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(54) Title: INTEGRATED FISCHER-TROPSCH PROCESSES USING NICKEL REVERSE WATER-GAS SHIFT CATALYSTS

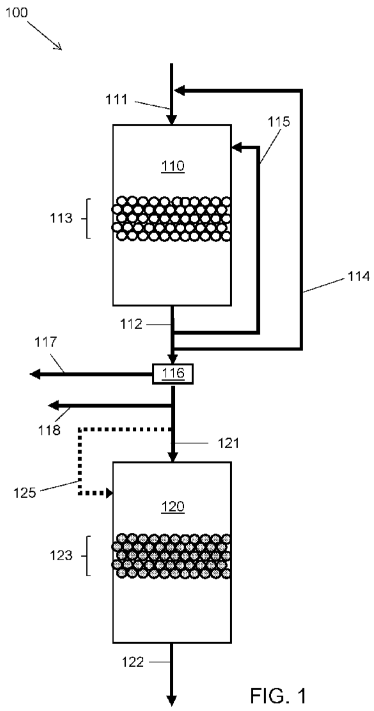

FIG. 1

(57) Abstract: The present disclosure relates generally to a process for performing an integrated Fischer-Tropsch process, the process comprising: providing a first feed stream comprising H_2 and CO_2; contacting at a first temperature in the range of 500-900°C and at a first pressure a reverse water-gas shift catalyst with the first feed stream to perform a reverse water-gas shift reaction to provide a first product stream comprising CO and H_2, the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first feed stream; contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream comprising H_2 and at least a portion of CO of the first product stream to provide a second product stream comprising C_{5+}hydrocarbons, wherein the reverse water-gas shift catalyst is a supported reverse water-gas shift catalyst comprising: a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support comprising a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide; nickel, present in an amount in the range of 0.05 to 10 wt%of the catalyst, based on the total weight of the catalyst; and manganese, present in an amount in the range of 0.5 to 20 wt%of the catalyst, based on the total weight of the catalyst.

[Continued on next page]

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INTEGRATED FISCHER-TROPSCH PROCESSES USING NICKEL REVERSE WATER-GAS SHIFT CATALYSTS

1. Field

[0001] The present disclosure relates generally to reverse water-gas shift catalysts, processes of making the same, and processes for performing reverse water-gas shift reactions. The present disclosure also relates to integrating processes for performing reverse water-gas shift reactions with processes for performing Fischer-Tropsch reactions.

2. Technical Background

[0002] The reverse water-gas shift reaction (rWGS) is an advantageous route to obtain carbon monoxide from carbon dioxide for further chemical processing. The rWGS converts carbon dioxide and hydrogen to carbon monoxide and water, as shown in Equation (1).

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^0_{298} = 42.1\ kJmol^{-1} \qquad \text{Eq. (1)}$$

This can be used, for example, to modify the $CO{:}H_2$ ratio of a gas mixture for further processing. The carbon monoxide and hydrogen so formed is a valuable feedstock for a number of chemical processes, for example, the well-known Fischer-Tropsch (FT) process, shown in Equation (2).

$$CO + 2\ H_2 \rightleftharpoons [-CH_2-] + H_2O \qquad \Delta H^0_{298} = -152\ kJmol^{-1} \qquad \text{Eq. (2)}$$

[0003] However, the rWGS reaction is not favored in all circumstances. For example, a competing reaction is the Sabatier reaction (Equation (3)), which decreases carbon monoxide yield in favor of methane production, which is not an active feedstock for FT.

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H^0_{298} = -165\ kJmol^{-1} \qquad \text{Eq. (3)}$$

The strongly exothermic Sabatier reaction is thermodynamically favored over the endothermic rWGS reaction at lower reaction temperatures. As such, minimizing the methanation during rWGS, especially at low temperatures, can become a significant challenge.

[0004] Similarly, the carbon monoxide product from rWGS can be hydrogenated to methane, as shown in Equation (4).

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^0_{298} = -206.5\ kJmol^{-1} \qquad \text{Eq. (4)}$$

Hydrogenation of carbon monoxide to methane is also an exothermic reaction, so it too is favored at lower temperatures. The stoichiometry of the reaction requires at least a 3:1 ratio of hydrogen to carbon monoxide. This means that performing the rWGS reaction with a large excess of hydrogen to drive the equilibrium toward carbon monoxide (see Equation (1)) is not always ideal because it runs the risk of hydrogenating the carbon monoxide product to form methane.

