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METHOD OF CONVERTING PYROLYSIS OILS, WAXES, AND/OR OLIGOMERS TO HIGHER VALUE CHEMICALS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims priority to each of European patent application no. 23187528.7, filed 25 July 2023, European patent application no. 23187529.5, filed 25 July 2023, European patent application no. 23187530.3, filed 25 July 2023, European patent application no. 23196604.5, filed 11 September 2023, India patent application no. 202341050195, filed 25 July 2023, the entire contents of each of which are incorporated herein by reference.

10

TECHNICAL FIELD

[0002] The present disclosure is directed to the production of high value chemical products from pyrolysis oils, particularly those from plastic waste, and waxes and/or oligomers.

15 BACKGROUND

[0003] The production of plastic has increased significantly in recent decades, with an estimated 400 million tons generated yearly. Unfortunately, only a small portion of this plastic waste is recycled.

[0004] The problem of plastic waste is complex and multifaceted and requires a comprehensive
20 solution. While mechanical recycling of plastics has been ongoing, recycling efforts have been met with limited success. Only certain types of plastics can be mechanically recycled, and even those that can be recycled must be sorted into their different types due to differences in their chemical properties, which require different processing conditions. It can be very expensive to sort and process these different plastics. Mechanical processing, where the plastic
25 waste is cleaned and shredded into small particles or flakes, which are then melted and reformed into new products, has a lower quality than virgin plastic that is formed from polymerization. This is due to the degradation of the polymer chains of the reformed plastic. Additionally, residual contaminants may still be present in the reformed plastic affecting its overall quality.

30 [0005] One promising solution is the conversion of plastic waste through chemical processes. This may eliminate the need to sort the recycled plastic into their different types. Plastics that typically cannot be mechanically processed may also be converted using chemical processes. Such mixed plastic wastes (MPW) can be converted into valuable chemicals, such as ethylene, propylene and other olefins and aromatics using these chemical processes. These chemicals

are the building blocks of many plastics and other products and can be used as a feedstock for the production of new or virgin plastics or other materials.

[0006] This conversion of mixed plastic waste into valuable chemicals offers a promising solution to make circular products that could significantly reduce the environmental impact of plastic waste while also creating value from a previously discarded resource.

[0007] One method of processing mixed plastic waste so that it can be used to form more valuable products involves converting the MPW to pyoil through pyrolysis. Pyrolysis is a thermal decomposition process that involves heating the mixed plastic waste in the absence of oxygen, leading to the breakdown of the plastic into smaller molecules. The process produces gases and vapors, which are then condensed into liquid form to create pyoil. The production of pyoil from plastic waste emits fewer greenhouse gases than incineration.

[0008] In chemical processing, steam cracking is typically used to convert pyoil into more valuable products, such as ethylene, propylene and aromatics. Before the pyoil can undergo steam cracking, however, it must first be pretreated in multiple operation units. This can include distillation, so that only the lighter fraction of the pyoil is cracked. Additionally, pyoil from MPW typically contains 50% or more unsaturated hydrocarbons. During the steam cracking process, these unsaturated hydrocarbons can cause coking, which can reduce the efficiency of the process and lead to equipment fouling. The pyoil may therefore be hydrogenated in a hydrotreater or undergo other processing steps before steam cracking. This requires added hydrogen, additional process steps, and additional processing units, increasing the cost and complexity of converting the pyoil. Moreover, even with the hydrogenation of the pyrolysis oil there is still potential for coking to occur during steam cracking.

[0009] What is needed therefore is a method of utilizing pyoils from mixed plastic waste that overcomes these shortcomings to produce more valuable products or chemicals.

SUMMARY

[0010] A method of converting pyrolysis oils, waxes, and/or oligomers to higher value products is carried out in a reactor system comprising a central axis, a feed assembly, and a reactor vessel that defines a reaction chamber. A fuel gas feed and an oxidizer gas feed are introduced into the feed assembly to produce a swirling fluid flow pattern about the central axis. The fuel gas feed and oxidizer gas feed are combusted in the feed assembly to form swirling combustion gases. A hydrocarbon reactant feed comprising a liquid hydrocarbon of at least one of (i) plastic-waste-derived pyrolysis oils, (ii) waxes, and (iii) oligomers having an average molecular weight (Mn) of from 1,000 g/mol to 50,000 g/mol is introduced into the feed

assembly. The liquid hydrocarbon has a dynamic viscosity from 0.1 cP to 1000 cP and is introduced as a liquid spray having a Sauter Mean Diameter (SMD) of droplets from 1 μm to 250 μm into the feed assembly. The hydrocarbon reactant feed is mixed with the swirling combustion gases to form a swirling, heated mixture. The heated mixture is passed into the reaction chamber and reacted within the reaction chamber under reaction conditions suitable to convert the hydrocarbons of the hydrocarbon reactant feed into a converted hydrocarbon product. The converted hydrocarbon product is removed from the reaction chamber.

[0011] In certain embodiments, the pyrolysis oils may be non-hydrogenated pyrolysis oils. The pyrolysis oils may be those derived from pyrolyzing mixed plastic waste materials. The pyrolysis oils may have a boiling point range of from 75 °C to 650 °C in some instances and in others the pyrolysis oils may be that fraction of pyrolysis oils having a boiling point range of from 75 °C to 500 °C.

[0012] The oligomers and waxes may be those derived from plastic waste materials and/or byproducts of the polymerization process. The oligomers may have an average molecular weight (M_n) of from 2,000 g/mol to 10,000 g/mol.

[0013] The liquid hydrocarbon may make up from 0.5 wt% to 100 wt% of the hydrocarbon reactant feeds. The liquid hydrocarbon may be introduced through a liquid feed inlet of the feed assembly in a flow pattern that is non-perpendicular to the central axis. In particular embodiments, the liquid spray may be introduced as a two-fluid spray through a two-fluid nozzle so that the liquid hydrocarbon is introduced through the two-fluid nozzle with a second fluid. The second fluid introduced through the two-fluid nozzle may be a gas. The liquid spray may be introduced in a spray angle of 40° or less.

[0014] The hydrocarbon reactant feed may further comprise a gaseous hydrocarbon. The converted hydrocarbon product may comprise at least one of an olefin, a C₂ to C₆ olefin, ethylene, a propylene, a butene, acetylene, a C₃ to C₆ alkyne, a butadiene, an aromatic compound, a xylene, benzene, toluene, and ethyl benzene.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] For a more complete understanding of the embodiments described herein, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying figures, in which:

[0001] **FIG. 1** is an elevational, cross-sectional view of a reactor system for the conversion of liquid plastic-waste-derived pyrolysis oils, waxes, and oligomers in accordance with various embodiments of the disclosure;

[0016] FIG. 2 is a perspective view of a feed assembly of the reactor system of FIG. 1 in accordance with various embodiments of the disclosure;

[0017] FIG. 3 is cross-sectional perspective view of the feed assembly and upstream end of a reaction chamber of the reactor system of FIG. 1;

5 [0018] FIG. 4 is a plot of the vaporization times as a function of droplet size using a simplified calculation with approximate conditions in a reactor systems, such as that of FIG. 1;

[0019] FIG. 5 is a plot showing the Computational Fluid Dynamics (CFD) calculations of spray evaporation in a reactor, such as that of FIG. 1, wherein all the liquid was vaporized within 5 mm from the injection point;

10 [0020] FIG. 6 is a plot of the results of testing of a FLOWMAX[®] FM3A two-fluid nozzle using liquid water and air showing the various droplet sizes under various flow conditions; and

[0021] FIG. 7 is a plot of selectivity in weight percent of light olefins and aromatics for either full range pyoil or polybutadiene oligomer in an ANJEVOC reactor.

15 **DETAILED DESCRIPTION**

[0022] In various embodiments of the present disclosure, unique reactor technology is utilized to convert pyoil from mixed plastic wastes (MPW), waxes and/or oligomers to produce high value chemicals, such as light olefins and aromatics. The pyoil may be whole-range pyoil or various fractions of pyoil produced from pyrolysis of the MPW. The waxes and/or oligomers
20 may be those obtained from fractional distillation of plastic waste pyoil and/or waxes or oligomers obtained from other sources, such as byproducts from the polymerization process. The conversion of these materials may be accomplished in single step of processing or with reduced or minimal processing steps and equipment, as compared to conventional steam cracking processing systems utilized to process pyoil, which requires additional processing
25 steps. More specifically, the conversion may be achieved by utilizing ANJEVOC (ANnular JEt VOrtex Chamber) reactor technology that produces annular highly swirled jets of feed gases where hydrogen (or other fuels such as natural gas, recycled syngas, etc.) and oxygen gases are mainly used to generate the heat required for cracking of hydrocarbons. Examples of such ANJEVOC reactors are described in U.S. Patent Nos. 11,020,719 and 11,123,705; and
30 International Publication Nos. WO2022/010821A1; WO2022/010822A1, and WO2022/010823A1, each of which is incorporated herein by reference in its entirety for all purposes, including the purpose of illustrating the configuration, construction and operation of such ANJEVOC reactors, and their various components.

[0023] The following includes definitions of various terms and phrases used throughout this specification.

[0024] For the purposes of this disclosure, if a numerical value, concentration or range is presented, each numerical value should be read once as modified by the term "about" (unless
5 already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the description, it should be understood that an amount range listed or described as being useful, suitable, or the like, is intended that any and every value within the range, including the end points, is to be considered as having been stated. For example, "a range from 1 to 10" is to be read as indicating each and every possible number
10 along the continuum between about 1 and about 10. Thus, even if specific points within the range, or even no point within the range, are explicitly identified or referred to, it is to be understood that the inventor appreciates and understands that any and all points within the range are to be considered to have been specified, and that inventor possesses the entire range and all points within the range.

15 [0025] The terms "about" or "approximately" are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting embodiment the terms are defined to be within 10%, preferably, within 5%, more preferably, within 1%, and most preferably, within 0.5%.

[0026] For the purposes of this disclosure, "X, Y, and/or Z" can be construed as X only, Y
20 only, Z only, or any combination of two or more items X, Y, and Z (e.g., XYZ, XY, XZ, YZ). Similarly, "at least one of X, Y, and Z" can be construed as X only, Y only, Z only, or any combination of two or more items X, Y, and Z (e.g., XYZ, XY, XZ, YZ)

[0027] The use of the words "a" or "an" when used in conjunction with the term "comprising,"
"including," "containing," or "having" in the claims or the specification may mean "one," but
25 it is also consistent with the meaning of "one or more," "at least one," and "one or more than one."

[0028] The words "comprising" (and any form of comprising, such as "comprise" and
"comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and
any form of including, such as "includes" and "include") or "containing" (and any form of
30 containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0029] Referring to FIG. 1, an elevational cross-sectional representation of a reactor system 10 for the conversion of liquid hydrocarbons is shown. The reactor system 10 is configured for the conversion of liquid hydrocarbons in the form of pyoil and waxes and/or oligomers, which

may be produced from the pyrolysis of plastic waste, such as MPW, or from other sources. The reactor system 10 can also be used to convert gaseous hydrocarbons in conjunction with the liquid hydrocarbons. The reactor system 10 may constitute an ANJEVOC reactor and includes a reactor vessel 12 having a reactor wall 14 that defines an interior reaction chamber 16. The reactor wall 14 may have a cylindrical configuration with a constant diameter along all or a portion of its length, which may constitute a majority (i.e., > 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, or 95%) of its length. In most instances, the reactor vessel 12 is oriented vertically so that the cylindrical reactor wall 14 is oriented in an upright orientation with downward flow. The reactor can have other orientations (e.g., horizontal, sloped, or upright with upward flow), however, because the process is controlled by the centrifugal force, which exceeds the gravitational force by several orders of magnitude. The reactor vessel 12 may be configured to provide a length to diameter ratio (L/D) of at least 2. In particular applications, the L/D ratio may range from 2-10, more particularly from 2-5.

[0030] The reactor vessel 12 may be formed from steel. In certain embodiments, a cooling jacket can be provided around all or portions of the reactor vessel 12, wherein a second steel wall 18 is positioned around and spaced from the inner reactor wall 14 and a cooling fluid, such as water, may be circulated through the jacket formed between the walls 14, 18. In other embodiments, the reactor wall 14 may be formed from one or more layers of refractory material that line the interior of an outer steel wall to reduce heat loss and sustain the high temperatures of the reactor 10. Because of the unique design and operation of the reactor 10, the reactor wall 14 is cooled internally by the high-velocity near-wall gas flow pushed by centrifugal forces against the reactor wall 14 so that in some applications no exterior cooling jacket is required. This also allows refractory materials to be used for the interior of the reactor wall 14. Refractory materials (without cooling) typically cannot be used with conventional cracking reactors with pure oxygen due to the higher temperatures (e.g., from 2000 °C to 2800 °C). Reaction temperature for the conversion of liquid hydrocarbons, such as crude oil, in the reactor system 10 will typically range from 800 °C to 2500 °C.

[0031] An outlet 20 is provided at a lower or downstream end of the reactor vessel 12 for removing or discharging cracked products from the reaction chamber 16. The outlet diameter can be same as the diameter of the reactor wall 14 or the outlet diameter may be reduced to accelerate the flow before quenching and collection downstream.

