprising:

converting a reactant to one or more products by subjecting to one or more heating cycles in a porous reactor, the reactant being provided to an inlet end of the reactor, the one or more
5 products being provided from an outlet end of the reactor, a first reactor portion at the inlet end of the reactor having a first pore size or porosity, a second reactor portion at the outlet end of the reactor having a second pore size or porosity, the inlet and outlet ends being separated from each other along an axial direction of the reactor,

wherein the second pore size or porosity is less than the first pore size or porosity,

10 the reactant is a polymer comprising carbon, and

at least some of the one or more products have a molecular weight less than a molecular weight of the reactant.

2. The method of claim 1, wherein the reactor comprises at least three reactor portions

15 with different pore sizes or porosities.

3. The method of claim 2, wherein each reactor portion is adjacent to and in direct contact with at least one other reactor portion along the axial direction.

20 4. The method of claim 2, wherein a third reactor portion of the reactor is disposed between the first and second reactor portions along the axial direction, the third reactor portion having a third pore size or porosity that is less than the first pore size or porosity and greater than the second pore size or porosity.

25 5. The method of claim 4, wherein:

the heating is such that one or more first intermediate products are generated in the first portion and conveyed along the axial direction to the third portion, and one or more second intermediate products are generated in the third portion and conveyed along the axial direction to the second portion;

30 at least some of the one or more first intermediate products have a first molecular weight less than the molecular weight of the reactant,

at least some of the one or more second intermediate products have a second molecular weight less than the first molecular weight, and

the molecular weight of the at least some of the one or more products is less than the second molecular weight.

6. The method of claim 4, wherein:

5 the first pore size is at least two times the third pore size;
the third pore size is at least two times the second pore size; or
both of the above.

7. The method of claim 4, wherein:

10 the first pore size is in a range of 500 μm to 2 mm, inclusive;
the third pore size is in a range of 200 nm to 1 mm, inclusive;
the second pore size is in a range of 100 nm to 300 μm , inclusive; or
any combination of the above.

15 8. The method of claim 2, wherein:

for each reactor portion, the pore size or porosity therein is substantially constant; and
the pore size or porosity for each downstream reactor portion is less than that for an
adjacent upstream reactor portion.

20 9. The method of claim 1, wherein the pore size or porosity of the reactor gradually
decreases from the first pore size or porosity at the inlet end to the second pore size or porosity at
the outlet end.

10. The method of claim 1, wherein the reactor is configured as a single Joule heating
25 element, and each heating cycle comprises passing an electrical current through the reactor along
the axial direction.

11. The method of claim 10, wherein the passing the electrical current is such that a
peak temperature in the first reactor portion is greater than a peak temperature in the second reactor
30 portion.

12. The method of claim 1, wherein each reactor portion in the reactor is configured as
a separate Joule heating element, and each heating cycle comprises passing a separate electrical
current through the respective reactor portion.

13. The method of claim 12, wherein the passing the separate electrical current is such that a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

5

14. The method of any one of claims 10 and 12, wherein the reactor is formed of carbon, metal, ceramic, or any combination of the foregoing.

15. The method of claim 14, wherein the reactor comprises carbon nanotubes, carbon felt, carbon cloth, or carbon foam.

10

16. The method of claim 1, wherein each heating cycle is such that a temperature gradient is formed within the reactor along the axial direction, with a peak temperature in the first reactor portion being greater than a peak temperature in the second reactor portion.

15

17. The method of claim 1, wherein each heating cycle comprises:
actively heating the reactor during a first time period; and
cooling the reactor during a second time period following the first time period,
wherein a peak temperature in each reactor portion occurs during the first time period.

20

18. The method of claim 17, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

25

19. The method of claim 18, wherein:
the heating cycle duration is less than or equal to 2 s;
the first time period is less than or equal to 150 ms;
the second time period is less than or equal to 1 s; or
any combination of the above.

30

20. The method of claim 17, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less than the corresponding peak temperature.

21. The method of claim 1, wherein a peak temperature in the first reactor portion during the heating is at least 500 °C.

22. The method of claim 1, wherein, during the converting, the reactant is flowed into and/or through the reactor via a carrier gas, gravity, capillary force, diffusion, or any combination of the foregoing.

23. The method of claim 1, wherein the polymer has a carbon-carbon backbone, and the one or more products comprise C₈-C₁₈ hydrocarbons.

24. The method of claim 23, wherein the reactant comprises polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyvinyl alcohol, polyvinyl acetate, rubber, polymethyl methacrylate, or acrylonitrile butadiene styrene.

25. The method of claim 24, wherein the reactant comprises polyethylene, and a yield for C₈-C₁₈ hydrocarbons in the one or more products is at least 60%.

26. The method of claim 1, wherein the polymer has a carbon-oxygen backbone or a carbon-hydrogen backbone.

27. The method of claim 26, wherein the reactant comprises polyethylene terephthalate, polybutylene terephthalate, polyurethane, nylon, unsaturated polyester, polycarbonate, epoxy, or polyether.

28. The method of claim 1, wherein the converting is performed without using a catalyst.

29. The method of claim 1, wherein:
a yield for C₈-C₁₈ hydrocarbons in the one or more products is at least 30%;
a weight-average molecular weight of the one or more products is less than or equal to 500 g/mol;
a polydispersity index for the one or more products is less than or equal to 1.5; or
any combination of the above.

30. The method of claim 1, wherein the heating comprises (i) a spatial temperature profile that varies along the axial direction, (ii) a temporal temperature profile with periods of heating separated by periods without heating, or both (i) and (ii).

5 31. The method of claim 1, wherein the one or more products comprises one or more components for gasoline, diesel fuel, and/or aviation fuel.

32. The method of claim 1, wherein the reactant comprises a thermoplastic.

10 33. A system comprising:

one or more porous reactors, each reactor having first and second reactor portions, the first reactor portion being at an inlet end of the respective reactor and having a first pore size or porosity, the second reactor portion being at an outlet end of the respective reactor and having a second pore size or porosity, the inlet and outlet ends being separated from each other along an axial direction of the respective reactor,

15 wherein the second pore size or porosity is less than the first pore size or porosity, and each porous reactor is configured to convert a reactant supplied to the inlet end into one or more products at the outlet end by subjecting to one or more heating cycles.

