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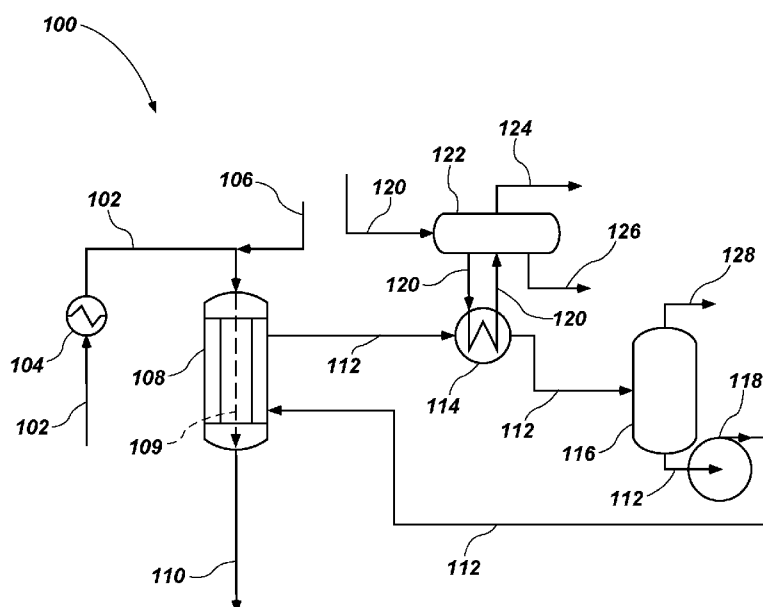


FIG. 1

(57) **Abstract:** A method of oxidizing a fluid includes providing a process fluid to a reactor at a first temperature, providing a heat transfer fluid in a recirculation loop to the reactor at a second temperature higher than the first temperature, and transferring heat from the heat transfer fluid to the process fluid within the reactor. At least one component of the process fluid is oxidized in an exothermic reaction to form a reaction product in the process fluid within the reactor after transferring heat from the heat transfer fluid to the process fluid. Heat is safely transferred from the process fluid to the heat transfer fluid within the reactor after formation of at least a portion of the reaction product.



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

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SYSTEMS AND METHODS OF OXIDIZING FLUIDS**PRIORITY CLAIM**

5 This application claims the benefit of the filing date of United States Provisional Patent Application Serial No. 62/555,727, filed September 8, 2017, for “Systems and Methods of Oxidizing Fluids.”

**STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT**

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This invention was made with government support under Contract Number DE-AC07-05ID14517 awarded by the United States Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

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Embodiments of the present disclosure relate generally to methods of oxidizing fluids using oxidative dehydrogenation reactions and methods of controlling such reactions.

BACKGROUND

20

Oxidative dehydrogenation (ODH) is a chemical reaction that involves the removal of hydrogen from an organic molecule. ODH is industrially important to convert alkanes to olefins, aldehydes, alcohols, polymers, and aromatics. ODH, in the presence of a metal catalyst, is exothermic and occurs at temperatures of 300°C and above. Generally, the reactants (a hydrocarbon and an oxygen-containing gas) are passed over the fixed bed catalyst directly to produce olefin product.

25

For example, ethylene may be produced by catalytic dehydrogenation of ethane in the presence of oxygen. ODH is an important process because the ethylene product is generally more pure than ethylene formed by other processes, and because high ethane conversion can be achieved with ODH at lower temperatures than with other methods of forming ethylene (*e.g.*, typical temperatures for steam cracking may be in the range of 900°C or above). As another example, ethylene may be reacted with an ODH reaction to form ethylene oxide.

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Because ODH reactions are exothermic, and because the reactants and products may be flammable and/or explosive, effective control of reaction temperatures is a topic of interest in the industry. Typically, ODH reactions may be performed in a reactor having a high surface area over which heat can be transferred. For example, an industrial ODH reactor may include tubes packed with catalyst material through which reactants pass. Boiler feed water (BFW) may be passed in a shell surrounding the tubes to maintain a selected temperature profile in the reactor. Even with such controls, a process fluid in an ODH reactor can have a significant temperature spike within the reactor, as shown in FIGS. 5-7 of the accompanying drawings.

DISCLOSURE

In some embodiments, a method of oxidizing a fluid includes providing a process fluid to a reactor at a first temperature, providing a heat transfer fluid in a recirculation loop to the reactor at a second temperature higher than the first temperature, and transferring heat from the heat transfer fluid to the process fluid within the reactor. At least one component of the process fluid is oxidized in an exothermic reaction to form a reaction product in the process fluid within the reactor after transferring heat from the heat transfer fluid to the process fluid. Heat is transferred from the process fluid to the heat transfer fluid within the reactor after formation of at least a portion of the reaction product.

A system for oxidizing a fluid includes a reactor configured to receive a process fluid at a first temperature and a recirculation loop. The recirculation loop is configured to provide a heat transfer fluid to the reactor at a second temperature higher than the first temperature and transfer heat from the heat transfer fluid to the process fluid within the reactor. The reactor is configured oxidize at least one component of the process fluid in an exothermic reaction to form a reaction product in the process fluid after heat is transferred from the heat transfer fluid to the process fluid. The recirculation loop is further configured to transfer heat from the process fluid to the heat transfer fluid within the reactor after formation of at least a portion of the reaction product.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a simplified process flow diagram of an ODH reaction using a heat transfer fluid according to the present disclosure.

FIG. 2 is a simulated temperature profile of a reactor operating and ODH reaction to convert ethane to ethylene.

FIG. 3 is a graph illustrating the concentration of oxygen in the simulated reactor for which a temperature profile is shown in FIG. 2.

FIG. 4 illustrates a simplified process flow diagram of an ODH reaction using steam as a heat transfer fluid according to the present disclosure.

FIGS. 5-7 are simulated temperature profiles of reactors operating conventional ODH processes.

10 MODE(S) FOR CARRYING OUT THE INVENTION

The illustrations presented herein are not actual views of any particular process or equipment, but are merely idealized representations that are employed to describe example embodiments of the present disclosure. Additionally, elements common between figures may retain the same numerical designation.

Methods of oxidizing a fluid as disclosed herein may be used for oxidative dehydrogenation (ODH) reactions. FIG. 1 illustrates a simplified process flow diagram for such a reaction. In a reaction process 100, an influent 102 may be preheated in a preheater 104. The influent 102 may include any hydrocarbon, such as ethane, ethylene, propane, propylene, butane, butylene, ethylbenzene, *etc.* In some embodiments, the influent 102 may include a diluent such as another hydrocarbon, steam, *etc.* The preheater may be a heat exchanger, an electric heater, *etc.* The influent 102 may be preheated to any selected temperature. For example, if the reaction process 100 is designed such that products are formed at about 310°C, the influent 102 may be preheated to about 100°C.

The influent 102 may be combined with an oxidizer 106 (typically oxygen) before entering a reactor 108. The reactor 108 may be a vessel including a catalyst material and may be configured to transfer thermal energy to or from the influent 102. Within the reactor 108, the influent 102 and the oxidizer 106 may react to form an effluent 110. Typically, one or more components of the effluent 110 may be formed by an exothermic reaction between the influent 102 and the oxidizer 106. The reaction continues along the length of the reactor 108. For simplicity in discussing heat transfer, the influent 102, the oxidizer 106, and/or the effluent 110 in any combination within the reactor 108 are referred to herein as the process fluid 109. The composition of the process fluid 109 typically changes along the length of the reactor 108 as the influent 102 and the oxidizer 106 react.

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As an example, the oxidizer 106 may compose from about 0.1 mol% to about 5 mol% of the process fluid 109 at the reactor 108 entrance. The reaction rate in the reactor 108 may be controlled at least in part by changing the concentration of the oxidizer 106 in the reactor 108.

