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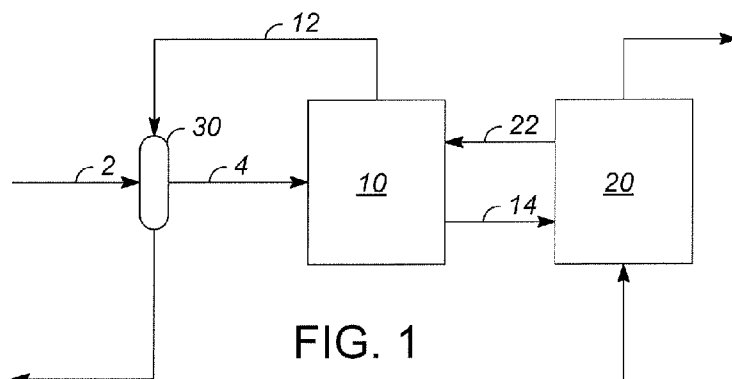
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(54) Title: MULTI-STAGE FLUIDIZED BED REACTOR FOR DEHYDROGENATION OF HYDROCARBONS



(57) Abstract: A reactor design and process for the dehydrogenation of hydrocarbons is presented. The reactor design includes a multibed catalytic reactor, where each of the reactor beds are fluidized. The catalyst in the reactor cascades through the reactor beds, with fresh catalyst input into the first reactor bed, and the spent catalyst withdrawn from the last reactor bed. The hydrocarbon feedstream is input to the reactor beds in a parallel formation, thereby decreasing the thermal residence time of the hydrocarbons when compared with a single bed fluidized reactor, or a series reactor scheme.

MULTI-STAGE FLUIDIZED BED REACTOR FOR DEHYDROGENATION OF HYDROCARBONS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 12/749,542 which was
5 filed on March 30, 2010.

FIELD OF THE INVENTION

[0002] The present invention relates to the production of light olefins from paraffins. Specifically, the invention is directed at propane dehydrogenation in the production of propylene.

BACKGROUND OF THE INVENTION

[0003] Continuous catalyst conversion processes are common in the refining and petrochemical industry. The fluidized catalyst cracking of hydrocarbons is an important process for the production of lighter hydrocarbon components, and as such, it is an important process for the production of propylene. The fluidized catalytic cracking process
15 continuously circulates a fluidized catalyst between a reactor and a regenerator.

[0004] Another route for the production of propylene can be obtained by the dehydrogenation of propane through catalytic dehydrogenation. The dehydrogenation catalysts generally comprise noble metal catalysts on acidic supports, such as alumina, or silica alumina, or zeolitic materials. However, the reaction is strongly endothermic, and
20 requires a high temperature for the reaction to proceed at a satisfactory rate. At the same time, the reactions need to be controlled to limit the degradation of the propane to form methane and ethylene, and where the ethylene can be hydrogenated by the hydrogen released through the dehydrogenation of the propane. The process also leads to coking of the catalyst, and deactivates the catalyst. The catalyst therefore needs to be regenerated on a regular basis
25 after relatively short periods of operation, or residence, in the dehydrogenation reactor.

[0005] The production of propylene through dehydrogenation is an endothermic process and requires a substantial amount of additional heating to allow the process to proceed. As a result, overall selectivity typically suffers due to temperature gradients across the catalyst bed. The hottest temperatures are desired at the outlet of the catalyst bed, but is not

achievable with current state-of-the-art designs. Another problem is the excessive non-catalytic thermal residence time, due to the required heating of the feed prior to feeding into the reactor.

SUMMARY OF THE INVENTION

5 **[0006]** The present invention provides a new reactor design. The reactor design comprises a multi-stage fluidized bed reactor, wherein there are a plurality of fluidized reactor beds. The reactor beds are arranged in a series configuration with respect to the flow of catalyst through the reactor, and in a parallel configuration with respect to the flow of a hydrocarbon feedstream. Each reactor bed has a catalyst inlet and a catalyst outlet, with the
10 first reactor bed outlet in fluid communication with the second reactor bed catalyst inlet. Each reactor bed has a catalyst inlet in fluid communication with a preceding reactor bed catalyst outlet, and a catalyst outlet in fluid communication with a subsequent reactor bed catalyst inlet. Each reactor bed also includes a hydrocarbon feedstream inlet, and there is a catalyst disengagement section for separating catalyst from a vapor product stream. The
15 present invention decreases the thermal residence time of the hydrocarbons when compared with a single bed fluidized reactor, or a series reactor scheme where at each stage the catalyst and intermediate product stream are separated before passing the intermediate product stream onto a subsequent reactor. The reduction in the thermal residence time provides for another benefit, in that a fired heater is no longer needed. The necessary heat for the reaction is
20 provided for by the heated catalyst returning from the regeneration unit. There is also a lower capital and real estate requirement. Eliminating high temperature thermal residence time minimizes thermal cracking of the feed, and improves the overall product selectivity.