20 34. The system of claim 33, wherein each reactor comprises at least three reactor portions with different pore sizes or porosities.

35. The system of claim 33, wherein, for each reactor, each reactor portion is adjacent to and in direct contact with at least one other reactor portion along the axial direction.

25 36. The system of claim 34, wherein, for each reactor, a third reactor portion thereof is disposed between the first and second reactor portions along the axial direction, the third reactor portion having a third pore size or porosity that is less than the first pore size or porosity and greater than the second pore size or porosity.

30 37. The system of claim 36, wherein, for each reactor:
the first pore size is at least two times the third pore size;
the third pore size is at least two times the second pore size; or
both of the above.

38. The system of claim 36, wherein, for each reactor:
the first pore size is in a range of 500 μm to 2 mm, inclusive;
the third pore size is in a range of 200 nm to 1 mm, inclusive;
5 the second pore size is in a range of 100 nm to 300 μm , inclusive; or
any combination of the above.

39. The system of claim 34, wherein, for each reactor:
the pore size or porosity for each reactor portion is substantially constant; and
10 the pore size or porosity for each downstream reactor portion is less than that for an
adjacent upstream reactor portion.

40. The system of claim 33, wherein, for each reactor, the pore size or porosity thereof
gradually decreases from the first pore size or porosity at the inlet end to the second pore size or
15 porosity at the outlet end.

41. The system of claim 33, wherein each reactor is configured as a single Joule heating
element constructed to be heated by passing an electrical current therethrough along the axial
direction.

42. The system of claim 41, wherein, for each reactor, an electrical resistance of the
first reactor portion is greater than an electrical resistance of the second reactor portion.

43. The system of claim 42, further comprising:
25 one or more power supplies electrically coupled to the one or more reactors and configured
to supply respective electrical currents to the one or more reactors; and

a controller operatively coupled to the one or more power supplies, the controller
comprising one or more processors and one or more non-transitory computer-readable storage
media storing computer-readable instructions that, when executed by the one or more processors,
30 cause the one or more processors to:

supply the respective electrical currents via the one or more power supplies to the
one or more reactors for each heating cycle, such that, for each reactor, a peak temperature
in the first reactor portion is greater than a peak temperature in the second reactor portion.

44. The system of claim 43, wherein the computer-readable storage media stores instructions that, when executed by the one or more processors, cause the one or more processors to, for each heating cycle:

supply, via the one or more power supplies, the respective electrical current to actively
5 heat each reactor during a first time period; and

cease, via the one or more power supplies, supply of the respective electrical current so as to cool each reactor during a second time period following the first time period,

wherein the peak temperature in each reactor portion occurs during the first time period.

10 45. The system of claim 44, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

15 46. The system of claim 44, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less than the corresponding peak temperature.

47. The system of claim 33, wherein, for each reactor, each reactor portion is configured as a separate Joule heating element constructed to be independently heated by passing
20 a separate electrical current through the respective reactor portion.

48. The system of claim 47, further comprising:

one or more power supplies electrically coupled to the one or more reactors and configured to supply respective electrical currents to the reactor portions; and

25 a controller operatively coupled to the one or more power supplies, the controller comprising one or more processors and one or more non-transitory computer-readable storage media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to:

30 supply the respective separate electrical currents via the one or more power supplies to the reactor portions for each heating cycle, such that, for each reactor, a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

49. The system of claim 48, wherein the computer-readable storage media stores
35 instructions that, when executed by the one or more processors, cause the one or more processors to, for each heating cycle:

supply, via the one or more power supplies, the respective electrical currents to actively heat each reactor portion during a first time period; and

cease, via the one or more power supplies, supply of the respective electrical currents so as to cool each reactor during a second time period following the first time period,

5 wherein the peak temperature in each reactor portion occurs during the first time period.

50. The system of claim 49, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

10

51. The system of claim 49, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less than the corresponding peak temperature.

15

52. The system of claim 33, further comprising:
one or more heating modules separate from the one or more reactors and configured to heat the one or more reactors; and

a controller operatively coupled to the one or more heating modules, the controller comprising one or more processors and one or more non-transitory computer-readable storage media storing computer-readable instructions that, when executed by the one or more processors, cause the one or more processors to:

20

heat, via the one or more heating modules, the one or more reactors during each heating cycle, such that, for each reactor, a peak temperature in the first reactor portion is greater than a peak temperature in the second reactor portion.

25

53. The system of claim 52, wherein the one or more heating modules comprise a Joule heating system, a microwave heating system, a laser heating system, an electron beam heating system, a spark discharge heating system, a plasma heating system, or any combination of the foregoing.

30

54. The system of claim 52, wherein the computer-readable storage media stores instructions that, when executed by the one or more processors, cause the one or more processors to, for each heating cycle:

heat, via the one or more heating modules, the one or more reactors during a first time period; and

35

cease, via the one or more heating modules, heating so as to cool each reactor during a second time period following the first time period,

wherein the peak temperature in each reactor portion occurs during the first time period.

5 55. The system of claim 54, wherein the first time period and second time periods together form a duration of the respective heating cycle, and the first time period is no more than 10% of the heating cycle duration.

10 56. The system of claim 54, wherein a minimum temperature in each reactor portion occurs during the second time period, and the minimum temperature is at least 50 °C less than the corresponding peak temperature.

15 57. The system of claim 33, wherein each reactor is formed of carbon, metal, ceramic, or any combination of the foregoing.

 58. The system of claim 53, wherein the reactor comprises carbon nanotubes, carbon felt, carbon cloth, or carbon foam.

20 59. A method comprising:
loading a reactant onto one or more surfaces of a reactor;
subjecting the reactor to heating at a first temperature such that the loaded reactant forms a reactant coating on the one or more surfaces;
after the subjecting to heating at the first temperature, converting at least part of the reactant coating to one or more products by subjecting to one or more heating cycles, the one or
25 more heating cycles comprising a peak temperature greater than the first temperature,
wherein the reactant is a thermoset plastic or biomass, and
at least some of the one or more products have a molecular weight less than a molecular weight of the reactant.