5 The reaction between the influent 102 and the oxidizer 106 may be controlled at least in part by heat transfer between a heat transfer fluid 112 and the process fluid 109. In some embodiments, the reactor 108 is configured similar to a shell-and-tube heat exchanger, with the process fluid 109 passing through the tubes, and with the reaction occurring within the tubes. The heat transfer fluid 112 may pass through the shell (*i.e.*,
10 around the tubes), such that the heat transfer fluid 112 can transfer heat to and from the process fluid 109, and the heat transfer fluid 112 may help to maintain the temperature of the reactor 108 (including the process fluid 109) within selected parameters.

 The heat transfer fluid 112 may recirculate through the reactor 108 and one or more other operations. For example, the heat transfer fluid 112 leaving the reactor 108 may
15 enter a heat exchanger 114, an accumulator 116, and/or a pump 118. Heat may be removed from the heat transfer fluid 112 in the heat exchanger 114 to boiler feed water 120 or another fluid. The boiler feed water 120 may be used for other heating needs, such as by passing the boiler feed water 120 into a flash tank 122 to form steam 124 and
blowdown 126. The steam 124 may be used as known in the art, such as for preheating,
20 reboiling, power generation, general heating, *etc.* In some embodiments, the boiler feed water 120 and/or the steam 124 may be used in a thermoelectric cooler, a Stirling engine, a chemical heat pump, or another device to generate electricity or to upgrade the energy level. The blowdown 126 may include liquid water and solids, and may be used as a purge stream to limit or prevent the buildup of settled solids in the flash tank 122. In some
25 embodiments, the blowdown 126 or a portion thereof may also be used for preheating, reboiling, power generation, general heating, *etc.*

 The accumulator 116 may be available to accumulate and store additional heat, such as by drawing off some of the heat transfer fluid 112 if conditions require. The output 128 of the accumulator 116 may normally have no flow if the process 100 is
30 operating at steady state. That is, the output 128 of the accumulator 116 may operate as a safety to accept excess heat from the heat transfer fluid 112 as needed. Make-up heat transfer fluid 112 (*e.g.*, cooled heat transfer fluid) may therefore be added at another point

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in the process 100 in the event that the heat transfer fluid 112 is extracted through the output 128 of the accumulator 116.

The pump 118 may be used to circulate the heat transfer fluid 112 through the reactor 108 and other unit operations. The process 100 may also include other unit
5 operations, such as a membrane filter to remove particulates leaving the reactor 108 and/or operations to remove water or carbon dioxide.

The reactor 108 may include a plurality of tubes having catalyst material therein. For example, the reactor 108 may include hundreds or even thousands of tubes, each configured to operate as a separate packed-bed reaction chamber. Though depicted as a
10 single flow, the process fluid 109 may be split into multiple streams, each of which may flow over and around particles of catalyst material, and the catalyst material may enable reaction of the influent 102 with the oxidizer 106 to form the effluent 110 (each being components of the process fluid 109). The tubes may be relatively small in diameter, such that each tube has a relatively large ratio of its surface area to its volume. This ratio may in
15 part determine the amount of heat transfer that can occur in the reactor 108. The tube diameter may be selected to be smaller to increase heat transfer at the expense of increased energy requirements in pumping the process fluid 109. Alternatively, the tube diameter may be selected to be larger to decrease energy requirements in pumping the process fluid 109 at the expense of increasing heat transfer between the process fluid 109 and the
20 heat transfer fluid 112. In some embodiments, each tube may have an inside diameter from about 1 cm to about 4 cm, such as about 3 cm.

In some embodiments, the reactor 108 may include another catalyst. For example, if the reactor 108 has tubes containing catalyst material, the final portion of each tube may include a different catalyst to convert residual oxidizer, a byproduct, or an impurity in the
25 process fluid 109 to another species. For example, a platinum catalyst in the last few centimeters of the tubes may cause conversion of CO to CO₂, which may be relatively less toxic and easier to separate from valuable products than CO. A second catalyst may overcome problems associated with nonselectivity of reactions in the reactor 108.

The reactor 108 has been described as having tubes and a shell. However, in other
30 embodiments, the reactor 108 may be a packed-bed reactor, a fluidized-bed reactor, or another selected design. If the reactor 108 is a packed-bed reactor, the oxidizer 106 may be inserted axially at various points along the length of the reactor 108, rather than be mixed with the influent 102 before entering the reactor 108. Such a configuration may enable

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better control of the reaction and may enable the reactor 108 to achieve a higher overall conversion of the influent 102 by adding more of the oxidizer 106 (which, if added all at the same point, may cause the reactor 108 to overheat).

In some embodiments, the reactor 108 may be a fluidized-bed reactor having
5 multiple beds of catalyst material. The process fluid 109 may pass through one or more cyclones to maintain the catalyst material in each bed. The oxidizer 106 may be added before each bed of catalyst material to improve conversion and reaction control. Furthermore, the process fluid 109 may be cooled as necessary between or within the beds.

The reactor 108 may include features to enhance a heat transfer coefficient (and
10 thus an amount of heat transfer) between the process fluid 109 and the heat transfer fluid 112, such as a roughened surface or metallic fibers connected to the wall of the reactor 108. The heat transfer fluid 112 and boiler feed water 120 typically may not limit the heat transfer coefficient (*i.e.*, a change in the flow rate of the heat transfer fluid 112 and/or the boiler feed water 120 may have little or impact on the heat transfer rate from the
15 process fluid 109 to the heat transfer fluid 112).

The reactor 108 may be configured similar to a counter-flow heat exchanger, with the process fluid 109 and the heat transfer fluid 112 entering at opposite ends of the reactor 108 (the heat transfer fluid 112 entering at the bottom and the process fluid 109 entering at the top, in the example depicted in FIG. 1). In some embodiments, the
20 reactor 108 may be configured similar to a parallel-flow heat exchanger, with the process fluid 109 and the heat transfer fluid 112 entering at the same end of the reactor 108. In either case, the temperature change of the heat transfer fluid 112 may be relatively small (as discussed below), such that the direction of flow of the heat transfer fluid 112 does not have a large influence on the temperature profile or heat-transfer driving force within the
25 reactor 108.

The heat transfer fluid 112 may be a material that is stable at temperatures of greater than about 300°C, greater than about 350°C, or even greater than about 400°C. Thus, the heat transfer fluid 112 may receive heat from the influent 102 at temperatures of greater than about 300°C, greater than about 350°C, or even greater than about 400°C. In
30 some embodiments, the heat transfer fluid 112 may include one or more alkane hydrocarbons, such as nonane. In other embodiments, the heat transfer fluid 112 may be a synthetic organic fluid, such as eutectic mixture of biphenyl and diphenyl oxide. Such fluids may be stable at temperatures of 400°C. For example, the heat transfer fluid 112

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may be DOWTHERM™ A, which is a heat transfer fluid available from The Dow Chemical Company, of Midland, Michigan. Such a synthetic organic fluid may be suitable because it may remain stable at temperatures expected to occur in the reactor 108, and within a margin of safety over such temperatures. As a comparison, the critical point of water is at a temperature of 373°C, and therefore, if water is used as the heat transfer fluid 112, the reactor 108 may be designed to be operate at a temperature low enough to maintain a margin of safety below the critical point (*e.g.*, a maximum design temperature may be selected to be about 325°C).

To operate efficiently and avoid runaway conditions, the reactor 108 may be configured such that heat is transferred between the process fluid 109 and the heat transfer fluid 112 to maintain a selected temperature profile of the process fluid 109. For example, the process fluid 109 may be heated by the heat transfer fluid 112 near an inlet of the reactor 108, and may be cooled by the heat transfer fluid 112 after a certain point through the reactor 108.