[0005] Coupled with Equations (3) and (4), further undesirable side reactions can occur. These side reactions can form undesirable carbon deposits on the surface of catalysts used to promote rWGS. Examples of these carbon-producing side reactions are shown in Equations (5), (6), and (7). All three of these reactions are endothermic and are favored at higher temperatures, just like the rWGS reaction.

$$CO + H_2 \leftrightarrow C + H_2O \qquad \Delta H^0_{298} = 131\ kJmol^{-1} \qquad Eq.\ (5)$$

$$CH_4 \leftrightarrow 2H_2 + C \qquad \Delta H^0_{298} = 75\ kJmol^{-1} \qquad Eq.\ (6)$$

$$2CO \leftrightarrow CO_2 + C \qquad \Delta H^0_{298} = 171\ kJmol^{-1} \qquad Eq.\ (7)$$

Accordingly, because the carbon-producing side reactions (Equations (5)-(7)) are also endothermic and are favored at higher temperatures, operation at higher temperatures to favor the desired carbon monoxide product can severely impact catalyst lifetime through the deposition of carbon.

[0006] Given the multiple reactions and competing thermodynamics at play, there remains a need in the art for new rWGS catalysts and processes, especially for integration with Fischer-Tropsch processes.

SUMMARY

[0007] In one aspect, the present disclosure provides for a process for performing an integrated Fischer-Tropsch process, the process comprising:

providing a first feed stream comprising H_2 and CO_2;

contacting at a first temperature in the range of 500-900 °C and at a first pressure a reverse water-gas shift catalyst with the first feed stream to perform a reverse water-gas shift reaction to provide a first product stream comprising CO and H_2, the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first feed stream;

contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream comprising H_2 and at least a portion of CO of the first product stream to provide a second product stream comprising C_{5+} hydrocarbons,

wherein the reverse water-gas shift catalyst is a supported reverse water-gas shift catalyst comprising:

a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support comprising a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide;

nickel, present in an amount in the range of 0.05 to 10 wt% of the catalyst, based on the total weight of the catalyst; and

manganese, present in an amount in the range of 0.5 to 20 wt% of the catalyst, based on the total weight of the catalyst.

[0008] In another aspect, the present disclosure provides for a method of making the catalyst as described herein, the method comprising:

providing a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support comprising a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide;

contacting the support with a liquid comprising one or more nickel-containing compounds and one or more manganese-containing compounds dispersed in a solvent;

allowing the solvent to evaporate to provide a catalyst precursor; and

calcining the catalyst precursor.

[0009] In another aspect, the present disclosure provides for a catalyst as described herein made by the method as described herein.

BRIEF DESCRIPTION OF FIGURES

[0010] FIG. 1 is a schematic of a process for performing an integrated Fischer-Tropsch process as described herein.

[0011] FIG. 2 is a schematic of a process for performing an integrated Fischer-Tropsch process as described herein.

[0012] FIG. 3 is a schematic of a process for performing an integrated Fischer-Tropsch process as described herein.

[0013] FIG. 4 is a schematic of a process for performing an integrated Fischer-Tropsch process as described herein.

[0014] FIG. 5 is a schematic of a process for performing an integrated Fischer-Tropsch process as described herein.

[0015] FIG. 6 is a schematic of a process for performing an integrated Fischer-Tropsch process as described herein.

DETAILED DESCRIPTION

[0016] As discussed above, the reverse gas-water shift reaction reacts carbon dioxide with hydrogen to form carbon monoxide and water and can be useful in providing a feedstock containing carbon monoxide and hydrogen -- often called “synthesis gas” -- for use in processes such as the Fischer-Tropsch process. However, the Sabatier reaction, carbon monoxide methanation, and carbon-producing side reactions can interfere with the rWGS reaction. The Sabatier reaction and CO methanation are exothermic and favored at lower temperatures, while the rWGS and carbon-producing side reactions are endothermic and favored at higher temperatures. Accordingly, there remains a need for rWGS catalysts that can provide good performance in spite of these complicating factors. Here, the present inventors have found rWGS processes that are particularly advantageous for integration with a Fischer-Tropsch process by using supported reverse water-gas shift catalysts that include a metal oxide support, nickel, and manganese.