[0032] The reactor 10 includes a reactor inlet assembly 22 that is coupled or joined to the upper or upstream end of the reactor wall 14 of the reactor vessel 12. Here, the reactor vessel 12 is oriented vertically with the inlet assembly 22 located above the reactor vessel 12. This is so

that any downstream liquid quenching fluids (e.g., water) that are used within the reaction chamber 16 to quench the reaction gases are carried by gravity to the outlet 20 and not towards the upstream end towards the inlet assembly 22.

[0033] The inlet assembly 22 defines a converging-diverging conduit 24 defined by a circumferential wall 26 that surrounds a central axis 28 of the reactor 10. is the central axis 28 of the reactor 10 may be the same or coincide with the central axis of each of the inlet assembly 22 or conduit 24 and reactor vessel 12. The circumferential wall 26 extends from opposite upstream and downstream ends of the converging-diverging conduit 24. As used herein, the terms “upstream” and “downstream” or similar expressions with respect to describing various components of the reactor system 10 shall refer to the position of the component with respect to the direction of overall fluid flow through the reactor 10 along the central axis 28.

[0034] As can be seen in FIG. 1, the circumferential wall 26 smoothly tapers in width or diameter from the upstream ends to define an annular constricted neck portion located between the downstream and upstream ends of the converging-diverging conduit 24. At the annular constricted neck portion, where the circumferential wall 26 of the conduit 24 transitions from converging or narrowing to diverging or widening, the circumferential wall 26 smoothly expands or diverges in width or diameter downstream from the annular constricted neck portion. The interior of the circumferential wall 26 may have a circular perpendicular transverse cross section with respect to the central axis 28 along all or a portion of its length. The circumferential wall 26 defines an interior flow path of the feed assembly 32, with the constricted neck portion being part of the smoothly curved and streamlined converging-diverging nozzle of the inlet assembly 22.

[0035] The nozzle geometry of the converging-diverging conduit 24 is configured based upon the theory relating to swirling conical jets of a viscous incompressible fluid. This phenomenon is described in the journal article by Pannala et al., entitled "Novel Annular Jet Vortex Reactor for High-Temperature Thermochemical Conversion of Hydrocarbons to Acetylene," published in ACS Engineering in 2022 (Pannala, S. et al. ACS Engineering 2022, 2(5), 406-420). The downstream or diverging portion of the conduit 24 is configured for non-supersonic fluid flow. Conduits or nozzles configured for supersonic flow, such as de Laval nozzles, are configured differently from the conduit 24 to provide supersonic flow downstream to form a shockwave. In various embodiments, the diverging conduit 24 does not form such supersonic flow or shockwave. Instead, the conduit 24 has a geometry that facilitates a recirculation and backflow of gases within the interior reaction chamber 16 near the central axis 28 in combination with annular swirling jet gas flow adjacent to the inner reactor wall 14. As such, the conduit 24 will

have a greater angle of divergence than the angle of divergence typically utilized in de Laval nozzles, which have an angle of divergence of 15° or less. In certain embodiments, the overall angle of divergence “A” (FIG. 1) relative to the central axis 28 may be from 25° or more. In particular instances, the angle of divergence A for the diverging portion of the conduit 24 discussed herein is from 25° to 55°. In some embodiments, the angle of divergence A is from at least, equal to, and/or between any two of 25°, 26°, 27°, 28°, 29°, 30°, 31°, 32°, 33°, 34°, 35°, 36°, 37°, 38°, 39°, 40°, 41°, 42°, 43°, 44°, 45°, 46°, 47°, 48°, 49°, 50°, 51°, 52°, 53°, 54°, and 55°. The large divergence angle leads to recirculation of fluid flow at the reactor wall 14, as a result of the upstream swirling flow coupled with the convergent divergent conduit 24.

[0036] The downstream end of the diverging portion of conduit 24 joins the reactor wall 14 at an inlet of the reaction chamber 16 around its perimeter so that the conduit 24 is in fluid communication with the reaction chamber 16 of the reactor vessel 12. The upstream end of the converging portion of conduit 24 forms an inlet for the reactor vessel 12.

[0037] A reactor feed assembly 32 is provided with the reactor system 10. A perspective view of the feed assembly 32 is shown in FIG. 2. The reactor feed assembly 32 joins the upstream end of conduit 24 and is in fluid communication with the conduit 24, with the central axis 28 passing through the reactor feed assembly 32. The feed assembly 32 includes a downstream feed assembly wall 34 that extends circumferentially around and joins the upstream end of the converging portion of conduit 24. The feed assembly wall 34 or circumferential portions thereof are oriented perpendicularly or substantially perpendicularly (i.e., ≤ 5 degrees from perpendicular about its circumference as it extends radially from the central axis) to the central axis 28.

[0038] Axially spaced upstream from the downstream wall 34 along the central axis 28 is an upstream feed assembly wall 36. The upstream wall 36 or circumferential portions thereof are oriented perpendicular to or substantially perpendicularly (i.e., ≤ 5 degrees from perpendicular about its circumference as it extends radially from the central axis) to the central axis 28.

[0039] An upstream gas partition wall 38 and a downstream gas partition wall 40 are axially spaced between the downstream and upstream feed assembly walls 34, 36 and are axially spaced from one another, with the upstream partition wall 38 being positioned upstream from the downstream partition wall 40. The partition walls 38, 40 or circumferential portions thereof are also each oriented perpendicularly to or substantially perpendicularly (i.e., ≤ 5 degrees from perpendicular about its circumference as it extends radially from the central axis) to the central axis 28. Each of the partition walls 38, 40 has a central opening 42, 44, respectively, that surrounds the central axis 28 and is concentric with the converging-diverging conduit 24. The

inner ends of the partition walls 38, 40 defining the openings 42, 44 terminate at a position upstream of the converging-diverging conduit 24. The central openings 42, 44 each have a circular configuration. Other continuously-curved shapes for the central openings 42, 44 (e.g., oval) may also be used provided such configuration facilitates the swirling of gases to provide the required swirling flow patterns described herein. This shape may also correspond to the cross-sectional shape of the circumferential wall 26 of the converging-diverging conduit 24. In most applications, however, the central openings 42, 44 will be circular in shape. The central openings 42, 44 may have a diameter or width that is the same or slightly different (smaller or larger) than the diameter or width of the constricted neck of the converging-diverging conduit 24 at its narrowest point.

[0040] Referring to FIG. 1, the upstream partition wall 38 defines an annular gas flow passage 46 located between the upstream feed assembly wall 36 and the upstream side of the upstream partition wall 36. In the embodiment shown, the flow passage 46 constitutes an upstream annular hydrocarbon reactant feed inlet flow passage for introducing a gaseous hydrocarbon to be converted, e.g., into high value chemicals such as light olefins and aromatics. Likewise, an annular gas flow passage 48 is defined by the downstream side of the downstream partition wall 40 and the downstream feed assembly wall 34. In the embodiment shown, the flow passage 48 may constitute an annular steam or water inlet flow passage.

[0041] An intermediate partition wall 50 is axially spaced between the downstream gas partition wall 40 and the upstream gas partition wall 38 to define downstream and upstream intermediate annular gas inlet flow passages 52, 54. The intermediate partition wall 50 also has a central opening 56 that surrounds the central axis 28 and is concentric with the converging-diverging conduit 24. The inner ends of the partition wall 50 defining the opening 56 terminate at a position upstream of the converging-diverging conduit 24. The central opening 56 may have a circular configuration. Other shapes for the central opening 56 (e.g., oval) may also be used provided such configuration facilitates the swirling of gases to provide the required swirling flow patterns described herein.

[0042] The intermediate partition wall 50, or circumferential portions thereof, is also oriented perpendicularly to or substantially perpendicularly (i.e., ≤ 5 degrees from perpendicular about its circumference as it extends radially from the central axis) to the central axis 28. In the embodiment shown, the annular flow passage 52 may constitute an oxygen or oxidizing gas flow passage to facilitate combustion. The annular flow passage 54 may constitute a fuel gas (e.g., H_2 , CH_4 , syngas or a combination of these) flow passage for introducing a fuel gas for combustion.

[0043] The area between the downstream and upstream feed assembly walls 34, 36 and spaced radially inward from the central openings 42, 44, 56 of the partition walls 38, 44, 50, respectively, forms a central chamber 58 of the feed assembly 32 that surrounds the central axis 28. The central axis 28 also coincides with and forms a central axis of the central chamber 58 and feed assembly 32.

[0044] This configuration provides flow passages through which gas feeds to be cracked, steam, oxygen gas, and hydrogen-rich fuel for providing combustion heat can each be separately introduced and passed through the flow passages 46, 48, 52, 54, respectively, into the central chamber 58 of the feed assembly 32 in a swirling fluid flow pattern about the central axis 28 such that the feeds combust in the central chamber to form swirling combustion gases. The feeds are introduced into the central chamber in a direction that is non-parallel to the central axis 28. To this end, one or more of the feed assembly wall 34, the upstream wall 36, the partition walls 38, and 40 the intermediate partition wall 50 (or circumferential portions thereof) are configured to introduce the feeds into the central chamber 58 of the feed assembly 32 in a swirling fluid flow pattern about the central axis 28 such that the feeds combust in the central chamber to form swirling combustion gases. The feed assembly wall 34, the upstream wall 36, the partition walls 38, and 40 the intermediate partition wall 50 (or circumferential portions thereof) may be oriented in a direction that is non-parallel to the central axis 28. In some embodiments, one or more of the feed assembly wall 34, the upstream wall 36, the partition walls 38, and 40 the intermediate partition wall 50 (or circumferential portions thereof) may be oriented less than or equal to 5 degrees, less than or equal to 10 degrees, less than or equal to 20 degrees, less than or equal to 30 degrees, less than or equal to 40 degrees from a direction perpendicular the central axis 28.

[0045] The upstream flow passage 46 can act as a gaseous hydrocarbon feed inlet flow passage. A fuel gas feed comprised of an hydrogen-rich gas feed (i.e., H_2) may be introduced into one of the first and second adjacent annular fuel gas inlet flow passages 52, 54, with an oxidizer (i.e., O_2) or oxygen-containing gas feed being introduced into the other of the flow passages 52, 54. Typically, the fuel and oxygen gas feeds will be introduced into flow passages that are immediately adjacent to one another to facilitate rapid combustion. In certain applications, the downstream flow passage 52 may be used for delivering the oxidizer or oxygen-containing gas and the upstream flow passage 54 will be used for delivering the hydrogen-rich fuel gas. The steam feed may be introduced into the downstream annular steam inlet flow passage 48. In other instances, the various feeds may be altered in sequences within the flow passages 46, 48, 52, 54. For example, any of flow passages 48, 52, 54 can act as a gaseous hydrocarbon feed

inlet flow passage. In certain applications, the steam feed may be combined or introduced with one or more of the other feeds. This may include combining the steam feed with the fuel-gas feed, the oxygen-containing gas feed, or the hydrocarbon gas feed.

5 [0046] In certain embodiments, one or more of the flow passages 46, 48, 52, 54 may remain idle or be omitted from the feed assembly 32. If a flow passage is omitted, one of the partition walls 38, 40, 50 need not be present and the number of flow passages will be reduced. In such instances, certain feeds may be combined and introduced together, such as the steam feed previously discussed.

10 [0047] In the illustrated reactor system 10, the flow passages 46, 48, 52, 54 are configured so that the different feeds pass through flow passages perpendicularly or substantially perpendicularly to the central axis 28 in an inwardly swirling fluid flow pattern within said flow passages so that the feeds flow about the central axis 28 within the central chamber 58. The swirling fuel gas and oxidizer feeds combust within the central chamber 58.

15 [0048] In the illustrated reactor system 10, the walls 34, 36, 38, 40, and 50 forming the different flow passages 46, 48, 52, 54 are parallel to one another. However, in other cases, walls 34, 36, 38, 40, and 50 may be non-parallel to one another. The walls 34, 36, 38, 40, and 50 are axially spaced apart to provide the desired volume and flow characteristics for the gases flowing through them. This may be based upon the desired flow rates or linear velocities of each of the feed gases and their relative amounts. For instance, the relative volume of oxygen gas needed
20 for the combustion is typically smaller than the volume of the hydrogen-rich fuel gas needed for the combustion. Therefore, the partition wall 50 may be spaced closer to the downstream partition wall 40 so that the flow passage 54 for the hydrogen fuel is larger and accommodates the greater flow of fuel gas. The particular spacing may depend on fuel gas and oxidizer combination, the desired volume for combustion, and nature of the hydrocarbon feeds.

25 [0049] Annular gas manifolds 60, 62, 64, 66 are provided around the outer periphery of the flow passages 46, 48, 52, 54, respectively. In an example, the gas manifold 60 may be fluidly coupled to a gaseous hydrocarbon feed source. The manifold 62 may be fluidly coupled to a steam source. The manifold 64 may be fluidly coupled to an oxygen-containing-gas source, such as a pure O₂ feed. And the manifold 66 is fluidly coupled to a hydrogen-rich or fuel feed
30 source, such as H₂. The manifolds 60, 62, 64, 66 are provided with the reactor feed assembly 32 to facilitate introduction of feed gases into the flow passages 46, 48, 52, 54. In other embodiments, the different feed sources to each manifold may be varied.