30 60. A system comprising:
a reactor having one or more surfaces coated with a reactant, the reactant being a thermoset plastic or biomass,
wherein the reactor is configured to convert the reactant coating into one or more products
by subjecting to one or more heating cycles.

35

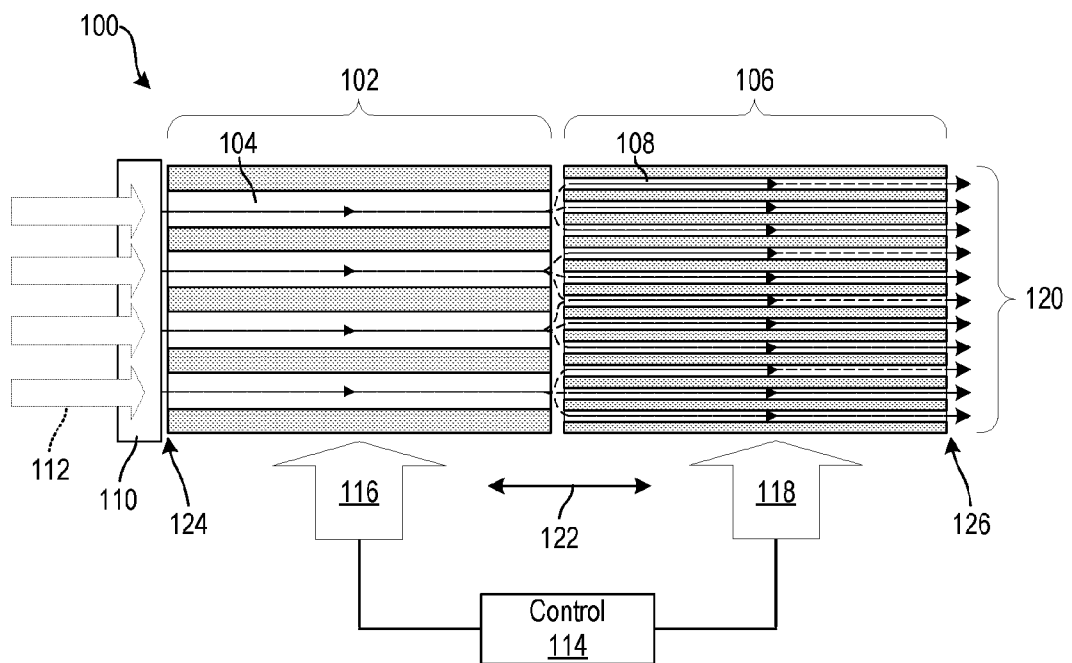


FIG. 1A

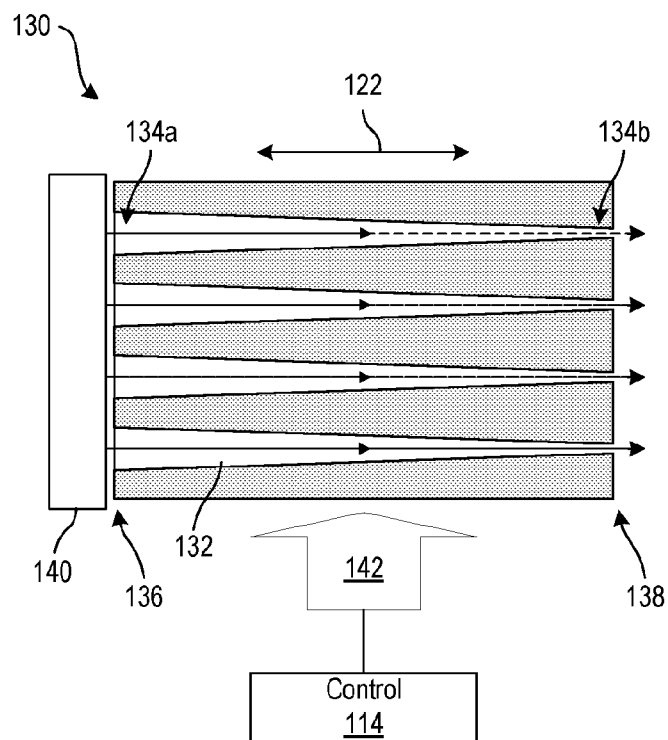


FIG. 1B

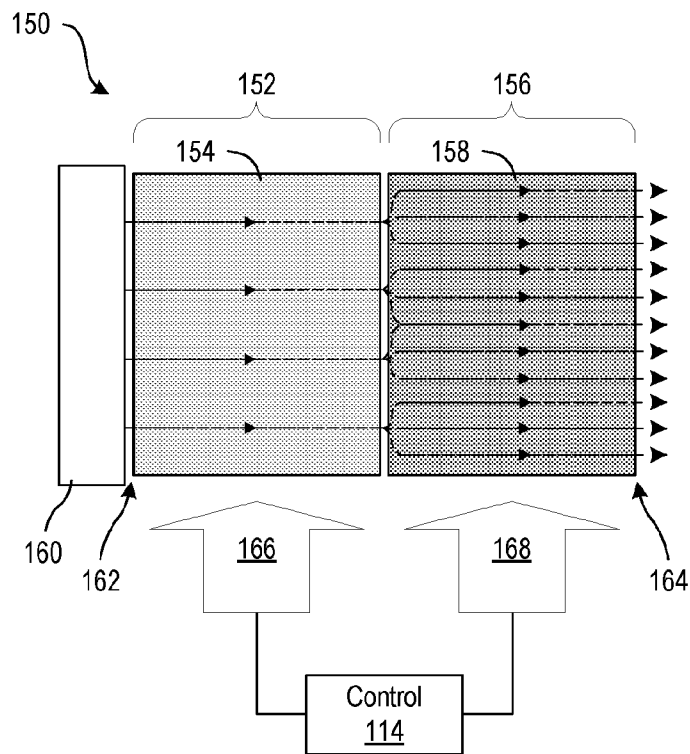


FIG. 1C

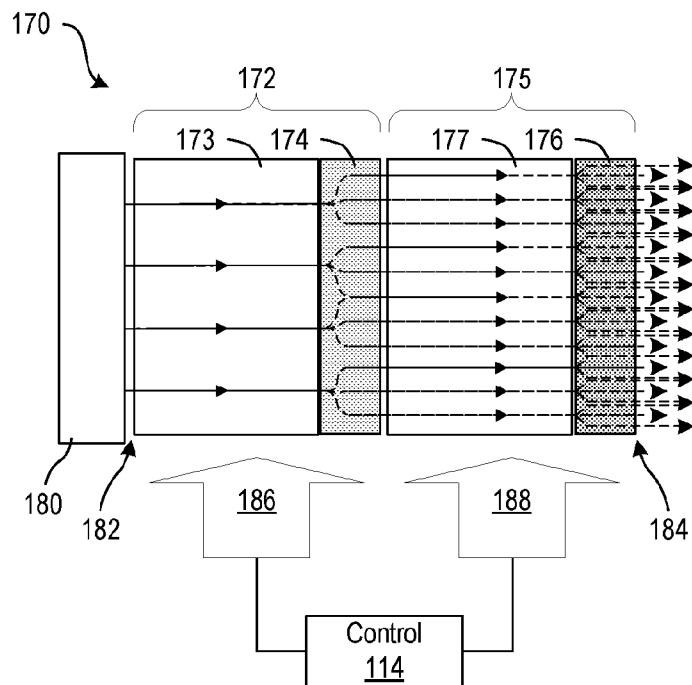


FIG. 1D

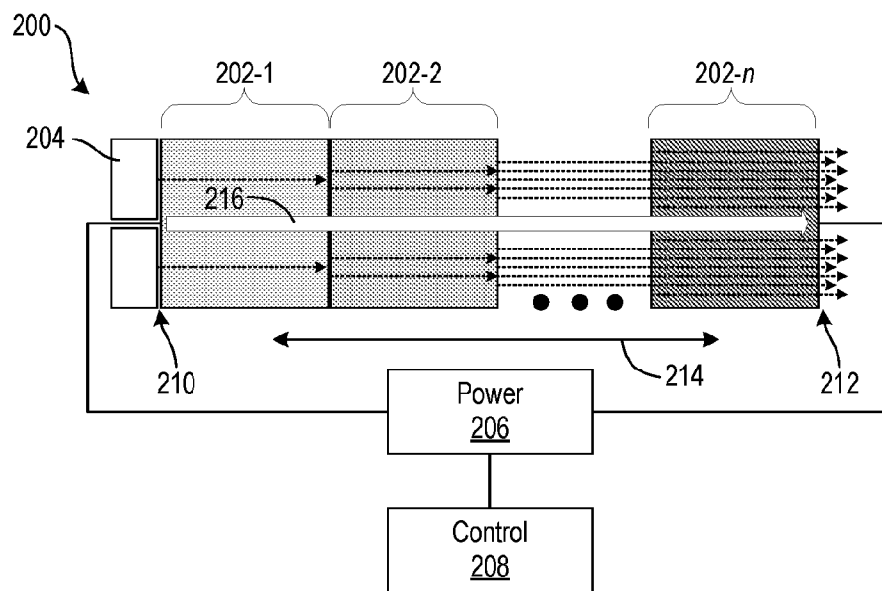


FIG. 2A

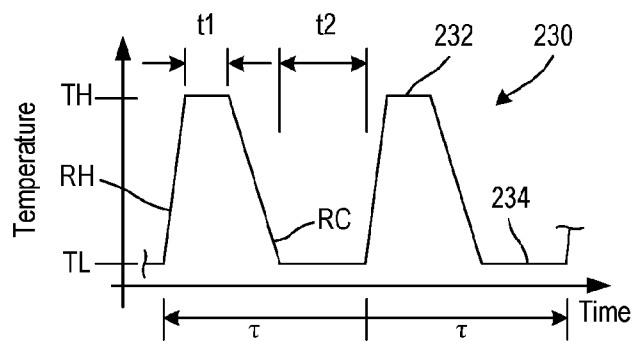