[0007] In one embodiment, each reactor bed includes a recirculation channel for the catalyst, wherein the catalyst flows out of the top of the bed and is recycled to the bottom of
25 the same bed, providing added control over residence times, density and heating or cooling of the catalyst.

[0008] Additional objects, embodiments and details of this invention can be obtained from the following drawings and detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1 is a schematic of a plant design for a hydrocarbon dehydrogenation process;

[0010] Figure 2 is a schematic of a reactor having three reactor beds; and

5 **[0011]** Figure 3 is a schematic of the three reactor beds showing the flow of catalyst between the reactor beds.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention is a new design for a dehydrogenation reactor. The new design allows for lower hydrogen partial pressure requirements, and reduces thermal residence times by allowing the reactor beds to operate with a staggered temperature profile with a lower average bed temperature than what could be achieved in a single fluidized bed reactor or by passing the feed and resultant products over a plurality of beds in series. By a plurality of beds, it is meant to indicate two or more beds. The design comprises multiple reactor beds that cascade the flow of the catalyst through the reactor, while having the hydrocarbon feedstream split, and directed to pass through the reactor beds in parallel. This reduces thermal residence times of the hydrocarbon feedstream, and the resulting product stream compared to state-of-the-art swing bed or moving bed dehydrogenation systems which use fired heaters. A specific embodiment of the present invention is the production of propylene from a propane feedstock. Propane dehydrogenation is an important source of propylene for use as the building block for polypropylene.

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[0013] The present invention comprises a multi-stage fluidized bed reactor. The multi-stage reactor comprises a plurality of reactor beds in a parallel configuration, comprising a first reactor bed and at least one subsequent reactor bed. Each reactor bed has a catalyst inlet and a catalyst outlet, and a hydrocarbon feedstream inlet. The reactor further includes a catalyst disengagement section for separating catalyst from a vapor product stream. The dehydrogenation process as shown in Figure 1 comprises passing a hydrocarbon feedstream 2 to a preheater 30. The preheated feedstream 4 is passed to the dehydrogenation reactor 10, where a product stream 12 comprising olefins is generated. A spent catalyst stream 14 is passed to a regeneration unit 20, where the catalyst is regenerated and the regenerated catalyst stream 22 is passed back to the dehydrogenation reactor 10. Regeneration of the

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catalyst typically comprises burning off carbon deposits on the catalyst and heating the catalyst for use in the dehydrogenation reactor 10.

[0014] In one embodiment, the reactor further includes a catalyst recirculation channel for each reactor bed, wherein each recirculation channel has a channel inlet in fluid communication with the reactor bed catalyst outlet and a channel outlet in fluid communication with each reactor bed catalyst inlet. Optionally, each recirculation channel can further include a heating unit for heating catalyst in each recirculation channel. The dehydrogenation reaction is an endothermic reaction, and the recirculation channel provides heat control to the reactor by adding supplemental heat to the catalyst as the catalyst is recirculated.

[0015] This design allows for a staggered temperature profile across the entire reactor, and allows for an increasing temperature profile for each subsequent reactor bed, thereby increasing the yield per reactor bed as the catalyst becomes less active as it passes from one reactor bed to a subsequent reactor bed. This increases selectivities and conversions of the hydrocarbon feedstream. This design also minimizes the hot residence time of the feedstream since only 1/3 of the feedstream is in contact with the hottest catalyst bed temperature.

[0016] In one embodiment, the design is aimed at the control of the reactor bed temperatures. The regenerated catalyst is divided and a portion is routed to each of the individual reactor beds. For a case that results in an ascending temperature profile, the catalyst is divided into three equal portions, with one portion passed to each reactor bed. The catalyst recirculation channels, or recirculation pipes, are adjusted to have circulation rates consistent with an operation of the reactor such that each reactor bed has the same density.