FIG. 2 is a simulated temperature profile of a reactor 108 (FIG. 1) in operation to convert ethane to ethylene. The simulated reactor 108 has a design temperature T_r of about 310°C, and a length of 7 meters. The design temperature T_r may correspond to the temperature of the process fluid 109 leaving the reactor 108. For about the first 1.5 m of reactor length (before a point X), the heat transfer fluid 112 is hotter than the process fluid 109. Thus, in this region of the reactor 108, the heat transfer fluid 112 heats the process fluid 109. At the point X, the temperatures of the heat transfer fluid 112 and the process fluid 109 are equal, and therefore there is no heat transfer between the heat transfer fluid 112 and the process fluid 109 at this point. After the point X, the heat transfer fluid 112 is cooler than the process fluid 109, and therefore heat is transferred from the process fluid 109 to the heat transfer fluid 112. The maximum difference ΔT between T_r and the temperature of the process fluid 109 may be relatively small, such as less than about 25°C, less than about 20°C, less than about 15°C, less than about 10°C, or even less than about 5°C. The heat of reaction between the influent 102 and the oxidizer 106 may drive up the temperature of the process fluid 109. The heat transfer fluid 112 may help to keep the reaction from thermal runaway, even though the heat transfer fluid 112 may heat the process fluid 109 before point X.

The process modeled in FIG. 2 may have the same inlet and outlet temperatures for the process fluid 109 as conventional processes. However, the maximum temperature of

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the process fluid 109 and the range of the temperature variation (*i.e.*, ΔT) of the process fluid 109 after point *X* may be relatively smaller than conventional processes. FIGS. 5-7 show simulated temperature profiles of reactors operating a conventional processes for comparison, showing the temperatures of process fluids 509, 609, and 709, respectively.

5 As illustrated, conventional processes have a maximum temperature variation significantly larger (*e.g.*, about 50°C) than the process modeled in FIG. 2. For example, in FIG. 5, a heat transfer fluid 512 enters the reactor at 325°C, and the process fluid 509 experiences a 50°C exotherm at the hottest part of the reactor. Though the conversion of reactants (*i.e.*, the limiting reagent) is complete, the hot spot is undesirable.

10 In the simulation depicted in FIG. 6, the heat transfer fluid 612 enters the reactor at 350°C, and the process fluid 609 experiences a 250°C exotherm at the hottest part of the reactor, which is not controllable. Even though the conversion of reactants is complete, the hot spot is very high and not controllable.

In the simulation depicted in FIG. 7, the heat transfer fluid 712 enters the reactor at
15 300°C, and the process fluid 709 experiences a 4°C exotherm at the hottest part of the reactor, which is controllable but undesirable. Furthermore, the conversion of reactants is incomplete, making the reactor unproductive. Also, excess reactive reagents leaving the reactor are a safety hazard.

Thus, the process described herein may be relatively safer (*e.g.*, less likely to
20 experience thermal runaway) and relatively easier to control. The maximum temperature of the process fluid 109 in the process described herein may be below about 400°C, below about 350°C, or even below about 330°C. The temperature variation ΔT may be kept low by increasing the flow rate of the heat transfer fluid 112. For example, the mass flow rate of the heat transfer fluid 112 may be higher than the mass flow rate of the process
25 fluid 109, and may be selected based on the heat capacity of the heat transfer fluid 112. A higher flow rate of the heat transfer fluid may correspond to a flatter temperature profile of the heat transfer fluid 112 within the reactor 108. For example, the mass flow rate of the heat transfer fluid 112 may be higher than at least about 10 times the mass flow rate of the process fluid 109, at least about 50 times the mass flow rate of the process fluid 109, or
30 even at least about 100 times the mass flow rate of the process fluid 109.

FIG. 3 is a graph illustrating the concentration of oxygen (*i.e.*, the oxidizer 106) in the simulated reactor 108 for which a temperature profile is shown in FIG. 2. The concentration of oxygen remains constant during the first portion of the reactor 108 as the

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process fluid 109 is heated to a temperature at which the reaction occurs, then begins to drop, eventually to zero. This indicates that there is no appreciable reaction in the first portion of the reactor 108 (*e.g.*, because the temperature in this portion of the reactor 108 is too low), but that the reaction still goes to completion in the reactor 108. Likewise, there is
5 no appreciable reaction between oxygen and ethane in the final portion of the reactor 108 (*e.g.*, because all of the oxidizer 106 has been consumed). This extra length within the reactor 108 may be purposefully included in the design to ensure that the oxidizer 106 reacts completely before the process fluid 109 exits the reactor 108. However, in these portions of the reactor 108, there may nonetheless be heat transfer between the heat transfer
10 fluid 112 and the process fluid 109, which may prevent the reactor 108 from becoming unstable. Furthermore, the last 15 cm of the reactor 108 may include a different catalyst to convert CO to CO₂.

The effluent 110 (*i.e.*, the process fluid 109 leaving the reactor 108) may include a portion of the original reactant, products of the reaction, water, byproducts, *etc.* For
15 example, if oxygen is supplied as the oxidizer 106 and is the limiting reagent, as in the simulation modeled in FIG. 3, the effluent 110 may include ethane, ethylene, water, and byproducts such as carbon dioxide. The effluent 110 may be subjected to one or more separation processes to remove impurities. In some embodiments, the effluent 110 or a portion thereof may be passed to another stage, which may include the same or similar unit
20 operations as those shown and described in FIG. 1. That is, the process 100 shown in FIG. 1 may be one of two, three, four, *etc.*, stages, each of which may enable an ODH reaction with a fresh supply of the oxidizer 106. A larger fraction of the original reactant may react by operating the process 100 multiple times in series. In some embodiments, the effluent 110 leaving the reactor 108 may be cooled before use as the influent 102 to another
25 reactor 108.

The effluent 110 may subsequently be treated by any other unit operations after leaving the reactor 108. For example, the effluent 110 may be transferred to a vapor-liquid separator, a filter, a distillation column, an absorption or adsorption device, *etc.*, to separate products from reactants or impurities.

30 In some embodiments, and as shown in FIG. 4, a process 400 may use supercritical water 412 as a heat transfer fluid. The process 400 may include a reactor 108 as shown in FIG. 1 and described above. The supercritical water 412 may be used instead of the heat transfer fluid 112 used in the process 100 of FIG. 1.

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The supercritical water 412 may recirculate through the reactor 108 and one or more other operations. For example, the supercritical water 412 leaving the reactor 108 may enter a cooler 414 and/or a pump 418. A makeup feed 416 entering the cooler 414 may include water having a temperature lower than the supercritical water 412 entering the cooler 414. High-pressure steam 420 may be separated from the supercritical water 412 for use in preheating, reboiling, power generation, general heating, *etc.* In some embodiments, the high-pressure steam 420 may be used in a thermoelectric cooler, a Stirling engine, a chemical heat pump, or another device to generate electricity.

The pump 418 may be used to circulate the supercritical water 412 through the reactor 108 and other unit operations. As advantage of using supercritical water 412 for thermal management of the reactor 108 is that the supercritical water 412 can used directly for various heating needs, and the heat exchanger 114 (FIG. 1) may be omitted. One disadvantage of using supercritical water 412 is that equipment must be designed to handle the relevant temperatures and pressures, which can entail significant costs.