FIG. 2B

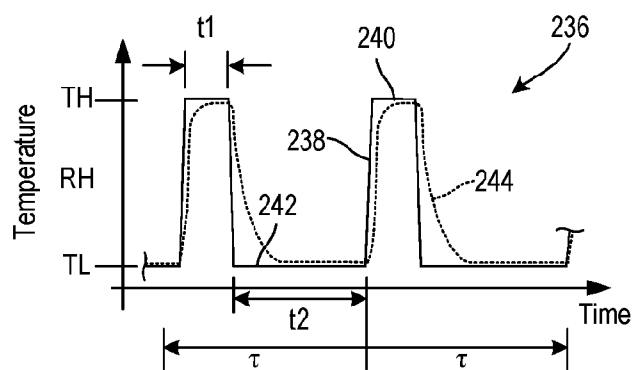


FIG. 2C

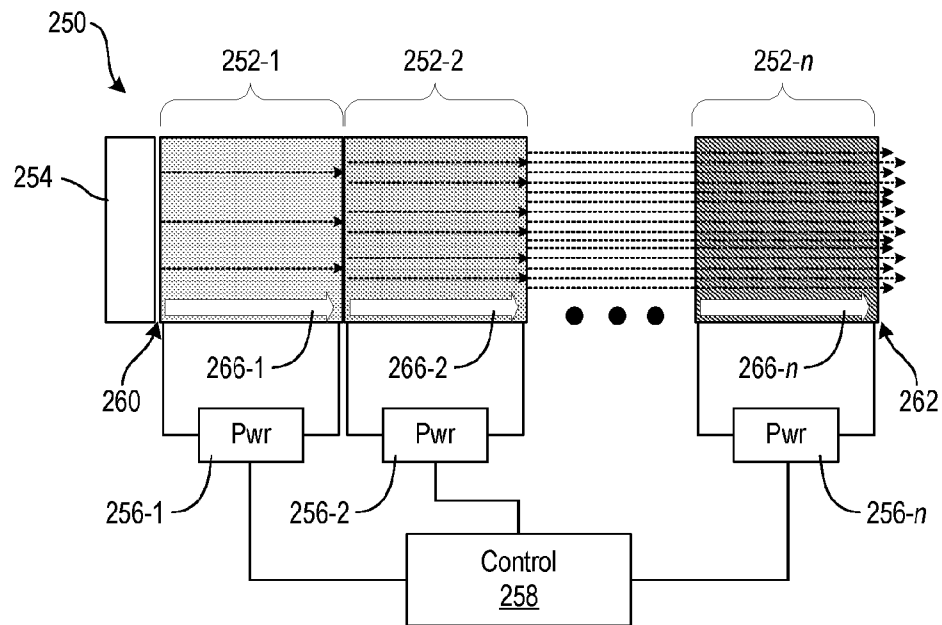


FIG. 2D

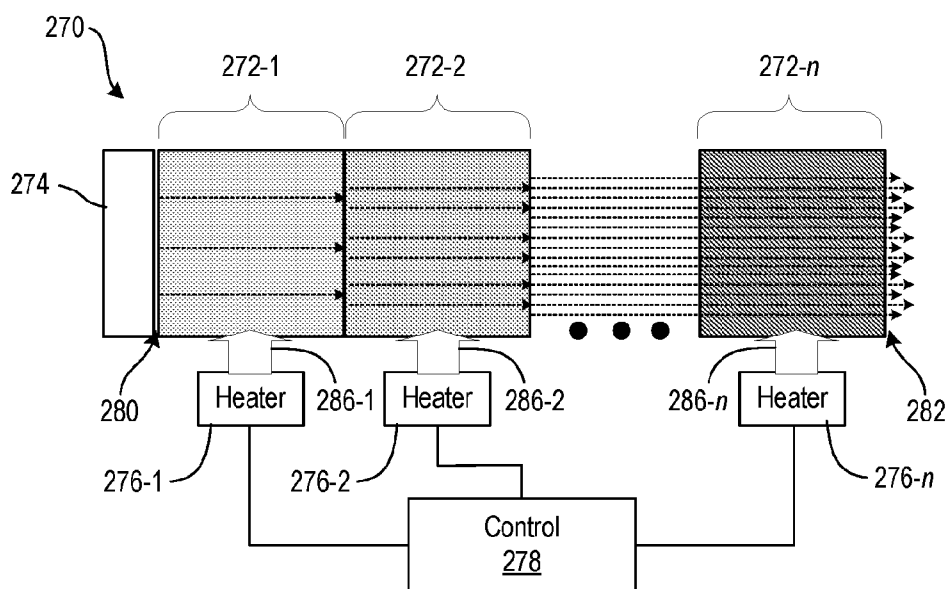


FIG. 2E

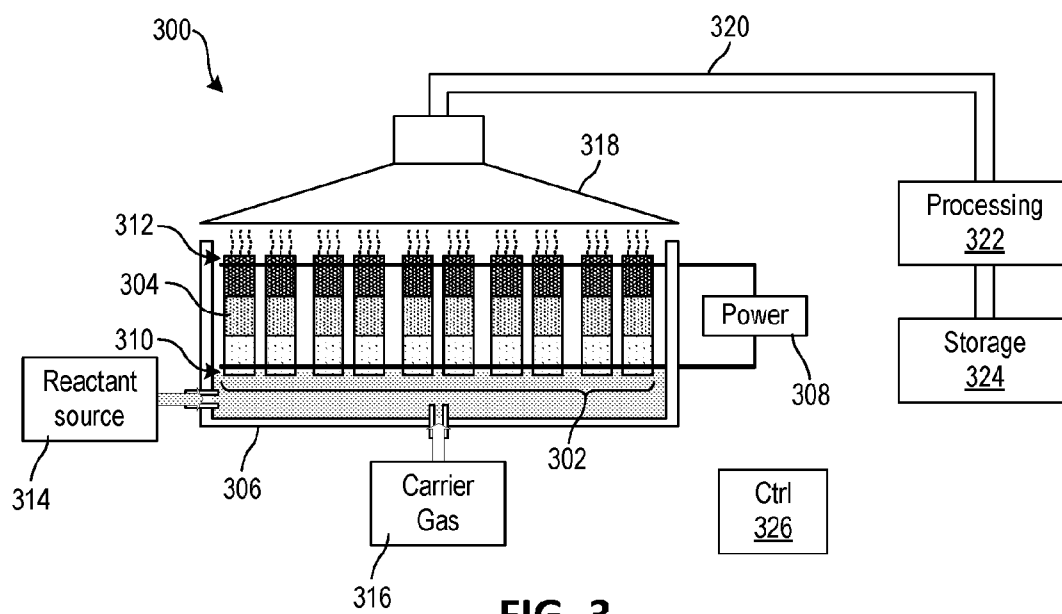


FIG. 3

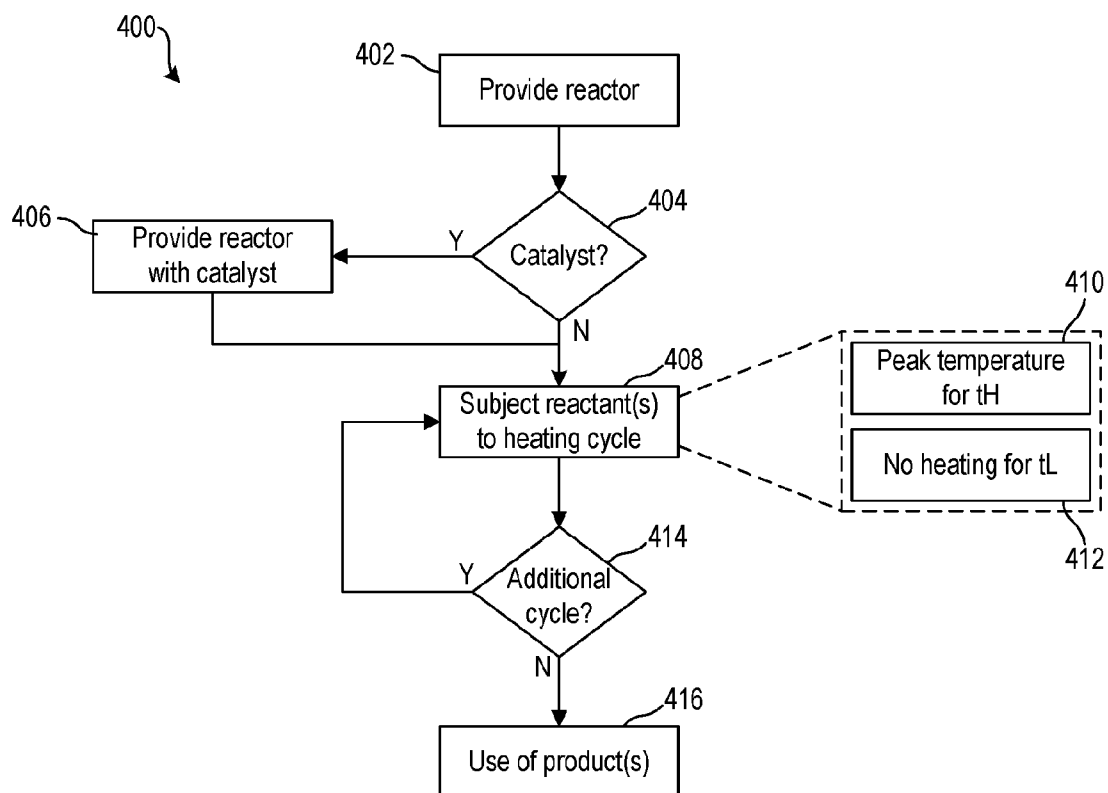


FIG. 4