[0017] As an alternate operation, the temperature of the reactor beds can be controlled through heating of the catalyst in the recirculation channels. Differential heat can be provided to heating the recirculation channels, to provide an ascending temperature profile across the reactor beds. The recirculation rates of the catalyst through the recirculation channels can be adjusted to maintain the desired catalyst bed densities. Vigorous catalyst mixing, associated with fluidized beds, assures that the hot regenerated catalyst quickly imparts its sensible heat into the respective reactor bed. In turn, the absence of intrabed temperature gradients leads to enhanced conversion, selectivity and prolonged catalyst life.

[0018] In one embodiment, the reactor comprises at least three reactor beds, as shown in Figure 2. Fresh or regenerated catalyst is fed into the first reactor bed 102, and catalyst

leaving the first reactor bed 102 flows to a second reactor bed 104. The catalyst leaving the second reactor bed 104 flows into the third reactor bed 106, with catalyst exiting the third reactor bed 106 being routed to a catalyst regeneration unit 20. A hydrocarbon feedstream 110 comprising paraffins is fed to each of the reactor beds 102, 104, 106 in parallel.

5 **[0019]** The operation of the parallel reactor beds allows for a minimization of the hydrogen partial pressure in the reactor 10. The feedstream 110 is frequently premixed with a hydrogen stream, such that the feed to the reactors is a combined hydrocarbon-hydrogen feedstream to the reactor 10. However, with the present invention, the amount of hydrogen at the inlet to the reactor 10 can be reduced such that the hydrogen to hydrocarbon ratio is zero
10 at the reactor inlet.

[0020] The design allows for a common separation system over all of the reactor beds, where catalyst fines and suspended catalyst are removed from the product stream before passing the product stream out of the reactor. The product stream can be used to preheat, or partially preheat, the hydrocarbon feedstream to the reactor 10.

15 **[0021]** In one embodiment, fresh or regeneration catalyst 120 enters the first reactor bed 102. A first feedstream flows through the first reactor bed, a stream comprising product and catalyst is carried out of the first reactor bed 102. The catalyst is separated from the product stream and at least partially directed to the second catalyst bed 104. A portion of the catalyst can be recycled to the first reactor bed 102. A second feedstream flows through the second
20 reactor bed 104, where a stream comprising product and catalyst is carried out of the second reactor bed 104. The catalyst from the second bed 104 is separated from the product stream and at least partially directed to the third catalyst bed 106. A third feedstream is fed to and flows through the third reactor bed 106. The catalyst is separated from the product stream and at least partially passed to the regeneration unit 20. The residence time of the
25 hydrocarbons can be minimized while maintaining longer times for the catalyst in the reactors. In turn, the feedstreams can be split in different amounts to account for aging of the catalyst, and changing temperatures across the reactor system 10.

[0022] In a specific embodiment, the catalyst flows do not need to be separated from the product stream. While it is mentioned that the catalyst flows do not need to be separated
30 from the product stream, it is meant that there is a disengagement of the catalyst from the product stream before passing the catalyst between the reactor beds. It is not necessary to achieve the separation associated with passing the catalyst and product stream to a separation

unit, such as including a cyclone, before passing the product stream out of the reactor. As shown in Figure 3, the catalyst can move through the reactor beds 102, 104, 106 without having to be separated from the product stream. Fresh, or regenerated, catalyst is added to the first reactor bed 102 at the bottom of the reactor bed. The catalyst flows up through the reactor bed, and flows out the top of the reactor bed. The catalyst from the top of the first reactor bed 102 is directed to the bottom of the second reactor bed 104 through a channel 122 connecting the top of the first reactor bed 102 to the bottom of the second reactor bed 104. Catalyst flows up through the second reactor bed 104 and is collected from the top of the second reactor bed 104. The catalyst is passed by a channel 124 to the bottom of the third reactor bed 106. The catalyst then flows up through the third reactor bed 106, and is drawn off the top of the reactor bed. The catalyst drawn off the final reactor bed is then passed through a channel 126 to the regeneration unit 20. This provides a series flow of catalyst through the reactor beds. In each reactor bed, the hydrocarbon feedstream makes only one pass and is collected at the top of the reactor beds. The piping for this specific embodiment provides for catalyst to flow up through the reactor beds. Other embodiments can allow for different catalyst flow patterns. While the drawings indicate three reactor beds, it is within the scope of this invention to have more than three reactor beds.