In other embodiments, water below its critical point may be used as the heat transfer fluid. In such embodiments, the reactor 108 may be isothermal (*i.e.*, the temperature of the heat transfer fluid may be constant within the reactor 108), due to the evaporation of liquid water to form steam within the reactor 108. Isothermal processes may be relatively easier to control, in part because the latent heat of vaporization is so much higher than the specific heat capacity of changing the temperature of a heat transfer fluid by a few degrees, and because the latent heat is available at a single temperature. Furthermore, steam from the reactor 108 may be used directly in other processes, without transferring the steam to another fluid. One drawback of using subcritical water as the heat transfer fluid is that a margin of safety should be built into the design. That is, the reaction temperature T_r should be kept far enough below 373°C, the critical temperature of water, that the danger of reaching 373°C is low. As known in the art, the properties of water change at its critical point, and thus a reaction that experiences thermal runaway up to 373°C is not likely to be controllable by the water. Thus, the reaction temperature T_r may be selected to be below about 350°C, below about 325°C, below about 310°C, or even below about 300°C. The reaction temperature T_r should be selected to be high enough to cause the reaction between the influent 102 and the oxidizer 106 to proceed. Therefore, a lower boundary on reaction temperature T_r may be about 250°C, about 275°C, or even 290°C, depending on the catalyst activation energy. A reactor 108 having a catalyst with a

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low activation energy may operate at a lower temperature, whereas a catalyst having a high activation energy requires a higher temperature to initiate and sustain the reaction.

ODH reactions using processes as described herein may be used for direct oxidation of alkanes (*e.g.*, ethane) to produce alkenes (*e.g.*, ethylene), or direct oxidation of alkanes to produce epoxides (*e.g.*, ethylene oxide, also known as epoxyethane or oxirane). The processes may be beneficial for any other oxidation reaction or other exothermic reaction. The processes described may enable safe operation and control of such reactions in tubular reactors, packed beds, fluidized beds, *etc.* The use of stable heat transfer fluids may be relatively safer than the use of steam, due to reaction temperatures in the range of the critical point of water.

Additional non limiting example embodiments of the disclosure are described below.

Embodiment 1: A method of oxidizing a fluid, comprising providing a process fluid to a reactor at a first temperature, providing a heat transfer fluid in a recirculation loop to the reactor at a second temperature higher than the first temperature, and transferring heat from the heat transfer fluid to the process fluid within the reactor. At least one component of the process fluid is oxidized in an exothermic reaction to form a reaction product in the process fluid within the reactor after transferring heat from the heat transfer fluid to the process fluid. Heat is transferred from the process fluid to the heat transfer fluid within the reactor after formation of at least a portion of the reaction product.

Embodiment 2: The method of Embodiment 1, wherein the process fluid comprises ethane.

Embodiment 3: The method of Embodiment 1, wherein the process fluid comprises ethylene.

Embodiment 4: The method of Embodiment 1 or Embodiment 2, wherein the reaction product comprises ethylene.

Embodiment 5: The method of Embodiment 1 or Embodiment 3, wherein the reaction product comprises ethylene oxide.

Embodiment 6: The method of any of Embodiments 1 through 5, wherein the reactor comprises a shell and a plurality of tubes comprising catalyst material.

Embodiment 7: The method of Embodiment 6, wherein the providing a reaction fluid to the reactor comprises providing the reaction fluid into the plurality of tubes.

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Embodiment 8: The method of any of Embodiments 1 through 5, wherein the reactor comprises a fluidized-bed reactor.

Embodiment 9: The method of any of Embodiments 1 through 5, wherein the reactor comprises a packed-bed reactor.

5 Embodiment 10: The method of any of Embodiments 1 through 9, further comprising heating the process fluid as the process fluid enters the reactor.

Embodiment 11: The method of any of Embodiments 1 through 10, further comprising preheating the process fluid before the process fluid enters the reactor.

10 Embodiment 12: The method of any of Embodiments 1 through 11, wherein the heat transfer fluid comprises an organic material.

Embodiment 13: The method of Embodiment 14, wherein the heat transfer fluid comprises biphenyl and diphenyl oxide.

Embodiment 14: The method of any of Embodiments 1 through 11, wherein the heat transfer fluid comprises water.

15 Embodiment 15: The method of Embodiment 14, wherein the heat transfer fluid comprises supercritical water.

Embodiment 16: The method of Embodiment 14, wherein the heat transfer fluid comprises subcritical water.

20 Embodiment 17: The method of any of Embodiments 1 through 13, wherein a difference between a maximum temperature of the process fluid and a temperature at which the process fluid leaves the reactor is less than about 20°C.

Embodiment 18: The method of Embodiment 17, wherein a difference between a maximum temperature of the process fluid and a temperature at which the process fluid leaves the reactor is less than about 15°C.

25 Embodiment 19: The method of Embodiment 18, wherein a difference between a maximum temperature of the process fluid and a temperature at which the process fluid leaves the reactor is less than about 10°C.

Embodiment 20: The method of any of Embodiments 1 through 19, wherein the process fluid is maintained below about 400°C at all points within the reactor.

30 Embodiment 21: The method of Embodiment 20, wherein the process fluid is maintained below about 350°C at all points within the reactor.

Embodiment 22: The method of Embodiment 21, wherein the process fluid is maintained below about 330°C at all points within the reactor.

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Embodiment 23: The method of any of Embodiments 1 through 22, wherein the providing a heat transfer fluid in a recirculation loop to the reactor comprises flowing the heat transfer fluid and the process fluid in opposite directions within the reactor.

Embodiment 24: The method of any of Embodiments 1 through 22, wherein the
5 providing a heat transfer fluid in a recirculation loop to the reactor comprises flowing the heat transfer fluid and the process fluid in a common direction within the reactor.

Embodiment 25: The method of any of Embodiments 1 through 24, wherein oxidizing at least one component of the process fluid in an exothermic reaction comprises contacting the process fluid with a catalyst within the reactor.

10 Embodiment 26: The method of Embodiment 25, further comprising contacting the process fluid with another catalyst to reduce a concentration of at least one byproduct in the process fluid.

Embodiment 27: The method of any of Embodiments 1 through 26, wherein a mass
15 flow rate of the heat transfer fluid in the reactor is at least about 10 times the mass flow rate of the process fluid in the reactor.

Embodiment 28: The method of Embodiment 27, wherein a mass flow rate of the heat transfer fluid in the reactor is at least about 50 times the mass flow rate of the process fluid in the reactor.

Embodiment 29: The method of Embodiment 28, wherein a mass flow rate of the
20 heat transfer fluid in the reactor is at least about 100 times the mass flow rate of the process fluid in the reactor.

Embodiment 30: A system for oxidizing a fluid comprising a reactor configured to receive a process fluid at a first temperature and a recirculation loop. The recirculation loop is configured to provide a heat transfer fluid to the reactor at a second temperature
25 higher than the first temperature and transfer heat from the heat transfer fluid to the process fluid within the reactor. The reactor is configured oxidize at least one component of the process fluid in an exothermic reaction to form a reaction product in the process fluid after heat is transferred from the heat transfer fluid to the process fluid. The recirculation loop is further configured to transfer heat from the process fluid to the heat transfer fluid within
30 the reactor after formation of at least a portion of the reaction product.

While the present disclosure has been described herein with respect to certain illustrated embodiments, those of ordinary skill in the art will recognize and appreciate that it is not so limited. Rather, many additions, deletions, and modifications to the illustrated

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embodiments may be made without departing from the scope of the invention as hereinafter claimed, including legal equivalents thereof. In addition, features from one embodiment may be combined with features of another embodiment while still being encompassed within the scope of the invention. Further, embodiments of the disclosure

5 have utility with different and various reactor types and configurations.