[0017] In one aspect, the present disclosure provides a process for performing an integrated Fischer-Tropsch process, the process includes providing a first feed stream comprising H_2 and CO_2; contacting at a first temperature in the range of 500-900 °C and at a first pressure a reverse water-gas shift catalyst with the first feed stream to perform a reverse water-gas shift reaction to provide a first product stream comprising CO and H_2, the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first feed stream; contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream comprising H_2 and at least a portion of CO of the first product stream to provide a second product stream comprising C_{5+} hydrocarbons, wherein the reverse water-gas shift catalyst is a supported reverse water-gas shift catalyst as described here.

[0018] In another aspect, the present disclosure provides a supported reverse water-gas shift catalyst, for example, for use in an rWGS process integrated with an FT process. The supported reverse water-gas shift catalyst includes a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support including a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide; at least one of nickel, present in an amount in the range of 0.05 to 10 wt% of the catalyst, based on the total weight of the catalyst; and manganese, present in an amount in the range of 0.5 to 20 wt% of the catalyst, based on the total weight of the catalyst.

[0019] As described above, the reverse water-gas shift catalysts of the present disclosure are supported catalysts. In various embodiments as otherwise described herein, the support makes up at least 70 wt%, e.g., at least 75 wt%, or 80 wt%, or 85 wt%, or 90 wt% of the catalyst on an oxide basis.

[0020] In various embodiments as otherwise described herein, the support is a cerium oxide support. As used herein, a "cerium oxide” support is a support that presents at least a surface layer (e.g., 50 microns in thickness) that is at least 50 wt% cerium oxide, on an oxide basis. In various embodiments of the disclosure as described herein, at least a surface layer of the cerium oxide support includes at least 60 wt% cerium oxide, e.g., at least 70 wt% cerium oxide, or at least 80 wt% cerium oxide. In some such embodiments, at least a surface layer of the cerium oxide support includes at least 90 wt% cerium oxide. For example, in some embodiments, at least a surface layer of the cerium oxide support includes at least 95 wt% cerium oxide or at least 98 wt% cerium oxide. In various examples, the cerium oxide support contains cerium oxide substantially throughout, e.g., at least 50 wt% of the cerium oxide support is cerium oxide on an oxide basis. For example, in various embodiments, the cerium oxide support includes at least 60 wt% cerium oxide, e.g., at least 70 wt% cerium oxide, or at least 80 wt% cerium oxide. In various embodiments, the cerium oxide support includes at least 90 wt% cerium oxide, e.g., at least 95 wt% cerium oxide, or at least 98 wt% cerium oxide. In some embodiments, the cerium oxide support may further include additional metals or metal oxides.

[0021] In various embodiments as otherwise described herein, the support is a titanium oxide support. As used herein, a "titanium oxide” support is a support that presents at least a surface layer (e.g., 50 microns in thickness) that is at least 50 wt% titanium oxide, on an oxide basis. In various embodiments of the disclosure as described herein, at least a surface layer of the titanium oxide support includes at least 60 wt% titanium oxide, e.g., at least 70 wt% titanium oxide, or at least 80 wt% titanium oxide. In some such embodiments, at least a surface layer of the titanium oxide support includes at least 90 wt% titanium oxide. For example, in some embodiments, at least a surface layer of the titanium oxide support includes at least 95 wt% titanium oxide or at least 98 wt% titanium oxide. In various examples, the titanium oxide support contains titanium oxide substantially throughout, e.g., at least 50 wt% of the titanium oxide support is titanium oxide on an oxide basis. For example, in various embodiments, the titanium oxide support includes at least 60 wt% titanium oxide, e.g., at least 70 wt% titanium oxide, or at least 80 wt% titanium oxide. In various embodiments, the titanium oxide support includes at least 90 wt% titanium oxide, e.g., at least 95 wt% titanium oxide, or at least 98 wt% titanium oxide. In some embodiments, the titanium oxide support may further include additional metals or metal oxides.