[0023] In addition, the system can include recycle channels to pass catalyst from the top of one reactor bed to the bottom of the same bed. This increases the average time the catalyst spends within one bed, provides density control and allows for additional heating of the catalyst during the passage through a recycle channel. Likewise, with the recycle channels, if the catalyst needs cooling, the catalyst temperature can be reduced before feeding the catalyst back into the reactor beds.

[0024] In another embodiment, each reactor bed can include a catalyst inlet for admitting regenerated catalyst. With this embodiment, the largest flow of regenerated catalyst is to the first reactor bed, with decreasing amounts of regenerated catalyst to each subsequent reactor bed. Using differential flow of regenerated catalyst to the reactor beds provides primarily for temperature control, but also provides for adjustment in catalytic activity.

[0025] One aspect of the present invention provides for a process for the dehydrogenation of hydrocarbons. The process comprises passing a hydrocarbon feedstream comprising paraffins in parallel to a plurality of fluidized reactor beds, where each reactor bed will generate a dehydrogenated product stream. Regenerated catalyst is passed to the first reactor

bed of the plurality of reactor beds. As catalyst passes through the first fluidized reactor bed, partially spent catalyst exits the first reactor bed. The partially spent catalyst is then passed to a second reactor bed. The catalyst in the second reactor bed passes through the fluidized reactor bed, and is increasingly deactivated, thereby creating a further deactivated catalyst.

5 This further deactivated catalyst is passed to a third reactor bed and flows through the fluidized reactor bed, thereby generating a spent catalyst stream. The spent catalyst is passed to a regeneration unit for regeneration of the catalyst. After regenerating the catalyst, the regenerated catalyst is passed to the first reactor bed.

[0026] The process of the present invention can be configured in numerous ways, but the preferred design utilized passing the catalyst into the reactor at the bottom of the reactor bed. The catalyst and hydrocarbon feedstream produces a fluidized bed that flow upward through the reactor bed. Catalyst is recovered at the top of the reactor bed from each reactor, and passed to the bottom of the reactor bed of a subsequent reactor bed.

[0027] For a dehydrogenation process, the reaction is endothermic, and additional heat is needed to maintain the reactor temperatures. The catalyst as it is drawn off can be passed through a heating unit, and catalyst can be recycled in one or more of the reactor beds, where catalyst is drawn off the top of a reactor bed and returned to the bottom of the same reactor bed. The amount of heating of catalyst and the average residence time of catalyst in an individual reactor bed can be controlled through this recycle, as well as the required catalyst circulation rate between the reactor and the regenerator.

[0028] The process can include passing lesser portions of regenerated catalyst to the second and/or third reactor beds. While the regenerated catalyst is generally passed to the first reactor bed, and the catalyst is allowed to cascade through the multiple reactor beds, a portion of the regenerated catalyst can be passed to subsequent reactor beds, i.e. the second and third reactor beds. The passing of lesser amounts of regenerated catalyst to the second and third reactor beds can provide control over the overall selectivity and conversion and operating temperature within a given reactor bed.

[0029] The operation of the dehydrogenation reaction includes operating the reactors at a pressure between 100 kPa and 500 kPa (14.5 psia to 72.5 psia), and preferably between 100 kPa and 300 kPa. The temperature of the reactors is operated in a range from 550°C and 700°C. The reaction is operated under a hydrogen partial pressure, and the hydrogen to hydrocarbon mole feed ratio at the reactor inlets is less than 0.8. Since this new design

provides for high selectivity and conversion while maintaining a low residence time for the catalyst, the process can be operated at hydrogen to hydrocarbon ratios near zero at the inlet. The level of hydrogen partial pressure depends on the type of catalyst used, and for many catalysts cannot be reduced to zero for optimum operation. The parallel nature of the beds with respect to the feedstream allows for hydrogen minimization at the inlet. The preferred usage is the production of propylene, and the preferred hydrocarbon feedstream is one which comprises propane. Another preferred hydrocarbon feedstream is butanes for the production of butylene.