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CLAIMS

What is claimed is:

- 5 1. A method of oxidizing a fluid, comprising:
providing a process fluid to a reactor at a first temperature;
providing a heat transfer fluid in a recirculation loop to the reactor at a second temperature
 higher than the first temperature;
transferring heat from the heat transfer fluid to the process fluid within the reactor;
10 after transferring heat from the heat transfer fluid to the process fluid, oxidizing at least one
 component of the process fluid in an exothermic reaction to form a reaction product
 in the process fluid within the reactor; and
transferring heat from the process fluid to the heat transfer fluid within the reactor after
 formation of at least a portion of the reaction product.
15 2. The method of claim 1, wherein the process fluid comprises ethane.

 3. The method of claim 1, wherein the process fluid comprises ethylene.

20 4. The method of claim 1, wherein the reaction product comprises ethylene.

 5. The method of claim 1, wherein the reaction product comprises ethylene
oxide.

25 6. The method of claim 1, wherein the reactor comprises a shell and a plurality
of tubes comprising catalyst material.

 7. The method of claim 6, wherein the providing a reaction fluid to the reactor
comprises providing the reaction fluid into the plurality of tubes.
30 8. The method of claim 1, wherein the reactor comprises a fluidized-bed
reactor.

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9. The method of claim 1, wherein the reactor comprises a packed-bed reactor.
10. The method of claim 1, further comprising heating the process fluid as the process fluid enters the reactor.
- 5 11. The method of claim 1, further comprising preheating the process fluid before the process fluid enters the reactor.
- 10 12. The method of claim 1, wherein the heat transfer fluid comprises an organic material.
13. The method of claim 12, wherein the heat transfer fluid comprises biphenyl and diphenyl oxide.
- 15 14. The method of claim 1, wherein the heat transfer fluid comprises water.
15. The method of claim 14, wherein the heat transfer fluid comprises supercritical water.
- 20 16. The method of claim 14, wherein the heat transfer fluid comprises subcritical water.
- 25 17. The method of claim 1, wherein a difference between a maximum temperature of the process fluid and a temperature at which the process fluid leaves the reactor is less than about 20°C.
- 30 18. The method of claim 17, wherein a difference between a maximum temperature of the process fluid and a temperature at which the process fluid leaves the reactor is less than about 15°C.
19. The method of claim 18, wherein a difference between a maximum temperature of the process fluid and a temperature at which the process fluid leaves the reactor is less than about 10°C.

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20. The method of claim 1, wherein the process fluid is maintained below about 400°C at all points within the reactor.

5 21. The method of claim 20, wherein the process fluid is maintained below about 350°C at all points within the reactor.

22. The method of claim 21, wherein the process fluid is maintained below about 330°C at all points within the reactor.

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23. The method of claim 1, wherein the providing a heat transfer fluid in a recirculation loop to the reactor comprises flowing the heat transfer fluid and the process fluid in opposite directions within the reactor.

15 24. The method of claim 1, wherein the providing a heat transfer fluid in a recirculation loop to the reactor comprises flowing the heat transfer fluid and the process fluid in a common direction within the reactor.

20 25. The method of claim 1, wherein oxidizing at least one component of the process fluid in an exothermic reaction comprises contacting the process fluid with a catalyst within the reactor.

25 26. The method of claim 25, further comprising contacting the process fluid with another catalyst to reduce a concentration of at least one byproduct in the process fluid.

27. The method of claim 1, wherein a mass flow rate of the heat transfer fluid in the reactor is at least about 10 times the mass flow rate of the process fluid in the reactor.

30 28. The method of claim 27, wherein a mass flow rate of the heat transfer fluid in the reactor is at least about 50 times the mass flow rate of the process fluid in the reactor.

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29. The method of claim 28, wherein a mass flow rate of the heat transfer fluid in the reactor is at least about 100 times the mass flow rate of the process fluid in the reactor.

- 5 30. A system for oxidizing a fluid, comprising:
a reactor configured to receive a process fluid at a first temperature, and after transferring
heat from a heat transfer fluid to the process fluid, oxidize at least one component
of the process fluid in an exothermic reaction to form a reaction product in the
process fluid; and
10 a recirculation loop configured to:
provide a heat transfer fluid to the reactor at a second temperature higher than the
first temperature;
transfer heat from the heat transfer fluid to the process fluid within the reactor; and
transfer heat from the process fluid to the heat transfer fluid within the reactor after
15 formation of at least a portion of the reaction product.