[0050] In general, the gas inlets from the manifolds 60, 62, 64, 66 are oriented to generate an inwardly swirling flow of gases within central chamber 58 (e.g., oriented nearly tangentially

with respect to an outer perimeter of the flow passages 46, 48, 52, 54). In other words, the gas inlets direct the incoming flow of gases along paths that extend inwardly from the walls of central chamber 58 but not along a radius of central chamber 58 directly toward the central axis 28 from the inlets. As an aside, one or more inlets may be provided for each flow passage 46, 48, 52, 54. Furthermore, the walls 34, 36, 38, 40, and 50 that form the different flow passages of the feed assembly 32 prevent the gases from flowing axially along the direction of central axis 28 while they are contained within the flow passages 46, 48, 52, 54. The manifolds 60, 62, 64, 66 can be configured as standard manifolds (e.g., snail-like) as may be typically used in vortex devices.

[0051] Referring to FIG. 2, in some embodiments, one or more or all of the flow passages 46, 48, 52, 54 may be provided with a plurality of circumferentially spaced guide vanes 68, 70, 72, 74 (e.g., 10 to 60 guide vanes for each flow passage). Each guide vane 68, 70, 72, 74 may be a planar member that is oriented in a plane that is parallel to the central axis 28 and extends between the walls 34, 36, 38, 40, and 50. The guide vanes 68, 70, 72, 74 may be circumferentially spaced an equal distance from one another. In certain embodiments, the guide vanes 68, 70, 72, 74 may be fixed in place, with the upper and lower side edges of the guide vanes being joined along their lengths or a portion of their lengths to the walls 34, 36, 38, 40, and 50 so that there are no air gaps between the side edges of the vanes 68, 70, 72, 74 and the walls 34, 36, 38, 40, and 50. In other embodiments, however, the guide vanes are movable. In such cases, the upper and lower side edges of the vanes 68, 70, 72, 74 may be closely spaced from the walls 34, 36, 38, 40, and 50 to provide a small clearance to allow movement. The close spacing may minimize air gaps through which gases may pass. Seals may also be used to effectively close these spaces or clearances while allowing movement. In other instances, the vanes 68, 70, 72, 74 may be oriented so that the plane of the vane is in a non-parallel or slanted orientation relative to the central axis 28. In such cases, the side edges may be fixed to the walls 34, 36, 38, 40, and 50 or remain closely spaced from walls 34, 36, 38, 40, and 50 to minimize air gaps. In certain applications, the guide vanes 68, 70, 72, 74 may be configured as airfoils, such as described in U.S. Patent No. 11,123,705.

[0052] In the illustrated reactor system 10, the guide vanes 68, 70, 72, 74 are provided adjacent to the outer perimeter of the flow passages 46, 48, 52, 54 and are spaced in an annular or circular ring pattern near the manifold inlets. In other reactor systems, they may be provided in an annular pattern at other positions located radially inward or further within the interior of the flow passages 46, 48, 52, 54. Alternatively, one or more additional annular sets of guide vanes

may be located radially inward from those located along the outer periphery to facilitate inwardly swirling fluid flow.

[0053] Feed gases from the manifolds 60, 62, 64, 66 are delivered nearly tangentially to the outer perimeter of the central chamber 58, where the guide vanes 68, 70, 72, 74 may direct the gas flow in an inwardly swirling or spiraling fluid flow pattern within the central chamber 58. In some embodiments, the inlets from the manifolds 60, 62, 64, 66 may be oriented or directed to impart the full inwardly swirling fluid flow without the use of or need for guide vanes. In other embodiments, the guide vanes 68, 70, 72, 74 may impart the full swirling flow of the introduced gases, such as in instances where the gas from the manifold inlets may be directed radially toward the central axis 28 or do not impart the full desired swirling flow. In such cases the guide vanes 68, 70, 72, 74 prevent flow directly toward the central axis 28 and direct the flowing gases nearly tangentially with respect to the inner walls of central chamber 58 to provide the inwardly swirling or spiraling fluid flow pattern.

[0054] The guide vanes 68, 70, 72, 74 of each flow passage 46, 48, 52, 54 may be mounted on actuators (not shown) so that they can be selectively movable to various positions to provide a selected inwardly spiraling flow pattern. The guide vanes 68, 70, 72, 74 may be pivotal about an axis that is parallel to the central axis 28 so that the vanes 68, 70, 72, 74 may be moved to various positions.

[0055] The orientation of the vanes 68, 70, 72, 74 and/or the orientation of the inlets of the manifolds 60, 62, 64, 66 of each flow passage will provide swirling or spiraling fluid jet flow that is in the same rotational direction about the central axis 28, i.e., clockwise or counterclockwise. Thus, gases within each of the flow passages will flow clockwise or counterclockwise about the central axis 28. In general, the vanes 68, 70, 72, 74 will all introduce gases at the same angle inner relative to the walls of central chamber 58 to provide the desired swirling fluid flow characteristics. If the vanes 68, 70, 72, 74 are movable, then they will typically be actuated to move in unison or close to unison.

[0056] In an example, oxygen and hydrogen fuel gases from flow passages 52, 54, gaseous hydrocarbon feed from flow passage 46, and steam from flow passage 48 may be discharged into the central chamber 58 of the feed assembly 32. Because the oxygen-containing gas and hydrogen-rich fuel gas are introduced separately from one another and not as mixture, this eliminates safety issues that would otherwise occur if these gases were premixed prior to their introduction into the feed assembly 32. Furthermore, the combustion reaction takes place rapidly, with most of the combustion occurring within a small space within the central chamber 58 where the two streams of oxygen-containing gas and hydrogen-rich fuel gas from the flow

passages 52, 54 are mixed after being discharged from the flow passages 52, 54. The combustible mixture can be ignited, e.g., using a spark, chemicals or pilot flame that extends through the bottom surface or side surfaces of the reactor. Suction from the swirling flow can transport heat from an ignition device to the combustion zone 58 to initiate the ignition.

5 [0057] The gaseous hydrocarbon feed from the upstream flow passage 46, and steam from flow passage 48 are discharged into the central chamber 58 so that gaseous hydrocarbon feed, steam and heated combustion gases are mixed together and form a swirling gas mixture within the chamber 58. This swirling gas mixture then passes through the converging-diverging conduit 24 and into the reaction chamber 16 of the reactor vessel 12.

10 [0001] A liquid feed inlet 76 is also formed in the upstream feed assembly wall 36 for introducing, into the feed assembly 32, all or a portion of the liquid hydrocarbons to be converted by the reactor system 10 into, e.g., high value chemicals such as light olefins and aromatics. In certain embodiments, there may be more than one or multiple liquid feed inlets 76. The liquid feed inlet 76 may be formed as a length of conduit that joins the feed assembly
15 wall 36. The conduit may include an inlet axis that is aligned with and/or parallel to the central axis 28 so that the liquid feeds or a majority (i.e., > 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, or 95%) of the liquid feeds introduced through the inlet 76 may be introduced axially or at a non-perpendicular angle with respect to the central axis 28 into the central chamber 58. In other words, the liquid feeds introduced through the inlet 76 are not introduced
20 perpendicularly to axis 28. A liquid feed manifold 80 may be used to introduce liquid feeds through the liquid feed inlet 76. The manifold 80 is fluidly coupled to a liquid feed source comprising the liquid hydrocarbon to be converted. The manifold 80 comprises one or more spray nozzles 78 that may be used to introduce the liquid feed as a liquid spray (i.e., a spray of liquid droplets) into the central chamber 58. Where multiple liquid feed inlets 76 are employed,
25 the manifold 80 may comprise multiple spray nozzles 78 positioned and oriented for introducing, into the central chamber 58 through the liquid feed inlets 76, the liquid feed as multiple sprays of droplets. In some embodiments, the droplets in the liquid feed define a non-swirling spray and/or a radially-extending fanned pattern so that all or a portion of the droplets are not parallel to the central axis, but will have axial and radial flow velocity components.
30 Moreover, the droplet pattern may be centered on or close to the central axis where the swirl velocities are lowest. In some embodiments, one or more spray nozzles 78 introduce liquid into the central chamber 58 of the feed assembly 32 where the swirl velocity of the swirling fluid flow is less than 5 m/s during operation of the reactor 10. One or more spray nozzles may be located within a certain placement radius ("PR") defined from a point where the central axis

28 intersects a plane defined by the upstream wall 36 of the feed assembly 32. In one embodiment, the PR is no greater than 30% of the radius of the central chamber 58. In other embodiments, the PR is no greater than 20% of the radius of the central chamber 58. As described below in various embodiments, using a nozzle that creates a particular droplet size and placing the nozzle in a central location within the feed assembly of the reactor system described below (i.e., aligned with or close to the central axis) results in hydrocarbon conversion efficiencies not seen in conventional reactor systems. As described below, the central location of the nozzle injects the liquid hydrocarbon reactant feed into an area of a reactor with a low swirl velocity (e.g., swirl velocity of less than 5 m/s). The location along with the droplet size allows the liquid droplets to vaporize before the droplets enter an area of the feed assembly with higher swirl velocities, thereby preventing rapid coking of the reactor. The combination of a location for the nozzle and a droplet size generated by the nozzle at that location thus provides certain unique advantages.

[0058] The combination of axial and radial flow velocity components defines a spray pattern that has a low spray angle and keeps the pattern close to the central axis 28. As a result, the droplets are directed primarily axially (e.g., to define a spray angle of 40° or less). Such a spray angle helps ensure that liquid droplets are vaporized before being caught in the swirling gas flow and forced by centrifugal forces against the reactor wall, which can lead to coking. In particular embodiments, the spray pattern may have a spray angle of at least, equal to, and/or between any two of 5°, 6°, 7°, 8°, 9°, 10°, 11°, 12°, 13°, 14°, 15°, 16°, 17°, 18°, 19°, 20°, 21°, 22°, 23°, 24°, 25°, 26°, 27°, 28°, 29°, 30°, 31°, 32°, 33°, 34°, 35°, 36°, 37°, 38°, 39°, and 40°. In certain embodiments, the spray pattern may be a solid conical, hollow-conical, linear stream, or flat spray pattern. In various embodiments, the liquid feed inlet 76 is does not include guide vanes, such as the vanes 68, 70, 72, 74, or other structures that may impart a swirling fluid flow to the liquid hydrocarbon before it enters the central chamber 58.

[0059] By introducing the liquid hydrocarbon axially, the atomized spray with liquid droplets is primarily concentrated close to the central axis 28 of the reactor 10 where the swirl velocity is lowest. In effect, the liquid droplets are concentrated at the “eye” of the swirling flow. Higher swirl velocities are encountered away from the central axis 28 or centerline and closer to the walls. These higher swirl velocities could deposit the atomized droplets on the walls and guide vanes causing coking and fouling. The small droplets interact with the counter current flow of the high temperature gases from the combustion and strong recirculation to vaporize the droplets and follow the other hydrocarbon gases to increase heat and crack in the reactor 10.

[0060] The spray nozzle(s) 78 may be selected and/or configured to provide a particular droplet size. The spray nozzle(s) may be constructed or configured to provide droplets under the selected flow conditions (e.g., pressure, velocity) having a Sauter Mean Diameter (SMD) or D_{32} from 1 μm to 250 μm . As used herein, the SMD or D_{32} size is defined as the ratio of droplet volume to the surface area of the droplets in a spray. Droplet measurements may be determined using phase doppler interferometer (PDI) techniques. In particular embodiments, the spray nozzle(s) at the liquid feed inlet 76 may provide a SMD size for the liquid hydrocarbon feed of from at least, equal to, and/or between any two of 1 μm , 2 μm , 3 μm , 4 μm , 5 μm , 6 μm , 7 μm , 8 μm , 9 μm , 10 μm , 11 μm , 12 μm , 13 μm , 14 μm , 15 μm , 16 μm , 17 μm , 18 μm , 19 μm , 20 μm , 21 μm , 22 μm , 23 μm , 24 μm , 25 μm , 26 μm , 27 μm , 28 μm , 29 μm , 30 μm , 31 μm , 32 μm , 33 μm , 34 μm , 35 μm , 36 μm , 37 μm , 38 μm , 39 μm , 40 μm , 41 μm , 42 μm , 43 μm , 44 μm , 45 μm , 46 μm , 47 μm , 48 μm , 49 μm , 50 μm , 55 μm , 60 μm , 65 μm , 70 μm , 75 μm , 80 μm , 85 μm , 90 μm , 95 μm , 100 μm , 105 μm , 110 μm , 115 μm , 120 μm , 125 μm , 130 μm , 135 μm , 140 μm , 145 μm , 150 μm , 155 μm , 160 μm , 165 μm , 170 μm , 175 μm , 180 μm , 185 μm , 190 μm , 195 μm , 200 μm , 205 μm , 210 μm , 215 μm , 220 μm , 225 μm , 230 μm , 235 μm , 240 μm , 245 μm , and 250 μm .

[0061] The smaller the droplet size, the faster the vaporization and less likely the droplets will enter the higher swirl regions of the reactor. The smaller the droplet size, however, there is a higher pressure drop across the nozzle and there is a limit to how fine an atomization can be achieved with the nozzle. Droplet size is therefore a compromise between the two competing requirements. The plot of FIG. 4 shows the vaporization times as a function of droplet size using a simplified calculation with approximate conditions in the reactor. FIG. 5 shows the Computational Fluid Dynamics (CFD) calculations of spray evaporation in the reactor, wherein all the liquid was vaporized within 5 mm from the injection point. The plot shows the volume fraction of liquid of the spray that ranges from approximately 2.5×10^{-5} at its introduction and goes to 0 (which indicates that all the liquid was vaporized).