[0030] The process, and design has been described with three reactor beds, but the process and design can be expanded to include more than three reactor beds, or can be for a two reactor bed system. The number of beds will be determined by the overall size of the dehydrogenation reactor system, the economics, and other variables normally encountered when designing a fluidized bed reactor system.

[0031] While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

CLAIMS:

1. A multi-stage fluidized bed reactor comprising:

a plurality of reactor beds in a parallel configuration, comprising first reactor bed and at least one subsequent reactor bed, with each reactor bed having a catalyst inlet and a

5 catalyst outlet, and a hydrocarbon feedstream inlet;

a catalyst transport means for passing catalyst between reactor beds; and

a catalyst disengagement section for separating catalyst from a vapor product stream.

2. The reactor of claim 1 further comprising a catalyst recirculation channel for each reactor
10 bed, wherein each recirculation channel has a channel inlet in fluid communication with the reactor bed catalyst outlet and a channel outlet in fluid communication with each reactor bed catalyst inlet.

3. The reactor of claim 2 further comprising a heating unit for heating the catalyst in each
15 recirculation channel.

4. The reactor of claim 1 wherein the plurality of beds comprises at least three reactor beds.

5. The reactor of claim 1 wherein the reactor beds are connected in series for the flow of
20 catalyst, while the reactor beds are connected in parallel for the flow of the hydrocarbon feedstream.

6. The reactor of claim 1 wherein each reactor bed further comprises a regenerated catalyst
inlet.

7. The reactor of claim 6 wherein the regenerated catalyst inlets are sized to direct the largest
flow of regenerated catalyst to the first reactor bed.

8. A multi-stage fluidized bed reactor comprising:

a plurality of reactor beds comprising:

a first reactor bed having a catalyst inlet and a catalyst outlet, and a hydrocarbon feedstream inlet;

at least two subsequent reactor beds, with each reactor bed having a catalyst inlet and a catalyst outlet, and a hydrocarbon feedstream inlet, wherein the reactor beds are in a series configuration with respect to the transport of catalyst and each catalyst inlet is in fluid communication with the catalyst outlet from a preceding reactor bed;

a catalyst transport means for passing catalyst between reactor beds;

a catalyst recirculation channel for each reactor bed, wherein each recirculation channel has a recirculation channel inlet in fluid communication with the reactor bed catalyst outlet and a channel outlet in fluid communication with each reactor bed catalyst recirculation inlet

a fresh catalyst inlet port for each reactor bed; and

a catalyst disengagement section for separating catalyst from a vapor product stream; wherein the reactor beds are connected in series for the flow of catalyst, while the reactor beds are connected in parallel for the flow of the hydrocarbon feedstream.

9. The reactor of claim 8 further comprising a heating unit for heating the catalyst in each recirculation channel.

10. The reactor of claim 8 wherein the fresh catalyst inlets are sized to direct the largest flow of regenerated catalyst to the first reactor bed.

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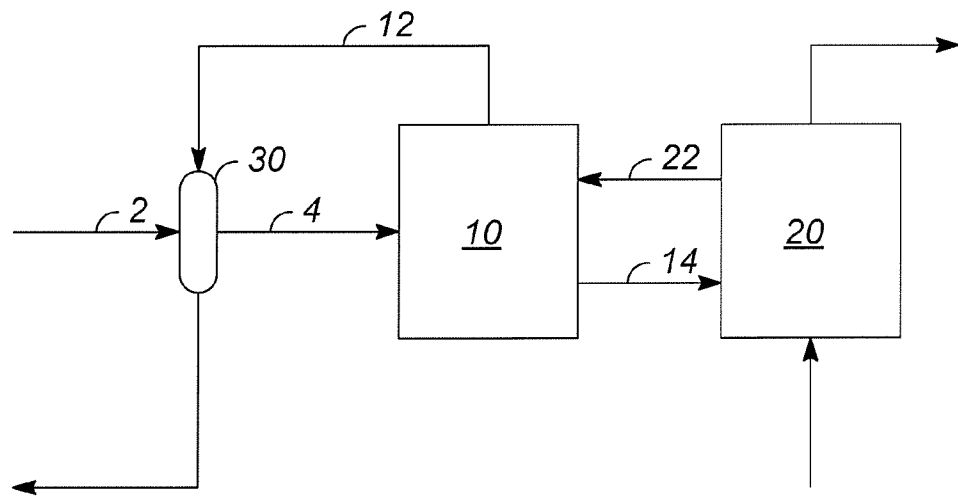