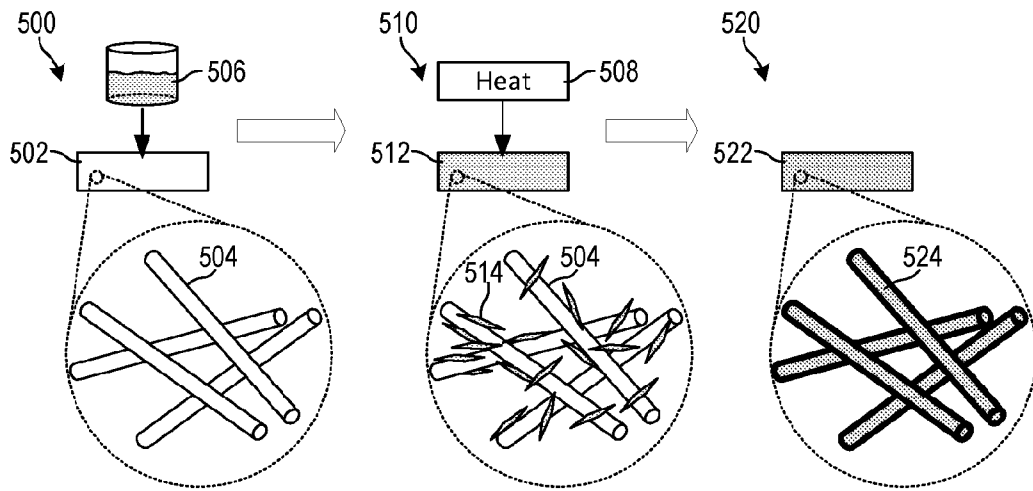


FIG. 5A

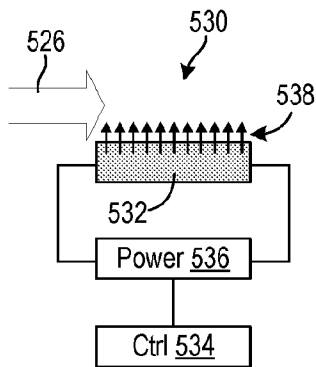


FIG. 5B

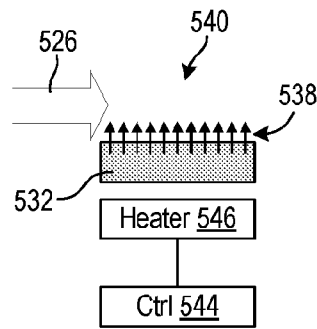


FIG. 5C

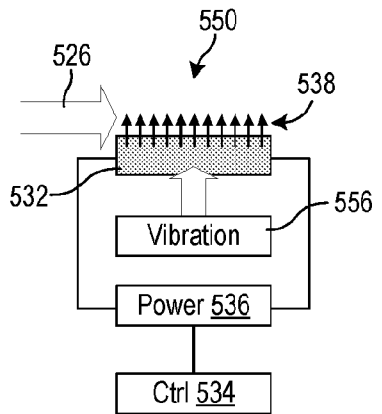


FIG. 5D

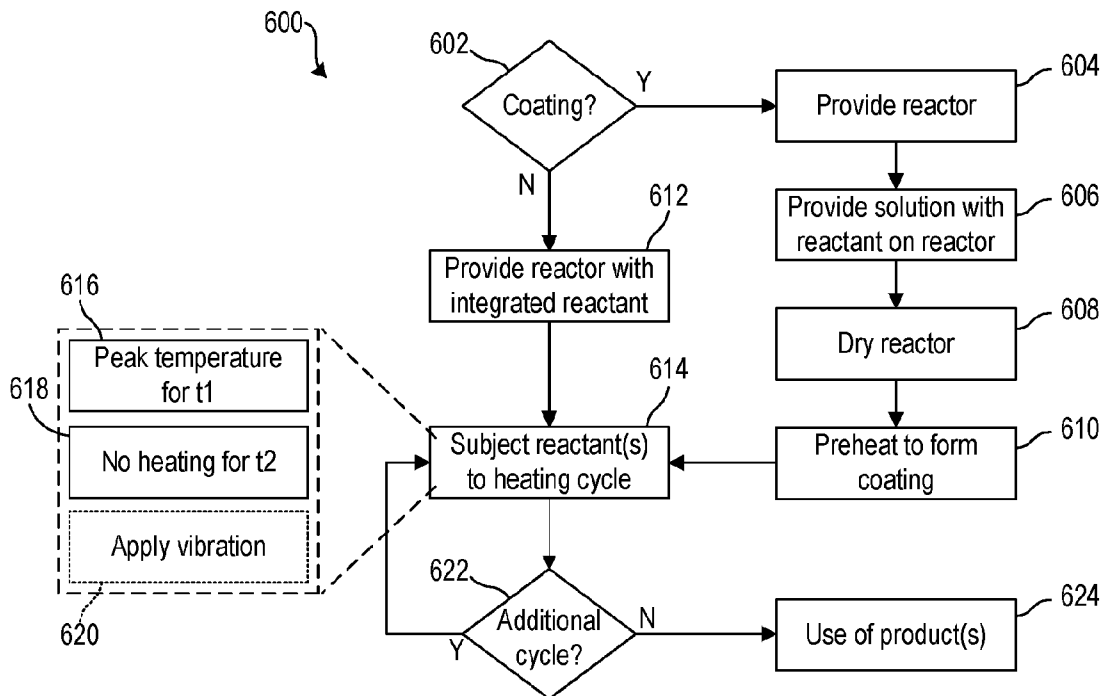


FIG. 6

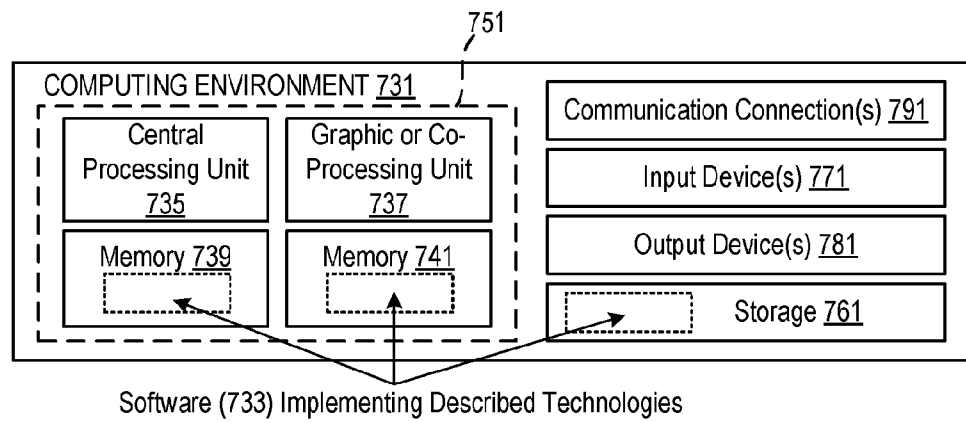