[0062] Other characteristics of the droplets generated by the spray nozzle(s) 78 may include the weighted average droplet size. Weighted average droplet size may include a mass (volume) median or 50% diameter ($D_{v0.5}$), which is the diameter at which 50% of the total volume of droplets are contained in particles with smaller diameters. In certain embodiments, the $D_{v0.5}$ of the droplets may be from at least, equal to, and/or between any two of 10 μm , 11 μm , 12 μm , 13 μm , 14 μm , 15 μm , 16 μm , 17 μm , 18 μm , 19 μm , 20 μm , 21 μm , 22 μm , 23 μm , 24 μm , 25 μm , 26 μm , 27 μm , 28 μm , 29 μm , 30 μm , 31 μm , 32 μm , 33 μm , 34 μm , 35

μm, 36 μm, 37 μm, 38 μm, 39 μm, 40 μm, 41 μm, 42 μm, 43 μm, 44 μm, 45 μm, 46 μm, 47 μm, 48 μm, 49 μm, 50 μm, 55 μm, 60 μm, 65 μm, 70 μm, 75 μm, 80 μm, 85 μm, 90 μm, 95 μm, 100 μm, 105 μm, 110 μm, 115 μm, 120 μm, 125 μm, 130 μm, 135 μm, 140 μm, 145 μm, 150 μm, 155 μm, 160 μm, 165 μm, 170 μm, 175 μm, 180 μm, 185 μm, 190 μm, 195 μm, 200 μm, 205 μm, 210 μm, 215 μm, 220 μm, 225 μm, 230 μm, 235 μm, 240 μm, 245 μm, and 250 μm. In one specific embodiment, the spray nozzle is configured to form droplets with a $D_{V0.5}$ from 10 μm to 50 μm.

[0063] The $D_{V0.1}$ is the diameter below which 10% of the total volume of droplets are found. In certain embodiments, the $D_{V0.1}$ of the spray may be from at least, equal to, and/or between any two of 5 μm, 6 μm, 7 μm, 8 μm, 9 μm, 10 μm, 11 μm, 12 μm, 13 μm, 14 μm, 15 μm, 16 μm, 17 μm, 18 μm, 19 μm, 20 μm, 21 μm, 22 μm, 23 μm, 24 μm, 25 μm, 26 μm, 27 μm, 28 μm, 29 μm, 30 μm, 30 μm, 31 μm, 32 μm, 33 μm, 34 μm, 35 μm, 36 μm, 37 μm, 38 μm, 39 μm, 40 μm, 41 μm, 42 μm, 43 μm, 44 μm, 45 μm, 46 μm, 47 μm, 48 μm, 49 μm, 50 μm, 55 μm, 60 μm, 65 μm, 70 μm, 75 μm, 80 μm, 85 μm, 90 μm, 95 μm, 100 μm, 105 μm, 110 μm, 115 μm, 120 μm, 125 μm, 130 μm, 135 μm, 140 μm, 145 μm, 150 μm, 155 μm, 160 μm, 165 μm, 170 μm, 175 μm. In one specific embodiment, the spray nozzle is configured to form droplets with a $D_{V0.1}$ from 5 μm to 25 μm.

[0064] The $D_{V0.9}$ is the diameter below which 90% of the total volume of droplets are found. In certain instances, the $D_{V0.9}$ of the spray may be from at least, equal to, and/or between any two of 20 μm, 21 μm, 22 μm, 23 μm, 24 μm, 25 μm, 26 μm, 27 μm, 28 μm, 29 μm, 30 μm, 30 μm, 31 μm, 32 μm, 33 μm, 34 μm, 35 μm, 36 μm, 37 μm, 38 μm, 39 μm, 40 μm, 41 μm, 42 μm, 43 μm, 44 μm, 45 μm, 46 μm, 47 μm, 48 μm, 49 μm, 50 μm, 55 μm, 60 μm, 65 μm, 70 μm, 75 μm, 80 μm, 85 μm, 90 μm, 95 μm, 100 μm, 105 μm, 110 μm, 115 μm, 120 μm, 125 μm, 130 μm, 135 μm, 140 μm, 145 μm, 150 μm, 155 μm, 160 μm, 165 μm, 170 μm, 175 μm, 180 μm, 185 μm, 190 μm, 195 μm, 200 μm, 205 μm, 210 μm, 215 μm, 220 μm, 225 μm, 230 μm, 235 μm, 240 μm, 245 μm, 250 μm, 255 μm, 260 μm, 265 μm, 270 μm, 275 μm, 280 μm, 285 μm, 290 μm, 295 μm, 300 μm, 305 μm, 310 μm, 315 μm, 320 μm, 325 μm, 330 μm, 335 μm, 340 μm, 345 μm, 350 μm, 355 μm, 360 μm, 365 μm, 370 μm, 375 μm, 380 μm, 385 μm, 390 μm, 395 μm, 400 μm, 405 μm, 410 μm, 415 μm, 420 μm, 425 μm, 430 μm, 435 μm, 440 μm, 445 μm, and 450 μm. In one specific embodiment, the spray nozzle is configured to form droplets with a $D_{V0.9}$ from 20 μm to 100 μm.

[0065] To facilitate forming a suitable fine spray of the liquid hydrocarbon feed having such small droplet sizes, the liquid hydrocarbon may be modified to have a dynamic viscosity from 0.1 cP to 1000 cP prior to or at its introduction, as measured using ASTM D445, but at the temperature of operation (i.e., the temperature of the liquid hydrocarbon when passed through the nozzle(s)). For example, as discussed below, the liquid hydrocarbon feed may in some cases be preheated to a temperature between 25 °C to 400°C and viscosity measured at this temperature. The droplet size is approximately proportional to dynamic viscosity to the power of 0.2 and thus lower dynamic viscosity leads to smaller droplet size. Typically, fluids with lower dynamic viscosity also have lower surface tension and the droplet size is approximately correlated to surface tension to the power of 0.5. In certain embodiments, the liquid hydrocarbon may be modified to have a dynamic viscosity from at least, equal to, and/or between any two of 0.1 cP, 0.2 cP, 0.3 cP, 0.4 cP, 0.5 cP, 0.6 cP, 0.7 cP, 0.8 cP, 0.9 cP, 1 cP, 2 cP, 3 cP, 4 cP, 5 cP, 6 cP, 7 cP, 8 cP, 9 cP, 10 cP, 15 cP, 20 cP, 30 cP, 40 cP, 50 cP, 60 cP, 70 cP, 80 cP, 90 cP, 100 cP, 150 cP, 200 cP, 250 cP, 300 cP, 350 cP, 400 cP, 450 cP, 500 cP, 550 cP, 600 cP, 650 cP, 700 cP, 750 cP, 800 cP, 850 cP, 900 cP, 950 cP, and 1000 cP. Modification of the hydrocarbon may include heating the hydrocarbon to a sufficient temperature and/or combining the liquid hydrocarbon with a solvent or low viscosity component to lower the dynamic viscosity. Such solvents may include an oligomer, wax or other liquid have a lower dynamic viscosity than the hydrocarbon being modified.

[0066] In certain applications, the spray nozzle(s) 78 may be configured or selected as a two-fluid nozzle. Such two-fluid nozzles may allow for the introduction of two different fluids, each having different properties from the other. For example, the liquids could include a liquid phase fluid and vapor phase fluid that are each sprayed simultaneously through the nozzle 78. The two-fluid nozzle 78 may have a mixing chamber where the two fluids are mixed prior to being discharged as a spray. Such two-fluid nozzles also provide internal mixing of the two fluids to prevent clogging, as well as providing a fine atomized spray having the above-stated droplet size. Such two-liquid spray nozzles are described, for example, in U.S. Pat. App. Pub. No. US2020/0147624, which is incorporated herein in its entirety for all purposes, including the description of the construction and use of such nozzles. Two-fluid nozzles may facilitate rapidly diffusing the mixture from the outlet, promoting atomization, and forming droplets, which can be conveyed easily by the atomization gas. This can reduce liquid deposition on the mixed gas outlet and prevent clogging. A suitable commercially available two-fluid nozzle for use as the spray nozzle(s) 78 may include that marketed as the FLOWMAX® X-Series or FLOWMAX® FM3A nozzle, available from Spraying Systems Co., Tokyo, Japan.

[0067] The energy input to the spray nozzle is equal to the pressure drop across the nozzle multiplied by the flow rate. To obtain a targeted droplet size distribution, the choice of single-phase or two-phase nozzle depends on the pressure drop of the nozzles. The selection of a single-phase or two-phase nozzle also depends on various requirements (e.g., (i) spray angle, (ii) hollow vs. full spray cone, and (iii) internal mixing and external mixing to address fouling, which can be achieved using a two-phase nozzle). Furthermore, for the current application with hydrocarbons, spray nozzle selection may depend on high temperature operability, coking and fouling characteristics, erosion, ability to detect and unplug the narrow openings of the nozzles, etc. In general, two-fluid nozzles provide a broad range of control over the droplet size distribution and ability to self-clean as the vapor phase can be steam. A disadvantage may be that slight variations in vapor phase or liquid phase flow rates or pressures can dramatically vary the droplet and spray characteristics.

[0068] In various embodiments of the present disclosure, the liquid hydrocarbon may be introduced into the liquid feed inlet 76 through the two-fluid spray nozzle 78 along with a gaseous hydrocarbon and/or steam (i.e., superheated steam) as the second fluid. The spray nozzle 78 is coupled to one end of the spray manifold 80 that is fluidly coupled to separate upstream liquid hydrocarbon and gas feed (i.e., steam and/or gaseous hydrocarbons) sources. The range of pressures for the liquid feed versus vapor feed depend on the design of the nozzle. For example, FIG. 6 shows the results of testing of a FLOWMAX[®] FM3A two-fluid nozzle using liquid water and air under different flow conditions and the various droplet sizes (i.e., D_{32} , $D_{v0.9}$, $D_{v0.99}$). The liquid pressure was varied in the range of 1-3 barg at a constant gas pressure of 4.14 barg. The corresponding liquid flow was in the range of 1-11 liters per minute and air flow rate was between 80-100 Nm³/hr. For these conditions, the SMD varied between 20 μ m to 55 μ m. Thus, these parameters may be tuned for any particular hydrocarbon used as liquid feed and paired with steam or other gas as the vapor phase in such two-fluid nozzles.

[0069] If the desired droplet characteristics are not achieved, the droplets can take a significantly longer time to vaporize. Droplet vaporization time is proportional to square of the droplet diameter. In addition, the droplets may encounter higher swirl velocities leading to high centrifugal acceleration (e.g., 100 g to 100,000 g forces), resulting in deposition of the droplets on the walls and coking and fouling of the reactor. This creates a positive feedback loop where any deposits will disrupt desirable hydrodynamics and accelerate additional maldistribution and deposition. This leads to coking and plugging of the reactor. For robust operations of the reactor with liquid feed, the droplet characteristics in terms of droplet size, spray angle, etc. are thus important.

[0070] In various embodiments of the present disclosure, the liquid hydrocarbon feed that can be converted by the reactor system 10 includes those pyrolysis oils derived from plastic wastes, including pyrolysis oils from MPW. Plastic wastes that may be pyrolyzed to form pyrolysis oils used for the liquid feed may include, but are not limited to, polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polylactic acid (PLA), nylon, expanded polystyrene (EPS), also known as Styrofoam, etc. These may include those plastic materials formed as microplastics, plastic films and wrappers, plastic fibers, fishing gear, plastic straws and utensils, plastic containers, plastic bottles and caps, and plastic toys and various consumer goods. Furthermore, these plastics do not need to be sorted or cleaned and can be a mixture of all types of plastics before they are pyrolyzed, eliminating a significant amount of the processing and costs that are typically associated with mechanical recycling.

[0071] The liquid hydrocarbon feed may include whole-range pyoil, which is that pyoil that has not undergone any fractionation or distillation. In other embodiments, the plastic waste pyoil may be a lighter fraction of pyoil or that portion of pyoil having a boiling point range of less than the final boiling point. Whole-range pyoil from MPW typically has a boiling point range from 75 °C to around 650 °C. The pyoils may have an average molecular weight (Mn) from 100 to 400. Lighter fractions of the pyoil may include those with a final boiling point from 600 °C, 550 °C, 500 °C, 450 °C, 400 °C or less. In certain applications, the liquid hydrocarbon feed may be that having boiling point range from at least, equal to, and/or between any two of 75 °C, 80 °C, 85 °C, 90 °C, 95 °C, 100 °C, 105 °C, 110 °C, 115 °C, 120 °C, 125 °C, 130 °C, 135 °C, 140 °C, 145 °C, 150 °C, 155 °C, 160 °C, 165 °C, 170 °C, 175 °C, 180 °C, 185 °C, 190 °C, 195 °C, 200 °C, 205 °C, 210 °C, 215 °C, 220 °C, 225 °C, 230 °C, 235 °C, 240 °C, 245 °C, 250 °C, 255 °C, 260 °C, 265 °C, 270 °C, 275 °C, 280 °C, 285 °C, 290 °C, 295 °C, 300 °C, 305 °C, 310 °C, 315 °C, 320 °C, 325 °C, 330 °C, 335 °C, 340 °C, 345 °C, 350 °C, 355 °C, 360 °C, 365 °C, 370 °C, 375 °C, 380 °C, 385 °C, 390 °C, 395 °C, 400 °C, 405 °C, 410 °C, 415 °C, 420 °C, 425 °C, 430 °C, 435 °C, 440 °C, 445 °C, 450 °C, 455 °C, 460 °C, 465 °C, 470 °C, 475 °C, 480 °C, 485 °C, 490 °C, 495 °C, 500 °C, 505 °C, 510 °C, 515 °C, 520 °C, 525 °C, 530 °C, 535 °C, 540 °C, 545 °C, 550 °C, 555 °C, 560 °C, 565 °C, 570 °C, 575 °C, 580 °C, 585 °C, 590 °C, 595 °C, 600 °C, 605 °C, 610 °C, 615 °C, 620 °C, 625 °C, 630 °C, 635 °C, 640 °C, 645 °C, and 650 °C.