[0022] In various embodiments as otherwise described herein, the support is an aluminum oxide support. As used herein, an "aluminum oxide” support is a support that presents at least a surface layer (e.g., 50 microns in thickness) that is at least 50 wt% aluminum oxide, on an oxide basis. In various embodiments of the disclosure as described herein, at least a surface layer of the aluminum oxide support includes at least 60 wt% aluminum oxide, e.g., at least 70 wt% aluminum oxide, or at least 80 wt% aluminum oxide. In some such embodiments, at least a surface layer of the aluminum oxide support includes at least 90 wt% aluminum oxide. For example, in some embodiments, at least a surface layer of the aluminum oxide support includes at least 95 wt% aluminum oxide or at least 98 wt% aluminum oxide. In various examples, the aluminum oxide support contains aluminum oxide substantially throughout, e.g., at least 50 wt% of the aluminum oxide support is aluminum oxide on an oxide basis. For example, in various embodiments, the aluminum oxide support includes at least 60 wt% aluminum oxide, e.g., at least 70 wt% aluminum oxide, or at least 80 wt% aluminum oxide. In various embodiments, the aluminum oxide support includes at least 90 wt% aluminum oxide, e.g., at least 95 wt% aluminum oxide, or at least 98 wt% aluminum oxide. In some embodiments, the aluminum oxide support may further include additional metals or metal oxides.

[0023] In various embodiments as otherwise described herein, the support is a zirconium oxide support. As used herein, a " zirconium oxide” support is a support that presents at least a surface layer (e.g., 50 microns in thickness) that is at least 50 wt% zirconium oxide, on an oxide basis. In various embodiments of the disclosure as described herein, at least a surface layer of the zirconium oxide support includes at least 60 wt% zirconium oxide, e.g., at least 70 wt% zirconium oxide, or at least 80 wt% zirconium oxide. In some such embodiments, at least a surface layer of the zirconium oxide support includes at least 90 wt% zirconium oxide. For example, in some embodiments, at least a surface layer of the zirconium oxide support includes at least 95 wt% zirconium oxide or at least 98 wt% zirconium oxide. In various examples, the zirconium oxide support contains zirconium oxide substantially throughout, e.g., at least 50 wt% of the zirconium oxide support is zirconium oxide on an oxide basis. For example, in various embodiments, the zirconium oxide support includes at least 60 wt% zirconium oxide, e.g., at least 70 wt% zirconium oxide, or at least 80 wt% zirconium oxide. In various embodiments, the zirconium oxide support includes at least 90 wt% zirconium oxide, e.g., at least 95 wt% zirconium oxide, or at least 98 wt% zirconium oxide. In some embodiments, the zirconium oxide support may further include additional metals or metal oxides.

[0024] In various embodiments as otherwise described herein, the support is a mixed oxide support. These can be provided, for example, by admixture of multiple of the oxides above and formation into a support that includes both. For example, in some embodiments, the mixed oxide support is a mixture of two or more metal oxides, such as cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide. In some embodiments, at least a surface layer of the support includes at least 50 wt% total of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide, on an oxide basis. In some embodiments, at least a surface layer of the mixed oxide support includes at least 60 wt% total, e.g., at least 70 wt%, or at least 80 wt% of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide. In some embodiments, at least a surface layer of the mixed oxide support includes at least 90 wt%, e.g., at least 95 wt%, or at least 98 wt% of two or more cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide. In various examples, the mixed oxide support contains the oxides substantially throughout, e.g., at least 50 wt% of the mixed oxide support is two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide. In various embodiments, the mixed oxide support includes at least 60 wt% total, e.g., at least 70 wt%, or at least 80 wt% of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide. In various embodiments, the mixed oxide support includes at least 90 wt% total, e.g., at least 95 wt%, or at least 98 wt% of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide. In some embodiments, the mixed oxide support may further include additional metals or metal oxides.

[0025] The present inventors have found that cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide can provide good performance in the absence of substantial amounts of other metals in the support. For example, in various embodiments of the disclosure as otherwise described herein, the support does not include additional metals in a total amount of additional metals in excess of 2 wt%, e.g., in excess of 1 wt% or in excess of 0.5 wt%, on an oxide basis.

[0026] However, the inventors have noted that in many cases performance can be desirably effected by the inclusion of other metals in the support. Accordingly, in other embodiments as otherwise described herein, the support includes at least one additional metal. In various embodiments, the total amount of the at least one additional metal is in the range of 0.5-20 wt%, e.g., 1-20 wt%, or 2-20 wt%, or 0.5-15 wt%, or 1-15 wt%, or 2-15 wt%, or 0.5-10 wt%, or 1-10 wt%, or 2-10 wt%, or 0.5-5 wt%, or 1-5 wt%, on an oxide basis.