FIG. 7

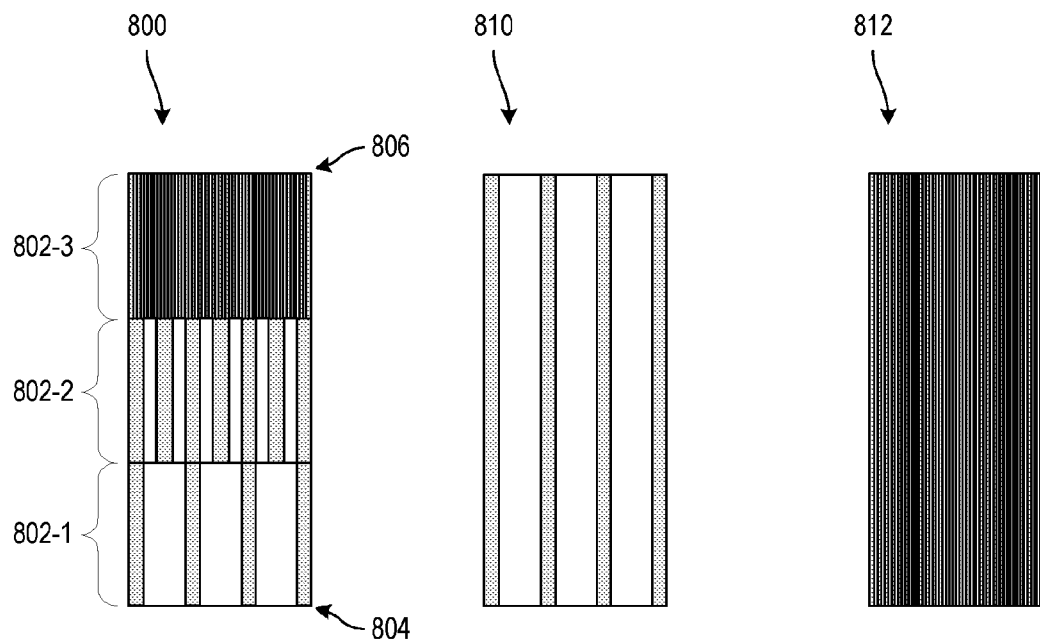


FIG. 8A

FIG. 8B

FIG. 8C

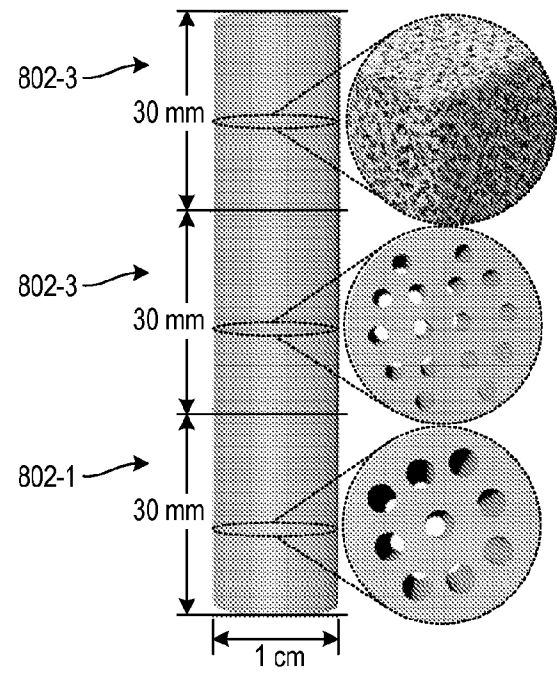


FIG. 9A

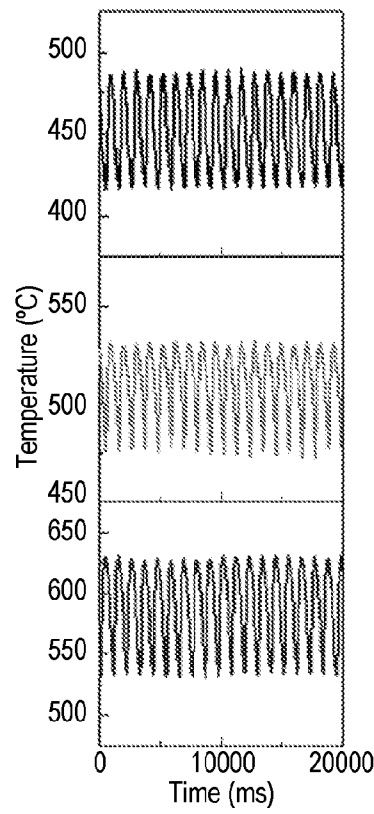


FIG. 9B

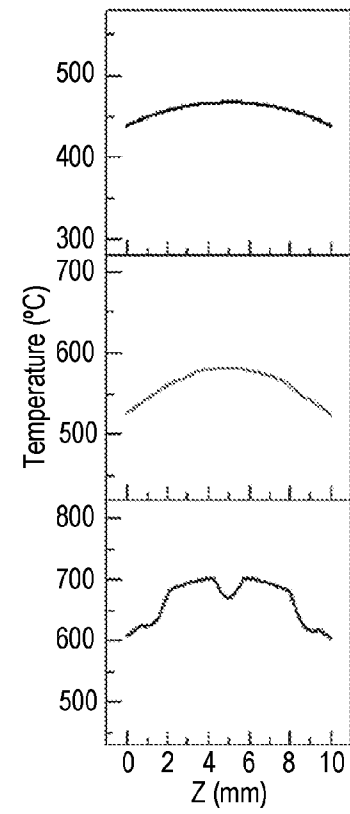


FIG. 9C

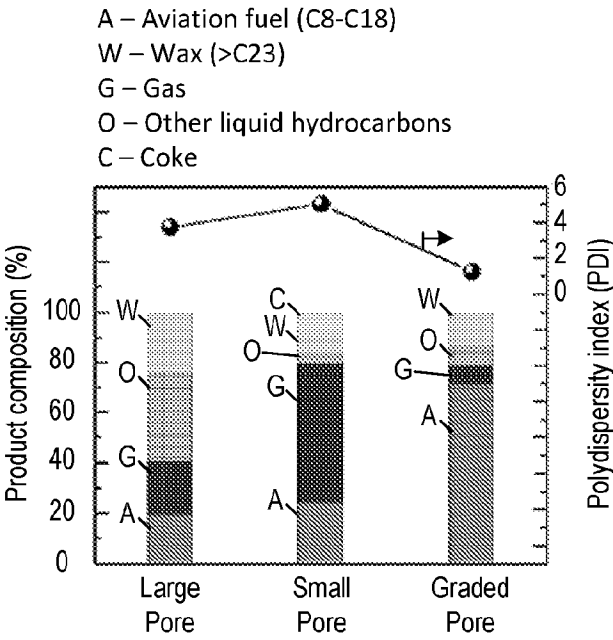