[0072] The plastic waste pyoils for the liquid feed may be non-hydrogenated pyrolysis oils. Such non-hydrogenated pyoils have not undergone any hydrogenation, such as in a

hydrotreater, after pyrolysis. Hydrogenated pyoils can also be used for the liquid feed, however, as well as a mixture of non-hydrogenated and hydrogenated pyoils. The pyrolysis oils do not need to be hydrogenated, as in conventional conversion systems (e.g., steam cracking), because of the reactor's ability to convert the pyoils without coking. This eliminates the additional processing steps required when processing pyoils in conventional steam cracking systems. It also allows the full range of plastic waste pyoils to be used, whereas steam cracking can only utilize the lighter 80-90% fraction of the pyoil, such as those in the C₄ to C₈ range. Heavier hydrocarbons, such as C₉ or higher, require longer residence times in the cracker, which can result in undesirable coking. Furthermore, pyoils cracked in steam crackers are typically combined with naphtha to improve the liquid feedstock quality and improve the processing and product yield.

[0073] In contrast, using the present reactor system 10, there is no such need to hydrogenate the pyoil or oligomers or combine the feeds with naphtha or other liquid hydrocarbons. The whole-range pyoil, as well as lighter pyoil fractions, waxes, and oligomers, can be used as the liquid feed. This is due to the extremely short contact or residence time and the reactant flow dynamics that occur within the reactor.

[0074] In various embodiments, waxes (i.e., paraffins) and/or oligomers may also be used as the liquid feed and processed in the reactor system 10. These may be waxes and oligomers derived from plastic waste pyoils, such as through distillation or fractionation. All or a portion of the waxes and oligomers may be those from other sources, as well, such as byproducts of the polymerization process.

[0075] The waxes may include those paraffins in the C₂₀ to C₅₀ range or higher. The waxes used for the liquid feed may have an average molecular weight (Mn) from 250 g/mol to 1,000 g/mol. In certain embodiments the waxes may have an average molecular weight (Mn) range from at least, equal to, and/or between any two of 250 g/mol, 260 g/mol, 270 g/mol, 280 g/mol, 290 g/mol, 300 g/mol, 310 g/mol, 320 g/mol, 330 g/mol, 340 g/mol, 350 g/mol, 360 g/mol, 370 g/mol, 380 g/mol, 390 g/mol, 400 g/mol, 410 g/mol, 420 g/mol, 430 g/mol, 440 g/mol, 450 g/mol, 460 g/mol, 470 g/mol, 480 g/mol, 490 g/mol, 500 g/mol, 510 g/mol, 520 g/mol, 530 g/mol, 540 g/mol, 550 g/mol, 560 g/mol, 570 g/mol, 580 g/mol, 590 g/mol, 600 g/mol, 610 g/mol, 620 g/mol, 630 g/mol, 640 g/mol, 650 g/mol, 660 g/mol, 670 g/mol, 680 g/mol, 690 g/mol, 700 g/mol, 710 g/mol, 720 g/mol, 730 g/mol, 740 g/mol, 750 g/mol, 760 g/mol, 770 g/mol, 780 g/mol, 790 g/mol, 800 g/mol, 810 g/mol, 820 g/mol, 830 g/mol, 840 g/mol, 850 g/mol, 860 g/mol, 870 g/mol, 880 g/mol, 890 g/mol, 900 g/mol, 910 g/mol, 920 g/mol, 930 g/mol, 940 g/mol, 950 g/mol, 960 g/mol, 970 g/mol, 980 g/mol, 990 g/mol, and 1000 g/mol.

[0076] The oligomers may be those formed from various monomers or combinations of monomers. In the present application, the oligomers may also be those produced from the partial or incomplete pyrolysis of the polymers or plastic materials. Typically, the monomers will be ethylene or propylene monomers, with ethylene monomers being the predominant monomers. The oligomers may include those having an average molecular weight (Mn) from 1,000 to 50,000. In particular embodiments, the oligomers may have an average molecular weight (Mn) of from 2,000 to 10,000. In certain cases, the oligomers may have an average molecular weight (Mn) from at least, equal to, and/or between any two of 1,000 g/mol, 1,500 g/mol, 2,000 g/mol, 2,500 g/mol, 3,000 g/mol, 3,500 g/mol, 4,000 g/mol, 4,500 g/mol, 5,000 g/mol, 5,500 g/mol, 6,000 g/mol, 6,500 g/mol, 7,000 g/mol, 7,500 g/mol, 8,000 g/mol, 8,500 g/mol, 9,000 g/mol, 9,500 g/mol, 10,000 g/mol, 11,000 g/mol, 12,000 g/mol, 13,000 g/mol, 14,000 g/mol, 15,000 g/mol, 16,000 g/mol, 17,000 g/mol, 18,000 g/mol, 19,000 g/mol, 20,000 g/mol, 21,000 g/mol, 22,000 g/mol, 23,000 g/mol, 24,000 g/mol, 25,000 g/mol, 26,000 g/mol, 27,000 g/mol, 28,000 g/mol, 29,000 g/mol, 30,000 g/mol, 31,000 g/mol, 32,000 g/mol, 33,000 g/mol, 34,000 g/mol, 35,000 g/mol, 36,000 g/mol, 37,000 g/mol, 38,000 g/mol, 39,000 g/mol, 40,000 g/mol, 41,000 g/mol, 42,000 g/mol, 43,000 g/mol, 44,000 g/mol, 45,000 g/mol, 46,000 g/mol, 47,000 g/mol, 48,000 g/mol, 49,000 g/mol, and 50,000 g/mol.

[0077] The liquid hydrocarbon feed may be comprised of one or more of whole-range pyoil, a pyoil fraction, waxes, and oligomers, and combinations of these. These may all be derived from plastic waste or MPW. The liquid hydrocarbon converted with the reactor system 10 will typically make up from 0.5 wt% to 100 wt% of the total weight of the hydrocarbon reactant feeds (i.e., both liquid and gas hydrocarbons). In particular embodiments, the liquid hydrocarbon may make up from at least, equal to, and/or between any two of 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt%, 0.9 wt%, 1.0 wt%, 1.1 wt%, 1.2 wt%, 1.3 wt%, 1.4 wt%, 1.5 wt%, 1.6 wt%, 1.7 wt%, 1.8 wt%, 1.9 wt%, 2.0 wt%, 2.1 wt%, 2.2 wt%, 2.3 wt%, 2.4 wt%, 2.5 wt%, 2.6 wt%, 2.7 wt%, 2.8 wt%, 2.9 wt%, 3.0 wt%, 3.1 wt%, 3.2 wt%, 3.3 wt%, 3.4 wt%, 3.5 wt%, 3.6 wt%, 3.7 wt%, 3.8 wt%, 3.9 wt%, and 4.0 wt%, 4.1 wt%, 4.2 wt%, 4.3 wt%, 4.4 wt%, 4.5 wt%, 4.6 wt%, 4.7 wt%, 4.8 wt%, 4.9 wt%, 5.0 wt%, 5.1 wt%, 5.2 wt%, 5.3 wt%, 5.4 wt%, 5.5 wt%, 5.6 wt%, 5.7 wt%, 5.8 wt%, 5.9 wt%, 6.0 wt%, 6.1 wt%, 6.2 wt%, 6.3 wt%, 6.4 wt%, 6.5 wt%, 6.6 wt%, 6.7 wt%, 6.8 wt%, 6.9 wt%, 7.0 wt%, 7.1 wt%, 7.2 wt%, 7.3 wt%, 7.4 wt%, 7.5 wt%, 7.6 wt%, 7.7 wt%, 7.8 wt%, 7.9 wt%, 8.0 wt%, 8.1 wt%, 8.2 wt%, 8.3 wt%, 8.4 wt%, 8.5 wt%, 8.6 wt%, 8.7 wt%, 8.8 wt%, 8.9 wt%, 9.0 wt%, 9.1 wt%, 9.2 wt%, 9.3 wt%, 9.4 wt%, 9.5 wt%, 9.6 wt%, 9.7 wt%, 9.8 wt%, 9.9 wt%, and 10.0 wt%, 11 wt%, 12 wt%, 13 wt%, 14 wt%, 15 wt%, 16 wt%, 17 wt%, 18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%, 23 wt%, 24 wt%, 25 wt%,

26 wt%, 27 wt%, 28 wt%, 29 wt%, 30 wt%, 31 wt%, 32 wt%, 33 wt%, 34 wt%, 35 wt%, 36 wt%, 37 wt%, 38 wt%, 39 wt%, and 40 wt%, 41 wt%, 42 wt%, 43 wt%, 44 wt%, 45 wt%, 46 wt%, 47 wt%, 48 wt%, 49 wt%, 50 wt%, 51 wt%, 52 wt%, 53 wt%, 54 wt%, 55 wt%, 56 wt%, 57 wt%, 58 wt%, 59 wt%, 60 wt%, 61 wt%, 62 wt%, 63 wt%, 64 wt%, 65 wt%, 66 wt%, 67 wt%, 68 wt%, 69 wt%, 70 wt%, 71 wt%, 72 wt%, 73 wt%, 74 wt%, 75 wt%, 76 wt%, 77 wt%, 78 wt%, 79 wt%, 80 wt%, 81 wt%, 82 wt%, 83 wt%, 84 wt%, 85 wt%, 86 wt%, 87 wt%, 88 wt%, 89 wt%, 90 wt%, 91 wt%, 92 wt%, 93 wt%, 94 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%, and 100 wt% by total weight of the hydrocarbon reactant feedstock.

[0078] In various embodiments of the present disclosure, the liquid hydrocarbon will be converted in the reactor system 10 along with a gaseous hydrocarbon. As used herein, “gaseous hydrocarbon” or similar expressions is meant to include those hydrocarbons that are at conditions, such as temperature and pressure with or without addition of steam dilution, where the hydrocarbon is in a gaseous or superheated state prior to its introduction into the reactor system 10. This may include those hydrocarbons that may be liquids at standard atmospheric conditions but are at elevated temperatures and/or reduced pressures, such that they are vaporized prior to their introduction into the reactor system 10. For example, the gaseous hydrocarbon may have a boiling point at one atmosphere no greater than 450 °C, no greater than 250°C, or no greater than 150°C. The gaseous hydrocarbon may include, but is not limited to, natural gas liquids (NGL), a natural gas condensate, a C₄ stream, and any one or more of a gaseous C₁ to C₂₀ hydrocarbon or mixtures thereof, and combinations of these.

[0079] In certain instances, all or a portion of the gaseous hydrocarbon can be cofed with the liquid hydrocarbon feed through the liquid feed inlet 76 and spray nozzle 78. In the case of the liquid hydrocarbon that is introduced using the two-fluid nozzle 78, the gaseous hydrocarbon may be mixed with the liquid hydrocarbon within the nozzle 78 itself, such as in a mixing chamber of the nozzle, prior to it being discharged as a spray. Where the spray nozzle 78 is not a two-fluid nozzle, the liquid and gaseous hydrocarbons may be mixed and combined upstream of the nozzle 78, where they both may be discharged together through the spray nozzle(s) 78. In still other instances, the gaseous hydrocarbon may be introduced separately from the liquid hydrocarbon through the liquid feed inlet 76.

[0080] In many instances, all or a portion of the gaseous hydrocarbon feed to be converted by the reactor system 10 is introduced through one of the annular gas flow passages 46, 48, 52, 54 of the feed assembly 32. Typically, this will be the upstream flow passage 46, which is immediately adjacent to the liquid feed inlet 76.

[0081] One or both of the liquid hydrocarbon feed and/or gaseous hydrocarbon feed may be mixed with steam. This is typically superheated steam that is combined with and fed with the hydrocarbon feed prior to its introduction into the feed assembly 32 or central chamber 58. In the case of the liquid hydrocarbon that is introduced using the two-fluid nozzle 78, the steam may be mixed with the liquid hydrocarbon within the nozzle 78 itself prior to it being discharged as a spray. Steam may also be separately introduced into the feed assembly 32 through one of the annular flow passages, such as the downstream flow passage 48.