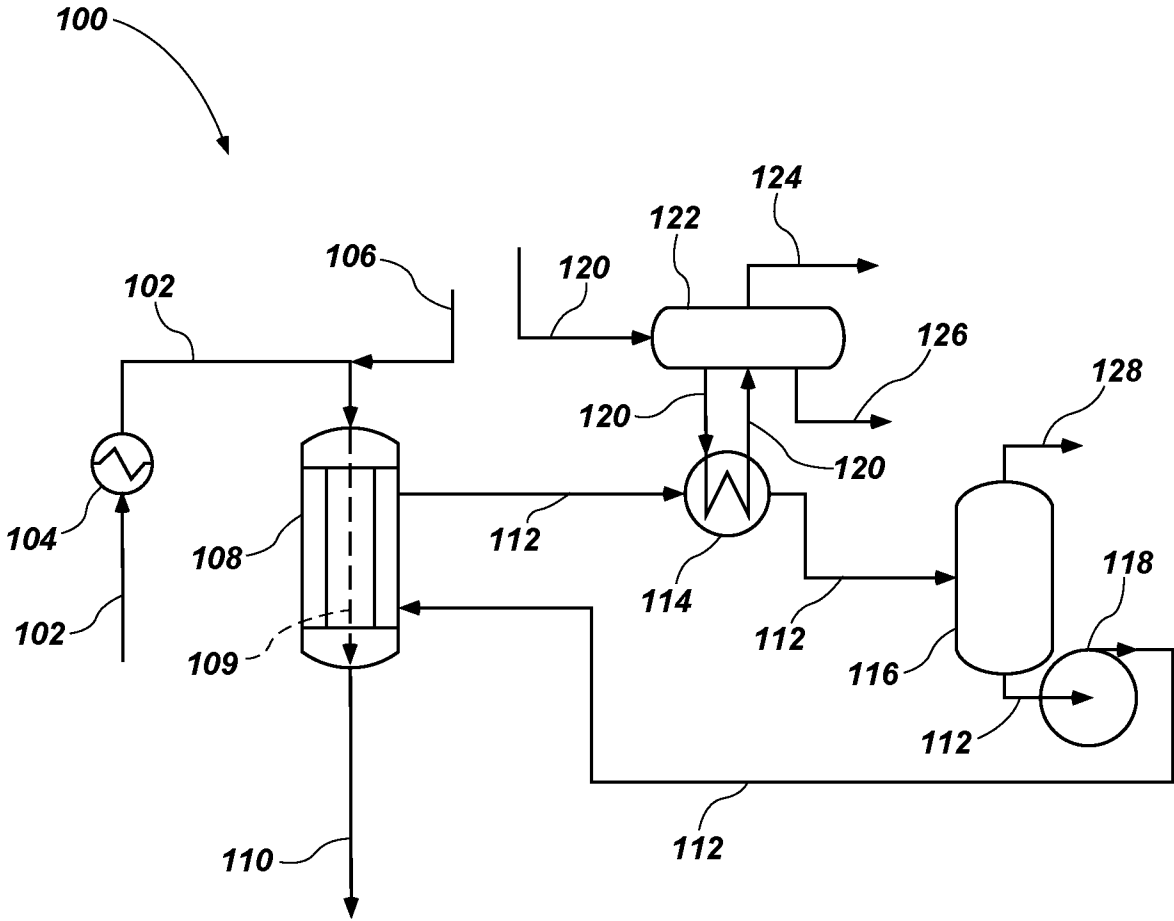


FIG. 1

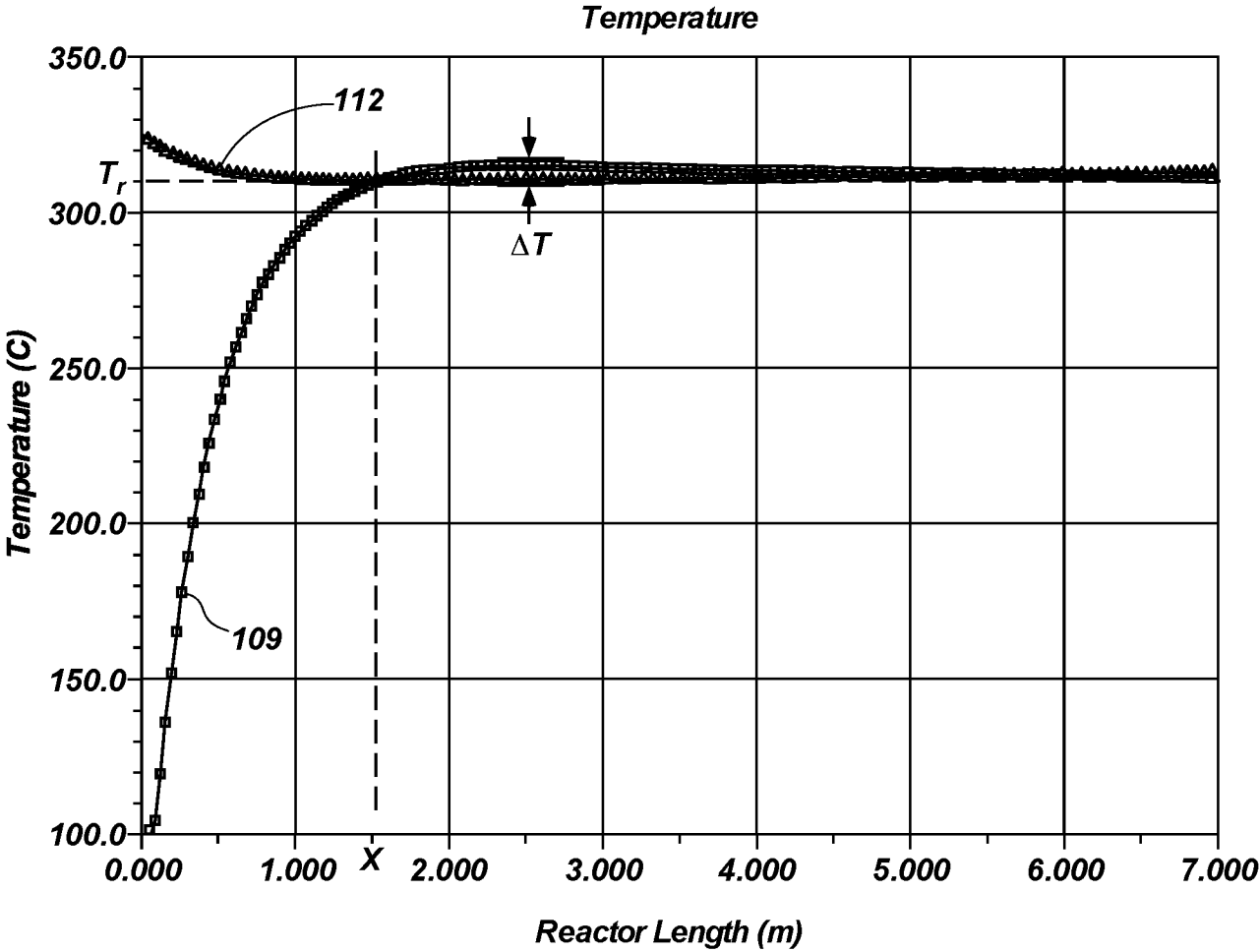


FIG. 2

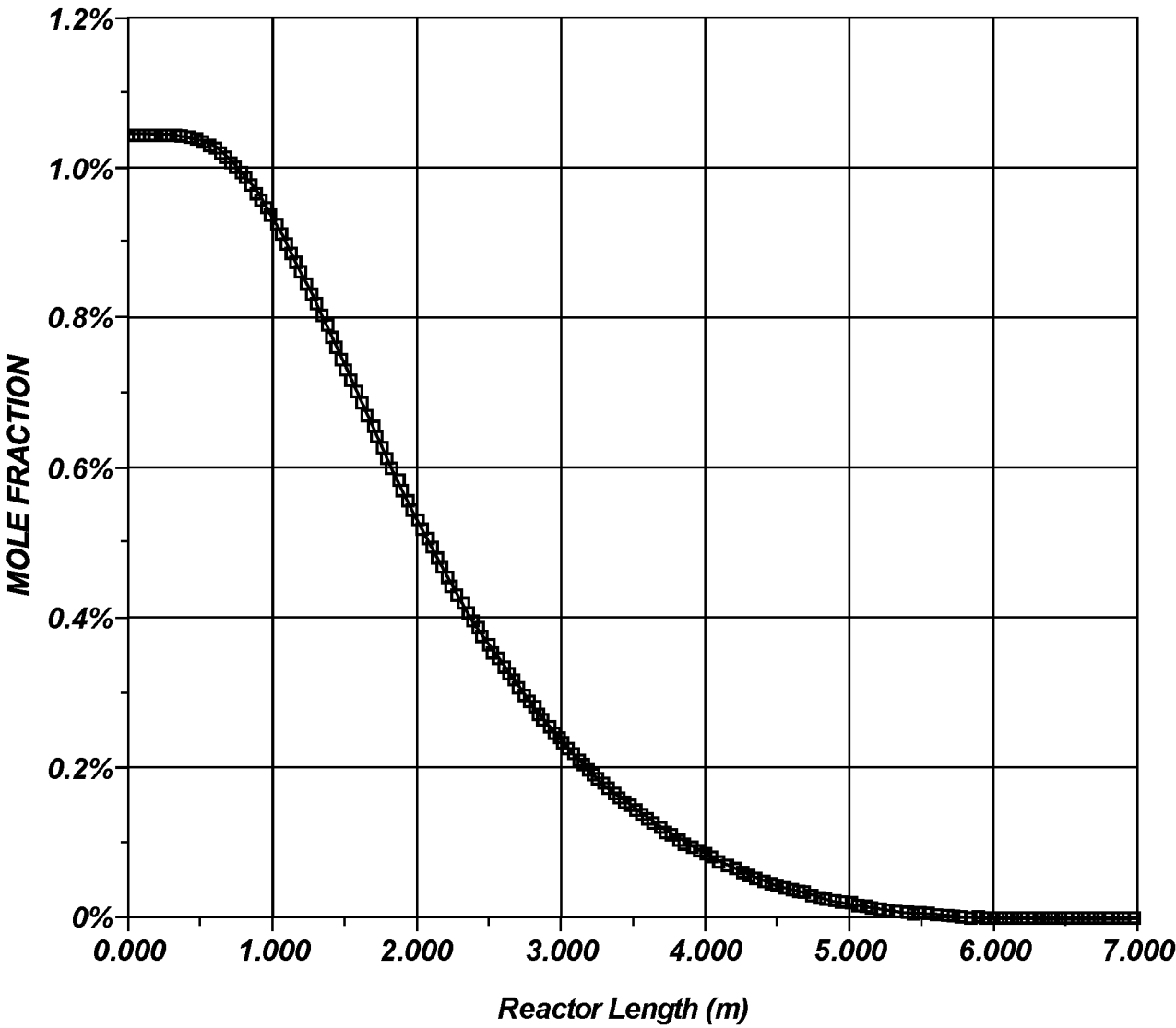