FIG. 10A

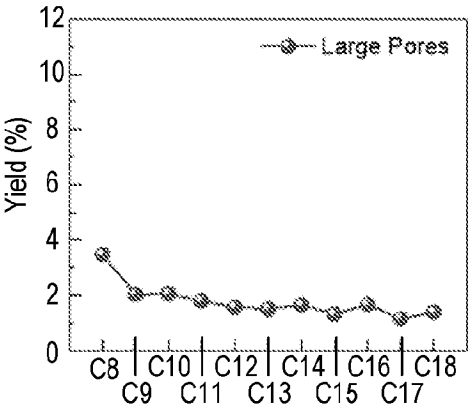


FIG. 10B

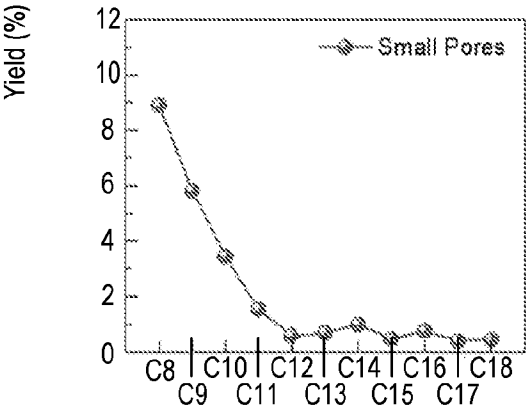


FIG. 10C

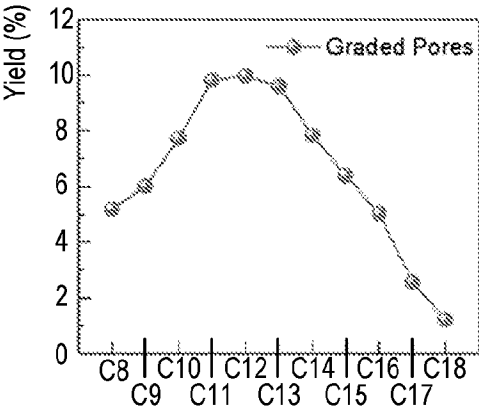


FIG. 10D

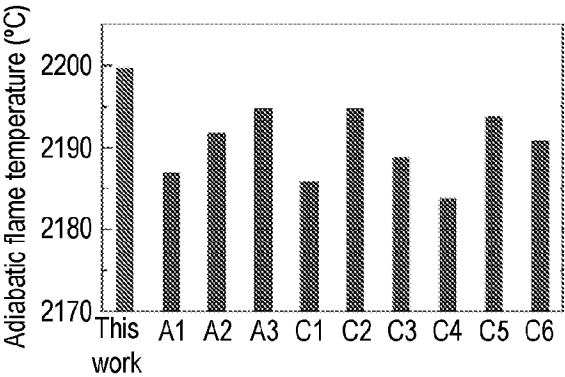


FIG. 11A

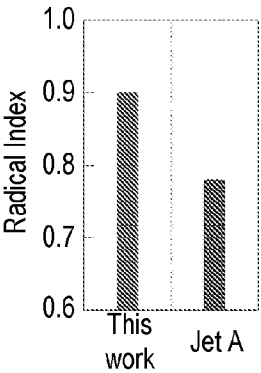


FIG. 11B