[0082] In an example of operation of the reactor system 10, a gaseous hydrocarbon feed, such as those discussed previously, is introduced from manifold 60 through an inlet into flow passage 46. A hydrogen-containing fuel gas is introduced from manifold 66 into flow passage 54. The hydrogen-containing fuel gas may be hydrogen gas (H_2), methane (CH_4), and/or CO/syngas or a combination of these. Here, the CH_4 is used as fuel for combustion. In certain embodiments where a combination of hydrogen gas and methane are used, the methane may be present in the fuel gas in an amount from 20 mol%, 15 mol%, 10 mol%, 5 mol% or less. Greater amounts of methane may impact the desired selectivity. In other embodiments, however, greater amounts of methane may be used, including 100% methane for the fuel gas. Natural gas may also be used as fuel gas.

[0083] The hydrogen-containing fuel gas may be a hydrogen-gas-rich stream composed primarily of hydrogen gas, which may be a recycled stream from downstream processing, or additional hydrogen gas. The hydrogen-gas-rich stream may contain other components such as methane, CO, steam, inert gases, and CO_2 . Other hydrocarbons can also be used as the fuel gas in certain embodiments and applications. Additionally, small amounts of N_2 can also be present. Sulfur can also be present in the fuel gas or other feed streams. If sulfur is present, additional separation upstream or downstream may be required. The reactor and process are sufficiently robust to accommodate the presence of sulfur, particularly since no catalyst is used. The ratio between the hydrocarbon feed (i.e., the total of liquid and gaseous hydrocarbons) to hydrogen-containing fuel will typically range from 1 to 15, more particularly from 1 to 10, based on mass.

[0084] An oxidizer or oxygen-containing gas, which may be a concentrated or pure oxygen gas, such as from an air separation unit (not shown), is introduced as the oxidizer feed through manifold 64 through inlets into the flow passage 52. Having the oxygen-containing gas introduced through the downstream flow passage 52 spaces it further from liquid feed inlet 76 and any hydrocarbons gas introduced through flow passage 46 to eliminate or minimize any combustion of the introduced hydrocarbon reactant feeds. In certain applications, the mole

ratio of H_2/O_2 may range from 2 to 9, more particularly from 2 to 5, and still more particularly from 2 to 4. The oxygen feed may provide an oxygen equivalent-to-fuel mole ratio from 0.2 to 1.0. An excess of hydrogen also helps to scavenge free radicals (e.g., O, OOH, OH) formed that would otherwise react with the hydrocarbon feeds. In some cases, a mole ratio of H_2/O_2 may be less than 2 to compensate for other fuel gases or to have excess O_2 in the mixing region to release heat to counter endothermic cracking reactions. In some cases, hydrogen is substoichiometric (below 1) to allow for additional exothermic reactions in the mixing zone. The oxygen feed may provide an oxygen equivalent-to-fuel mole ratio from 0.125 to 0.50. Furthermore, the ratio between the hydrocarbon feeds to hydrogen fuel will typically range from 1.0 to 15 based on mass depending on the hydrocarbon feed.

[0085] Steam or water may be introduced through manifold 62 and through inlets into the flow passage 48. Steam may be introduced upstream of the other feeds and may be used to cool the walls of the converging-diverging conduit 24 and reactor vessel 12. The introduced steam also reduces the reaction temperatures within the reactor 10. Steam may also be pre-mixed with the various feeds, such as with the liquid and gaseous hydrocarbon feeds, fuel gas, and/or oxygen-containing feed. Steam may be used in a mass ratio of steam-to-fuel from greater than 0 to 10.0, more particularly from 0 to 2.0, in certain applications.

[0086] In practice, all of the oxygen gas and at least a portion of the hydrogen-containing fuel gas are typically combusted to form heated combustion products that are almost entirely mixed with the other feeds prior to exiting the converging-diverging conduit 24 and entering the reaction chamber 16. With the high centrifugal force of the swirling gases, the denser gases (e.g., cracking feed) flow closer to the reactor wall, while the hotter combustion products tend to flow through the center of the reactor. The device geometry and the swirling gas-mixture from chamber 58 results in a back flow of the gas mixture within the reaction chamber 16. This mixture flows upstream and radially inward from the thin, outer annular mixed gas flow layers circulating within the reaction chamber 16. Internal cooling of the walls may occur due to the high swirling steam delivered through flow passage 48 in FIG. 3. Additional cooling (if necessary) occurs by a water jacket located between walls 14 and 18 in FIG. 1.

[0087] The liquid hydrocarbon feed comprising one or more of pyoil, plastic waste pyoil, MPW pyoil, waxes, and oligomers is introduced through the inlet 76 from nozzle 78 as a spray is immediately vaporized. The low liquid viscosity and resulting small droplet size increase the speed with which the liquid feed is heated and vaporized. In various embodiments, there may be no need for preheating the liquid hydrocarbon prior to its introduction into the reactor system 10. In certain instances, the liquid hydrocarbon may be preheated. This may be

particularly true for oligomers and waxes, which are typically solid (or highly viscous) at room temperature. This may be to reduce the viscosity to the viscosity range, previously discussed, to facilitate optimal droplet formation. Typical temperatures for the preheated liquid may range from 30 °C to 350 °C. Other methods of reducing the viscosity may include combining the hydrocarbon with a solvent (e.g., oligomers and/or waxes with lower viscosities) and/or using that fraction (i.e., distillation fraction) of the hydrocarbon material having the desired viscosity.

[0088] Based upon the type of hydrocarbon feeds, the operational conditions of the reactor may vary. The gas residence time within the reactor may range from 50 milliseconds or less, more particularly from 20 milliseconds or less. In particular embodiments, the residence time may range from 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 millisecond or less, with 10 microseconds being the approximate lowest residence time. The pressure at the reactor outlet may vary. A suitable pressure at the reactor outlet may range from 0 kPa (g) to 10,000 kPa (g), more particularly from 0 kPa (g) to 1,000 kPa (g).

[0089] Reaction temperatures may range from 800 °C to 2500 °C where the lowest temperatures are found at the reactor exit when all the endothermic reactions are completed and the highest temperatures are encountered in the combustion regions of the reactor (flame). The reaction temperature within the reactor and recirculation zone may range from 900 °C to 1300 °C. In particular embodiments, the temperature within the reactor and recirculation zone may range from 1000 °C to 1300 °C, more particularly from 1200 °C to 1250 °C. In some embodiments, the reactor temperature is higher than what is achieved in conventional cracking reactors, such as tube furnace reactors, which typically operate at 800 °C to 900 °C. As discussed earlier, this is due to the temperature limitations of the metallic materials used for such conventional reactors. In the reactor, the swirling gas mixture facilitates keeping the walls of the reactor much cooler than in such conventional cracking reactors. The use of such higher temperatures also allows a shorter residence or contact times shorter contact times resulting in better selectivity and conversion without formation of unwanted products. Operating temperatures for the reactor may be selected to avoid excess production of such unwanted compounds, such as CO and CO₂, or optimize the olefin-to-acetylene ratio, as acetylene is typically not desired.

[0090] The gases are introduced and flow through the flow passages 46, 48, 52, 54 so that the axial velocity (i.e., relative to the central axis 28) is zero or nearly zero prior to being discharged into the central chamber 58. The inlets (not shown) and/or the orientation of the guide vanes 68, 70, 72, 74 may be set for each flow passage 46, 48, 52, 54 so that a selected azimuthal-to-radial velocity ratio for each of the feed streams that flow through the flow passages 46, 48,

52, 54 is achieved, wherein the azimuthal and radial directions are defined in a cross-section perpendicular to the central axis 28 of the reactor 10. In particular, for each inlet, the radial direction is along a line that extends from the inlet to the central axis 28. The azimuthal direction is perpendicular to both this radial direction and the axial direction (i.e., the direction of the central axis 28). Returning to the azimuthal-to-radial velocity ratio, in particular embodiments, it may range from greater than 0 to 30 or more, more particularly from > 0 , 1, or 2 to 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30. In some applications the azimuthal-to-radial velocity ratio may range from > 0 to 5, more particularly from 2 to 4. The particular azimuthal-to-radial velocity ratio may vary depending upon the particular reactor configuration and composition of the various streams, however. This is more intimately related to the mixing times and reaction times depending on the flow rates, composition of the fuel and feedstocks used for cracking.

[0091] Converted hydrocarbon products produced in the reactor are removed from the reactor vessel 12 through outlet 20. The converted hydrocarbon products may be quenched within a quench zone of the reactor 10 or they may be quenched exterior to the reactor 10 in a quenching unit, such as a water-droplet-spray quench vessel, or other suitable gas quench device. The quenched products may be further processed and recycled.

[0092] In a variation of the reactor described, additional hydrocarbon feed gas can be introduced as a secondary feed stream at an intermediate position along the length of reactor vessel 12, such as at inlet 82 (FIG. 1). One or more such inlets 82 may be provided at various locations and in the reactor vessel 12, which may be circumferentially and longitudinally spaced apart. The inlets 82 may be oriented or configured so that gases are introduced at an angle, as well, to facilitate swirling fluid flow, similar to that delivered from the inlets of the feed assembly 32. Feed assemblies provided on the reactor vessel 12 similar to the feed assembly 32 may be used for the introduction of such cracking feed gas so that the cracking feed is introduced as a swirling fluid flow.

[0093] In some embodiments, a plurality of reactor inlet assemblies and corresponding feed assemblies can be provided in a single reactor while maintaining the high performance.

[0094] By utilizing the reactor system 10, the plastic wastes, including MPW and wastes that typically cannot be recycled using mechanical recycling, can be converted into higher value products, such as light olefins and aromatics. The pyoil from such plastic wastes, and waxes and oligomers, both from plastic waste and from other sources, can be processed in a single step process, without hydrogenation or other processing steps that are typically employed in converting these materials. The system features high conversion of the feed and higher

selectivity for olefins. Due to the short residence time, olefins, unsaturates and/or aromatic content in the feedstock will not hinder cracking or conversion nor create excessive coking behaviors during the reaction, as these will merely pass through the reactor unchanged.

[0095] The reactor system 10 utilizing the hydrocarbon reactant feeds, such as those described previously, can be used to provide a variety of higher value products. These include any one or more of olefins, C₂ to C₆ olefins, ethylene, propylenes, butenes, acetylene, C₃ to C₆ alkynes, butadienes, aromatic compounds, xylenes, benzene, toluene, and ethyl benzene. Furthermore, at least a portion of any one or more of these products, such as C₂ to C₆ alkanes, xylenes, benzene, and toluene, in the reactor product stream may be separated from the reactor product stream and recycled to form at least a portion of the hydrocarbon reactant feeds.

[0096] The following examples serve to further illustrate various embodiments and applications.

EXAMPLE

[0097] In the Example below, different experimental runs were made in an ANJEVOC reactor system 10 as described herein using various liquid hydrocarbons with gaseous hydrocarbons. Each experimental run is shown as a different data point along the x-axes of Figure 7.

EXAMPLE 1

[0098] FIG. 7 shows selectivity in weight percent of light olefins and aromatics for either full range pyoil or polybutadiene oligomer with ethane in the ANJEVOC reactor 10,. The ethane gas was introduced through the gas feed 46 of the reactor, while the pyoil and polybutadiene oligomer were each introduced through a single-fluid nozzle 78. The pyoil and polybutadiene oligomer each had a dynamic viscosity of less than 10 cP. The pyoil and polybutadiene oligomer were each introduced as a spray non-perpendicularly and non-tangentially to the central axis of the central chamber of the feed assembly of the reactor. The spray had a SMD size from 10 μ m to 130 μ m during injection. In all experiments, the H₂ flow rate was fixed at 4.2 lb/hr and the steam flow rate was fixed at 5 lb/hr. The flow rate of O₂ varied from 14.5 to 20 lb/hr. The weight percentage of polybutadiene oligomer and full range pyoil varied between 25 to 50% with respect to the ethane flow. The average molecular weight (Mn) of the full range pyoil was 280. The average molecular weight (Mn) for polybutadiene was 1,100. The overall selectivity for olefins and aromatics ranged between 62 – 67 wt% at a conversion level between 83 and 91%.

[0099] While the disclosure has been shown in some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes and modifications without departing from the scope of the disclosure based on experimental data or other optimizations considering the overall economics of the process. Accordingly, it is
5 appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the disclosure.

CLAIMS

1. A method of converting pyrolysis oils, waxes, and/or oligomers to higher value products in a reactor system comprising a central axis, a feed assembly, and a reactor vessel
5 that defines a reaction chamber, the method comprising:
introducing a fuel gas feed and an oxidizer gas feed into the feed assembly to produce a swirling fluid flow pattern about the central axis;
combusting the fuel gas feed and oxidizer gas feed in the feed assembly to form swirling combustion gases;
10 introducing a hydrocarbon reactant feed into the feed assembly, wherein the hydrocarbon reactant feed comprises a liquid hydrocarbon of at least one of (i) plastic-waste-derived pyrolysis oils, (ii) waxes, and (iii) oligomers having an average molecular weight (M_n) of from 1,000 g/mol to 50,000 g/mol, wherein the liquid hydrocarbon has a dynamic viscosity from 0.1 cP to 1000 cP at the temperature at which the liquid hydrocarbon is introduced and
15 the liquid hydrocarbon is introduced as a liquid spray of droplets having a Sauter mean droplet diameter (SMD) from 10 μm to 250 μm ;
mixing the hydrocarbon reactant feed with the swirling combustion gases to form a swirling, heated mixture in the feed assembly;
passing the heated mixture from the feed assembly into the reaction chamber;
20 reacting the heated mixture within the reaction chamber under reaction conditions suitable to convert the hydrocarbons of the hydrocarbon reactant feed into a converted hydrocarbon product; and
removing the converted hydrocarbon product from the reaction chamber.
- 25 2. The method of claim 1, wherein the pyrolysis oils are non-hydrogenated pyrolysis oils.
3. The method of any of claims 1-2, wherein the pyrolysis oils are derived from pyrolyzing mixed plastic waste materials.
- 30 4. The method of any of claims 1-3, wherein the pyrolysis oils have a boiling point range of from 75 °C to 650 °C.
5. The method of any of claims 1-3, wherein the pyrolysis oils are a fraction of pyrolysis oils having a boiling point range of from 75 °C to 500 °C.