FIG. 3

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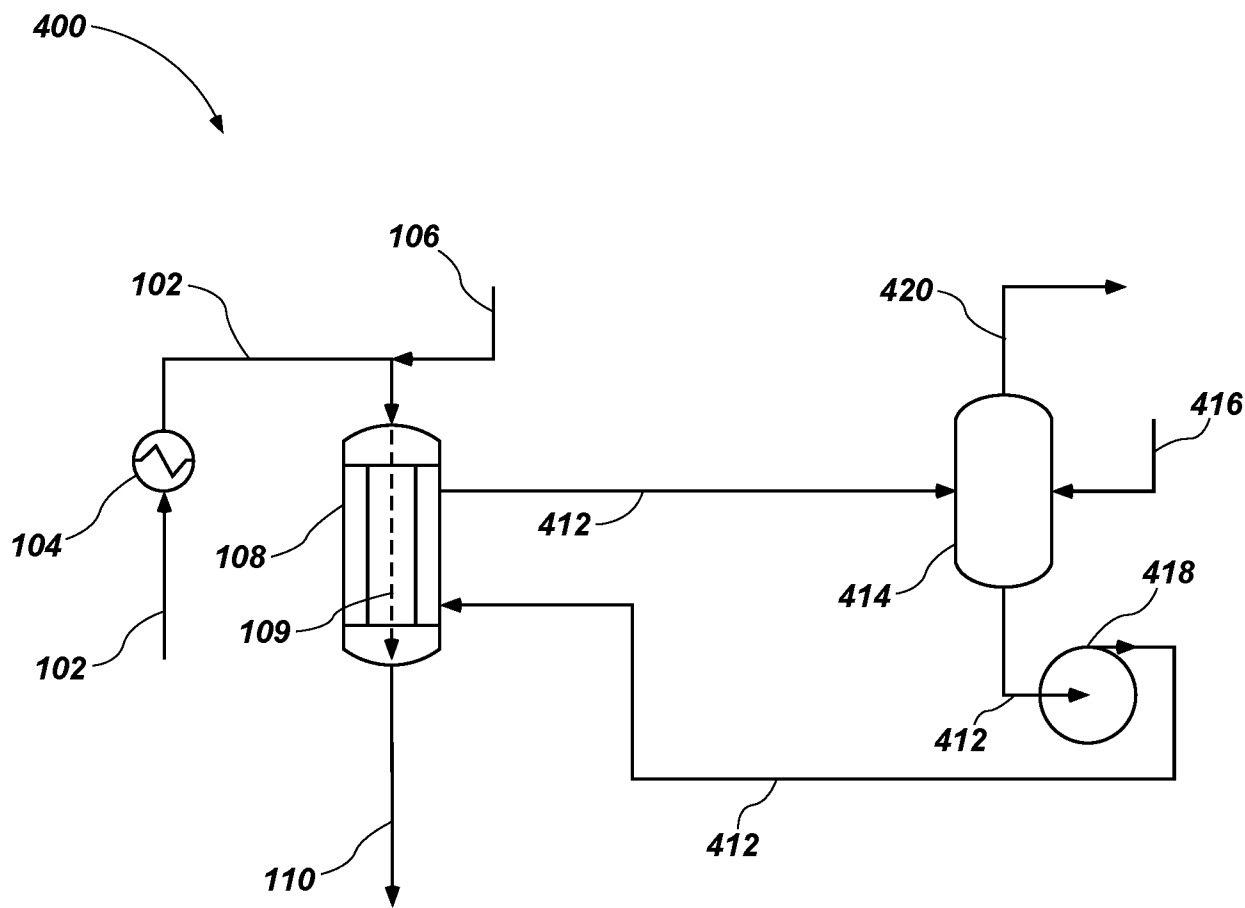