FIG. 1

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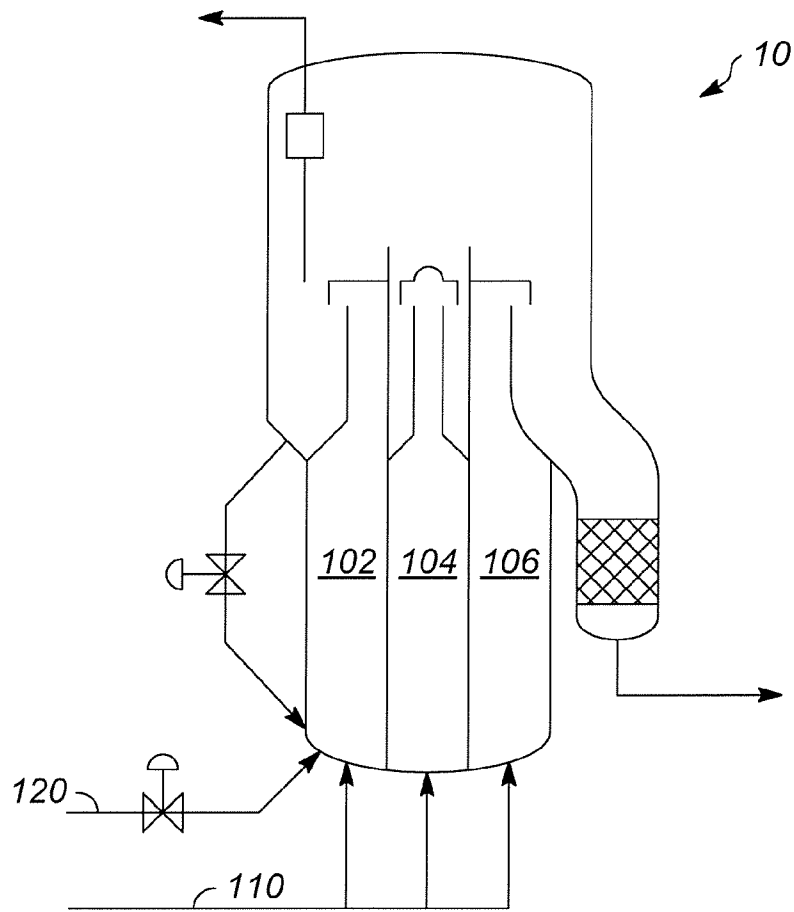


FIG. 2

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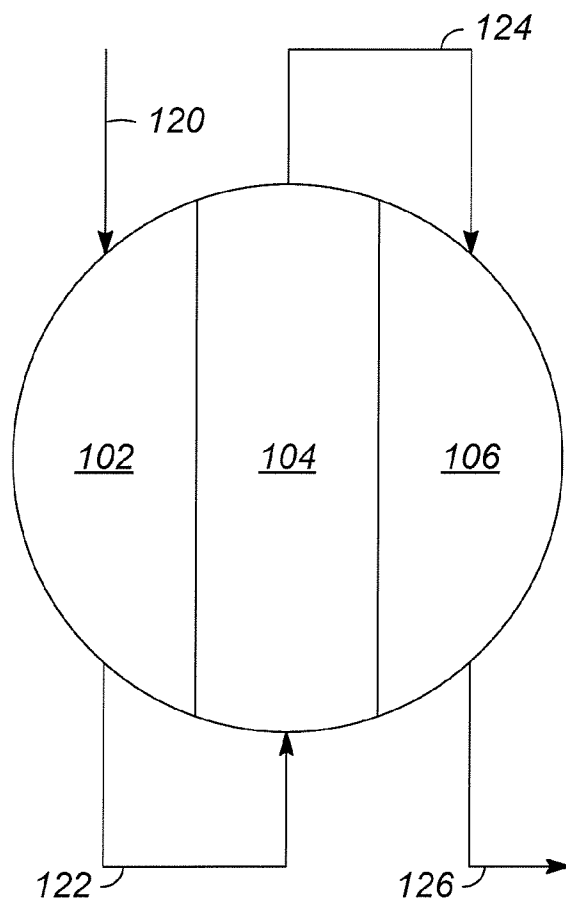


FIG. 3