6. The method of any of claims 1-5, wherein the oligomers and waxes are derived from plastic waste materials and/or byproducts of the polymerization process.

5 7. The method of any of claims 1-6, wherein the oligomers have an average molecular weight (Mn) of from 2,000 g/mol to 10,000 g/mol.

8. The method of any of claims 1-7, wherein the liquid hydrocarbon is from 0.5 wt% to 100 wt% of one or more hydrocarbon reactant feeds introduced into the feed assembly.

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9. The method of any of claims 1-8, wherein the liquid hydrocarbon is introduced into the feed assembly in a flow pattern that is non-perpendicular to the central axis.

10. The method of any of claims 1-9, wherein the liquid spray is introduced as a two-fluid
15 spray through a two-fluid nozzle so that the liquid hydrocarbon is introduced through the two-fluid nozzle with a second fluid.

11. The method of claim 10, wherein the second fluid introduced through the two-fluid nozzle is a gas.

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12. The method of any of claims 1-11, wherein the liquid spray is introduced in a spray angle of 40° or less.

13. The method of any of claims 1-12, wherein the hydrocarbon reactant feed further
25 comprises a gaseous hydrocarbon.

14. The method of any of claims 1-13, wherein the converted hydrocarbon product comprises at least one of an olefin, a C₂ to C₆ olefin, ethylene, a propylene, a butene, acetylene, a C₃ to C₆ alkyne, a butadiene, an aromatic compound, a xylene, benzene, toluene, and ethyl
30 benzene.

15. The method of any of claims 1-14, wherein the reactor system is an annular jet vortex reactor chamber (ANJEVOC) reactor system.

16. The method of any of the preceding claims, wherein the liquid hydrocarbon is mixed with a second fluid, and a mixture of the liquid hydrocarbon and the second fluid are introduced as a spray through the nozzle.

5 17. The method of any one of the preceding claims, wherein the liquid hydrocarbon and the second fluid are mixed upstream of the nozzle.

18. The method of any one of the preceding claims, wherein the second fluid comprises a gaseous hydrocarbon

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19. The method of any one of the preceding claims, further comprising mixing the liquid hydrocarbon with steam.

20. The method of any one of the preceding claims, further comprising mixing the gaseous
15 hydrocarbon with steam.

21. The method of any one of the preceding claims, wherein the steam comprises superheated steam.

20 22. The method of any one of the preceding claims, further comprising preheating the liquid hydrocarbon.

23. The method of any one of the preceding claims, wherein the liquid hydrocarbon is preheated in a temperature ranging between 30 °C to 350 °C.

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24. The method of any one of the preceding claims, further comprising combining the hydrocarbon with a solvent before introducing the hydrocarbon reactant feed into the feed assembly.

30 25. The method of claim 1, wherein passing the heated mixture from the feed assembly into the reaction chamber comprises passing the heated mixture through a converging-diverging conduit.

26. The method of claim 25, wherein the converging-diverging conduit comprises a constricted neck portion located between the downstream and upstream ends of the converging-diverging conduit.

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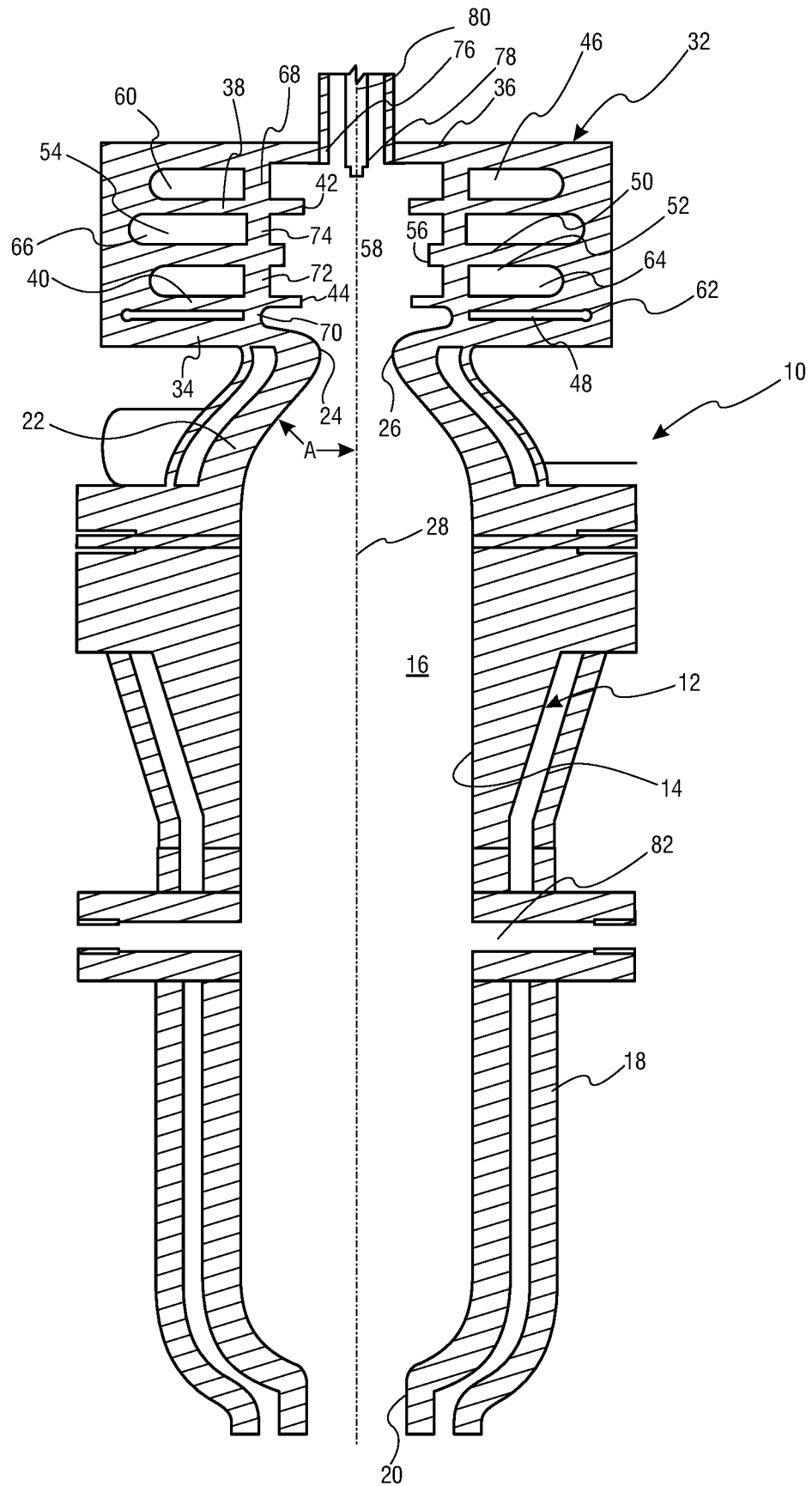