FIG. 4

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Temperature

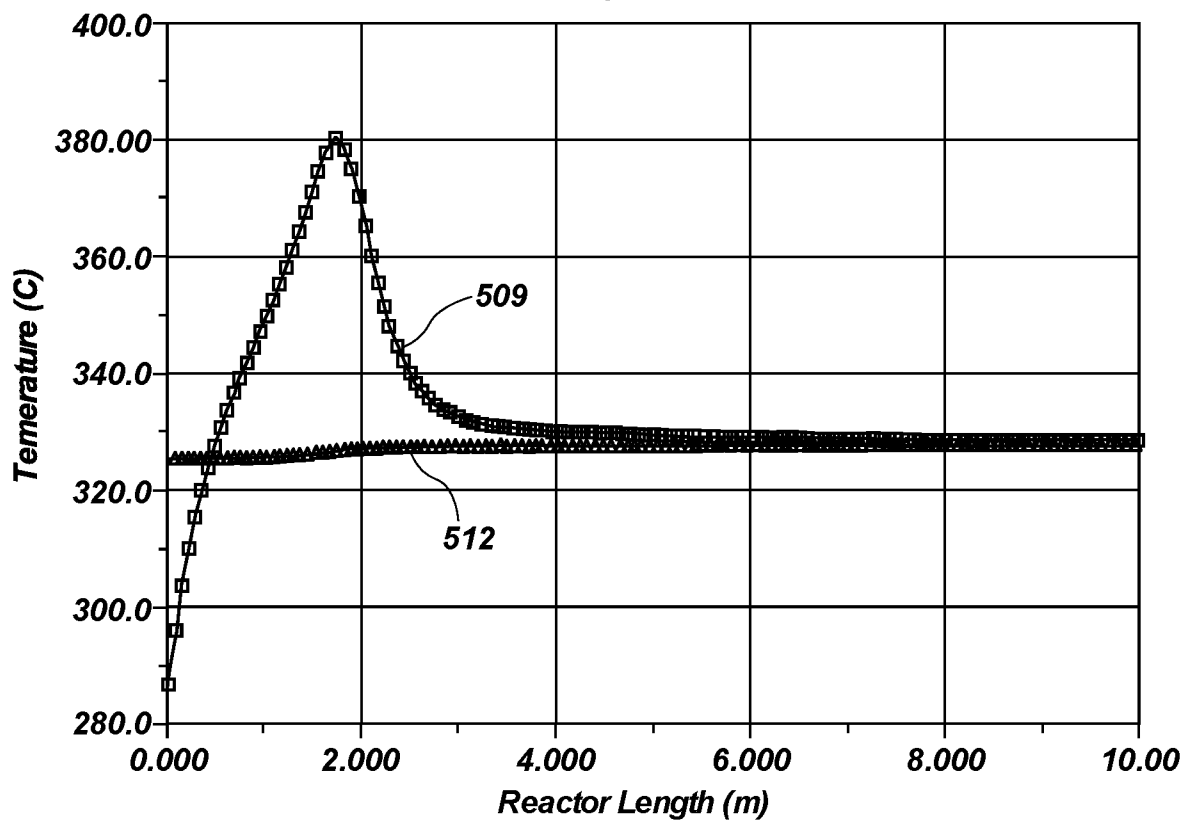


FIG. 5

Temperature

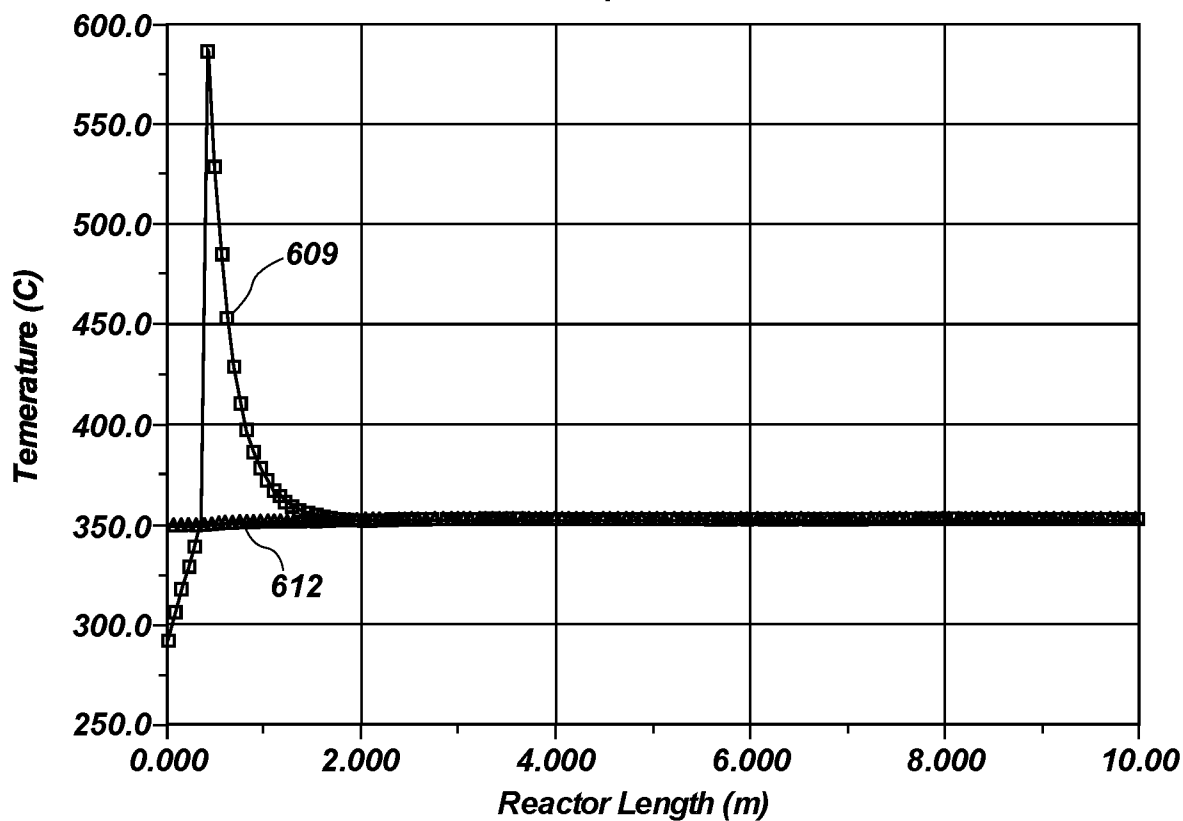
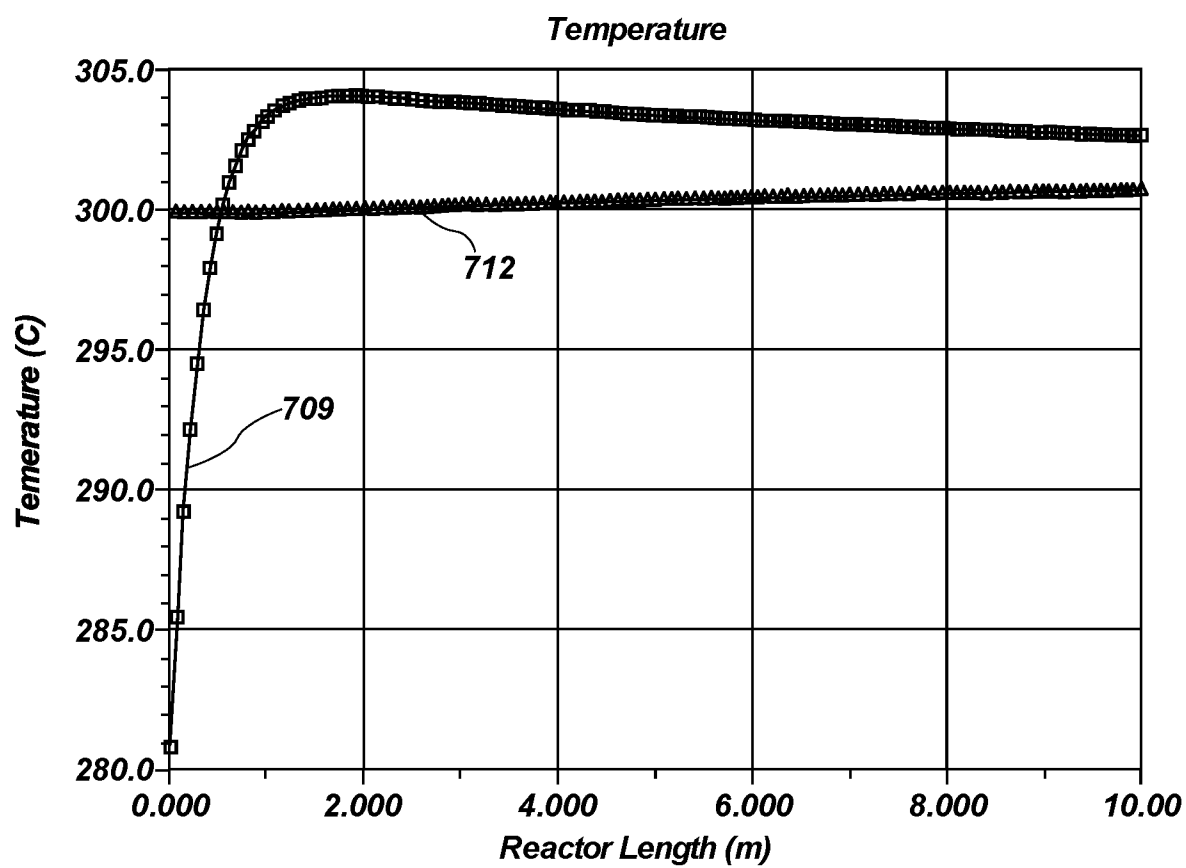


FIG. 6





INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/48000

A. CLASSIFICATION OF SUBJECT MATTER
 IPC - B01J 8/08; C07C 5/32, 5/48 (2018.01)
 CPC - C07C 5/321, 5/324, 11/04

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/0255985 A1 (GAFFNEY, AM, et al.) 07 October 2010; figure 1; paragraphs [0055]-[0056], [0059], [0062]-[0066], [0070],[0078], [0085], [0089], [0092], [0094]	1-2, 4, 6-11, 14, 16, 23, 25-26, 30
Y		3, 5, 12-13, 15, 17-22, 24, 27-28
Y	EP 0339748 A2 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 02 November 1989; column 1, lines 1-14	3, 5
Y	US 3907696 A (JACKSON, LL et al.) 23 September 1975; column 1, lines 31-35, 39-41	12-13
Y	Silin, VA, et al. "THE LIGHT WATER INTEGRAL REACTOR WITH NATURAL CIRCULATION OF THE COOLANT AT SUPERCRITICAL PRESSURE V-500 SKD"; Nuclear Engineering and Design 144 (1993); page 123, Introduction, third and fourth paragraphs	15
Y	US 2006/0003402 A1 (ADRI, AEM et al.) 05 January 2006; figures 8, 11; paragraphs [0029], [0061], [0093], [0096]-[0100]	17-22, 24
Y	WO 02/088851 A1 (ASHE MORRIS LIMITED) 07 November 2002; page1, lines 3-8, 14-23; page 27, lines 2-27; page 28, lines 1-28	27-28
A	GB 1268152 A (MONSANTO) 22 March 1972; page 5, lines 66-72; page 6, lines 117-128; page 7, lines 2-5	29



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

06 October 2018 (06.10.2018)

Date of mailing of the international search report

22 OCT 2018

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