FIG 1

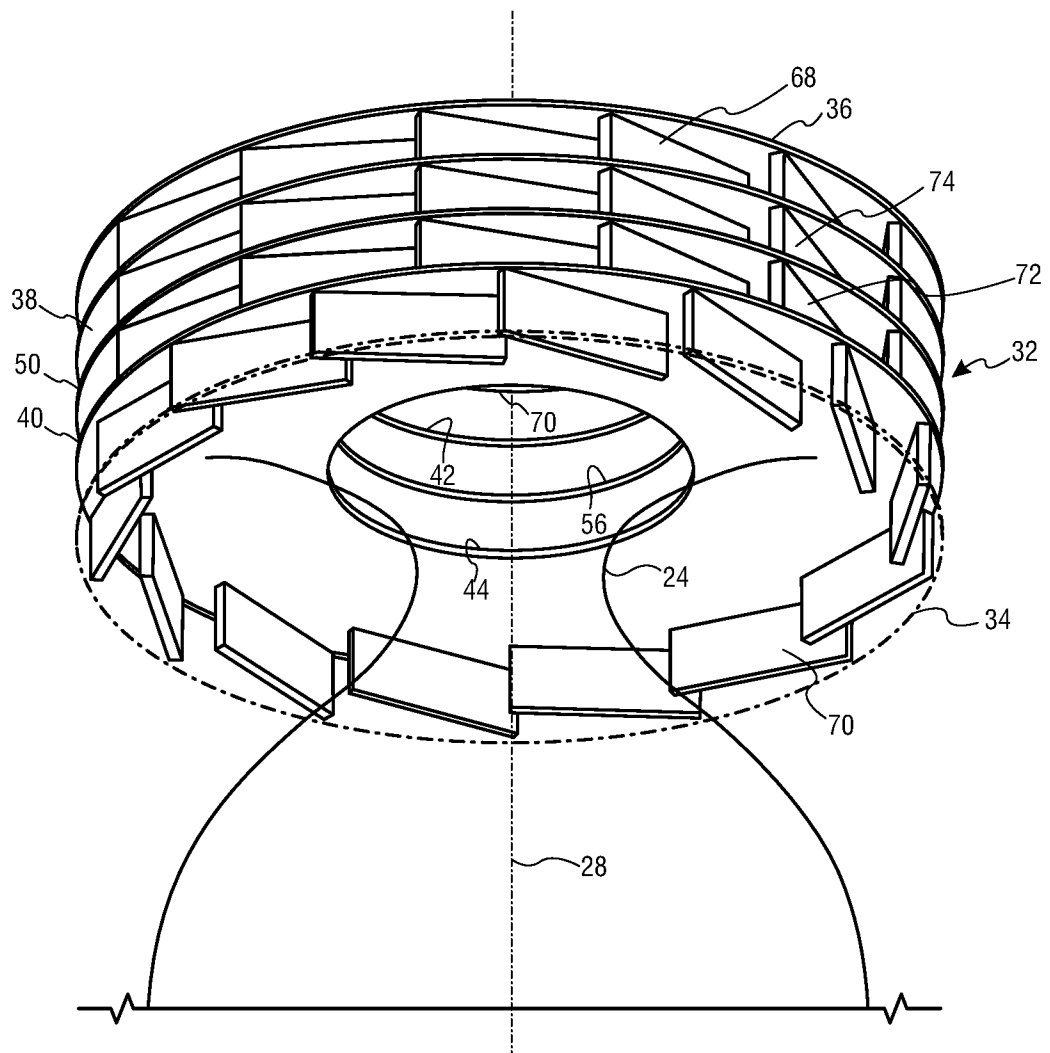


FIG 2

3/6

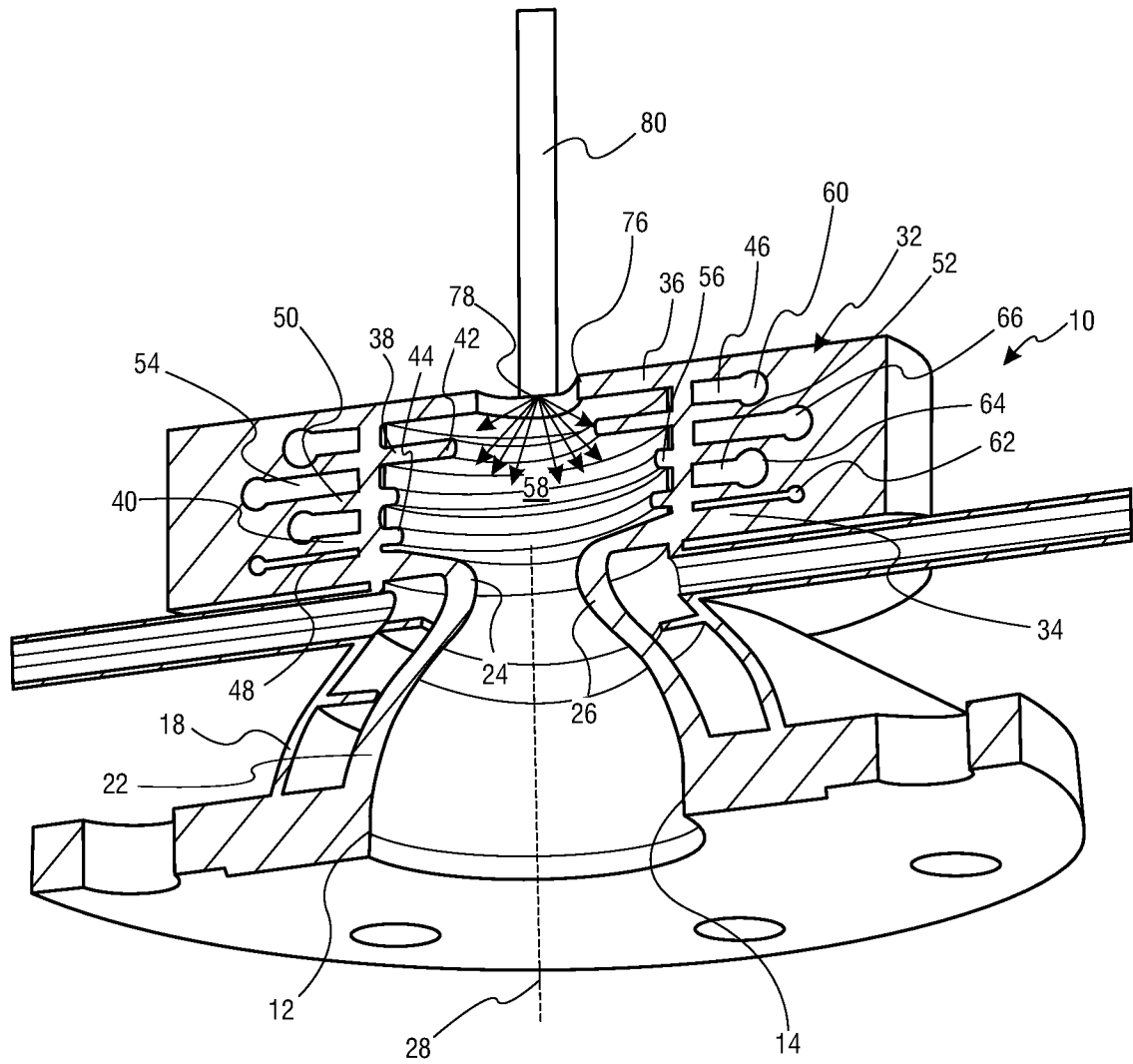


FIG 3

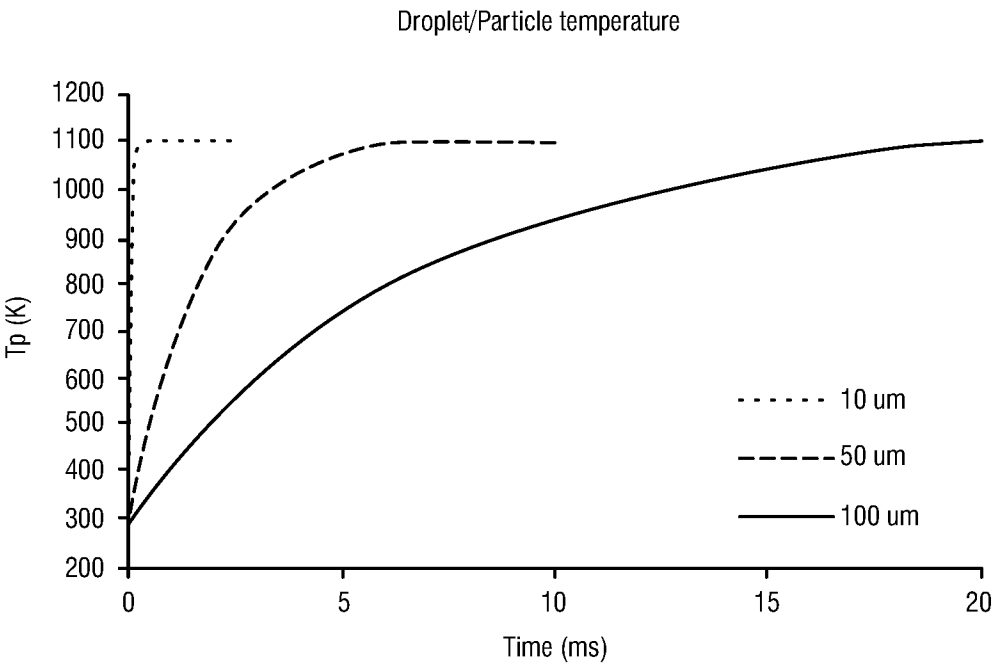


FIG 4

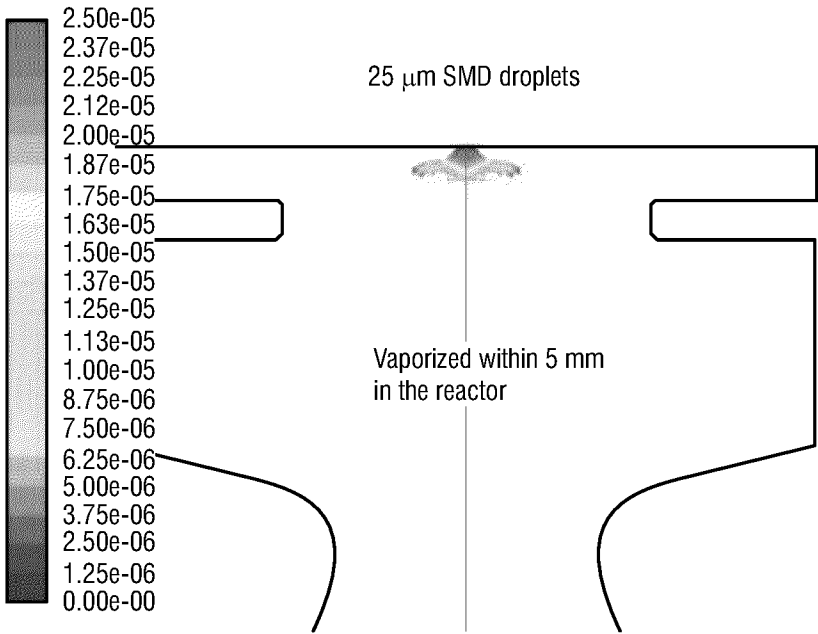


FIG 5

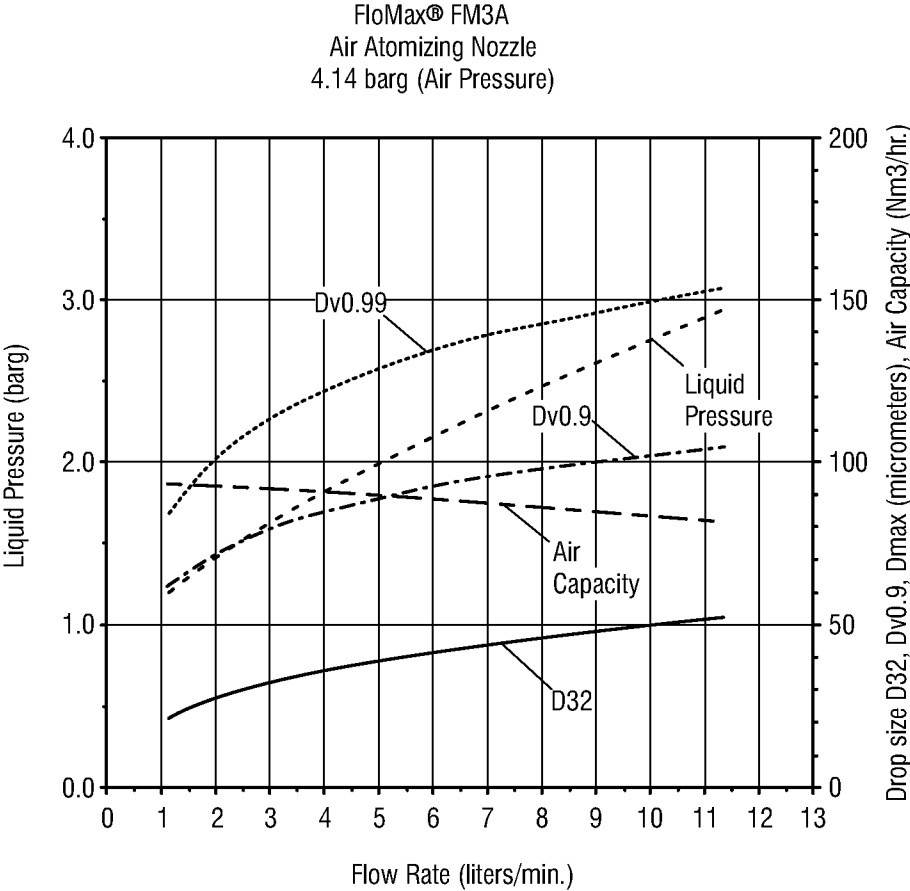


FIG 6

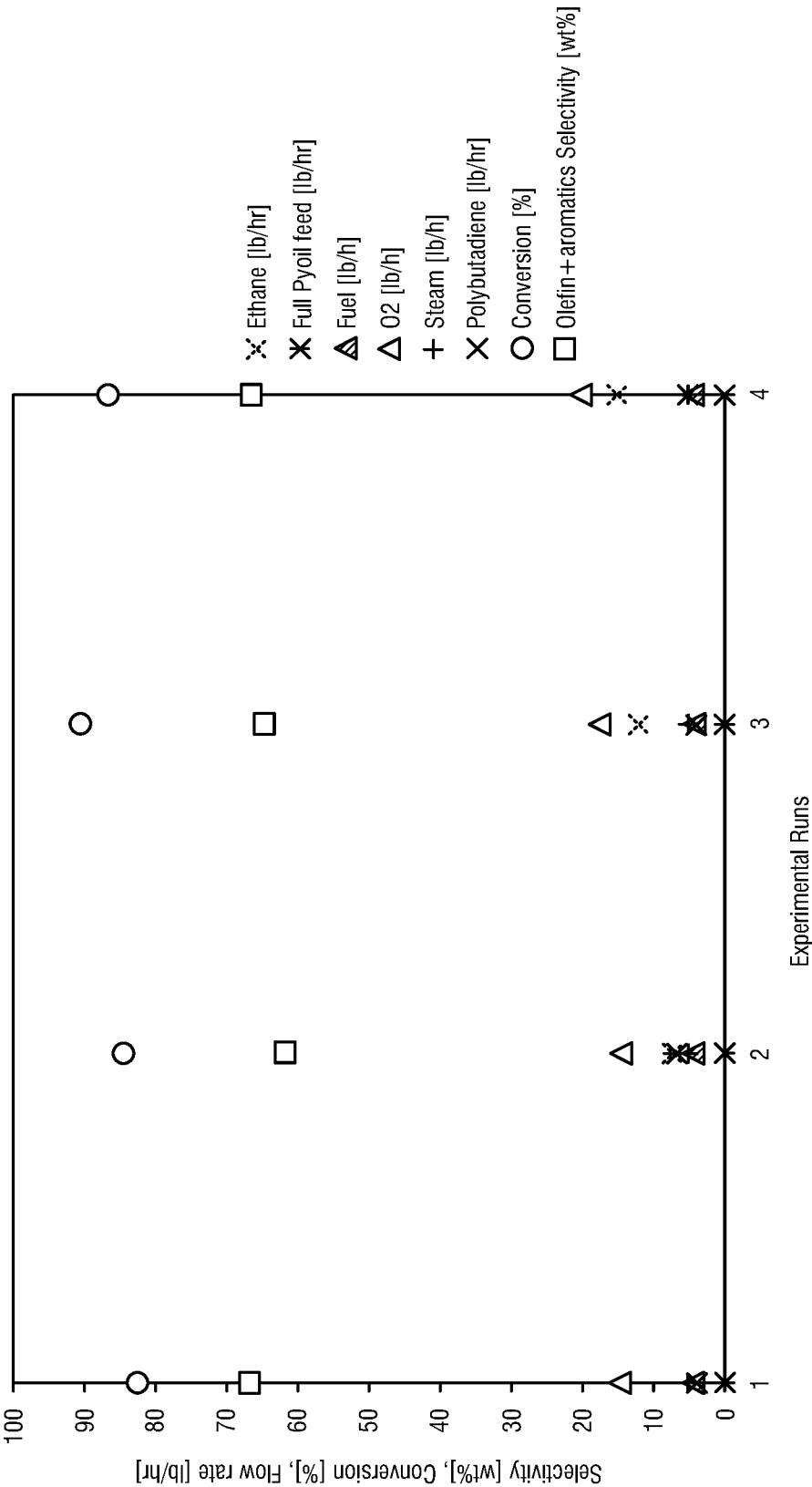


FIG 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/071072

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G9/38 B01J4/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G B01J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2022/010823 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]; PANNALA SREEKANTH [US]) 13 January 2022 (2022-01-13) cited in the application paragraphs [0001], [0006] - [0023], [0081] - [0086] figures 1,2,5,6 claims 1-20 -----	1 - 26
Y	WO 2022/010822 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]; CHEN LEI [US]) 13 January 2022 (2022-01-13) cited in the application figures 1,2,6,7 paragraphs [0006], [0019], [0036], [0043], [0045], [0066], [0079], [0090] - [0097] claims 1-20 ----- - / - -	1 - 26



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

10 October 2024

Date of mailing of the international search report

22/10/2024

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Zuurdeeg, Boudewijn

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/071072

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 166 830 A (ARAND JOHN K [US] ET AL) 4 September 1979 (1979-09-04) figures 1a,1b claims 1-40 paragraph bridging columns 9 and 10 -----	1-26
A	WO 2022/189343 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]) 15 September 2022 (2022-09-15) claims 1-14 figures 1-4 -----	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/071072

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