[0027] Supports suitable for use herein can be provided with a range of pore volumes. The person of ordinary skill in the art will select a pore volume appropriate for a desired catalytic process. For example, in various embodiments as otherwise described herein, the pore volume is at least 0.05 mL/g, e.g., at least 0.1 mL/g. In various embodiments as otherwise described herein, the pore volume is at most 1.5 mL/g, e.g., at most 1 mL/g. In various embodiments of the present disclosure as described herein, the pore volume is in the range of 0.05-1.5 mL/g, e.g., 0.1 mL/g to 1 mL/g. Pore volumes are measured by mercury porosimetry, for example, as measured according to ASTM D4284-12.

[0028] As described above, the supported reverse water-gas shift catalysts of the disclosure includes nickel. For example, in various embodiments as otherwise described herein, nickel is present in the catalyst. For the purposes of this disclosure, the amount of nickel present is calculated as a weight percentage of nickel atoms in the catalyst based on the total weight of the catalyst, despite the form in which that nickel may be present. The nickel may be present in the catalyst in a variety of forms; most commonly, nickel is principally present as metal, metal oxide, or a combination thereof. In some embodiments of the present disclosure as described herein, nickel is present in the catalyst in an amount in the range of 0.05 to 10 wt%, e.g., in the range of 0.1 to 10 wt%, or 0.5 to 10 wt%, 1 to 10 wt%, or 2 to 10 wt%, or 5 to 10 wt%, based on the total weight of the catalyst. For example, in some embodiments, nickel is present in the catalyst in an amount in the range of 0.05 to 7 wt%, e.g., in the range of 0.1 to 7 wt%, or 0.5 to 7 wt%, or 1 to 7 wt%, or 2 to 7 wt%, based on the total weight of the catalyst. In some embodiments, nickel is present in the catalyst in an amount in the range of 0.05 to 5 wt%, e.g., in the range of 0.1 to 5 wt%, or 0.5 to 5 wt%, or 1 to 5 wt%, or 2 to 5 wt%, based on the total weight of the catalyst. For example, in some embodiments of the present disclosure as described herein, nickel is present in the catalyst in an amount in the range of 0.05 to 2 wt%, e.g., in the range of 0.1 to 2 wt%, or 0.3 to 2 wt%, or 0.5 to 2 wt%, based on the total weight of the catalyst. In some embodiments, nickel is present in the catalyst in an amount in the range of 0.05 to 1.5 wt%, e.g., in the range of 0.1 to 1.5 wt%, or 0.3 to 1.5 wt%, or 0.5 to 1.5 wt%, based on the total weight of the catalyst. In some embodiments, nickel is present in an amount in the range of 0.05 to 1 wt%, e.g., in the range of 0.1 to 1 wt%, or 0.3 to 1 wt%, or 0.5 to 1 wt%, based on the total weight of the catalyst. In some embodiments, nickel is present in the catalyst in an amount in the range of 0.05 to 0.8 wt%, e.g., in the range of 0.1 to 0.8 wt%, or 0.3 to 0.8 wt%, or 0.5 to 0.8 wt%, based on the total weight of the catalyst.

[0029] As described above, the supported reverse water-gas shift catalysts of the disclosure also include manganese. The present inventors have determined that inclusion of manganese in the catalyst can provide improved performance, as described in the Examples below. For the purposes of this disclosure, the amount of manganese present is calculated as a weight percentage of manganese atoms in the catalyst based on the total weight of the catalyst, despite the form in which that manganese may be present. The manganese may be present in the catalyst in a variety of forms; most commonly, manganese is principally present as metal oxide, metal, or a combination thereof. In various embodiments of the present disclosure as otherwise described herein, manganese is present in the catalyst in an amount in the range of 0.5 to 20 wt%, based on total weight of the catalyst. For example, in various embodiments, manganese is present in the catalyst in an amount in the range of 0.5 to 15 wt%, or 0.5 to 12 wt%, or 0.5 to 10 wt%, based on the total weight of the catalyst. In various embodiments of the present disclosure as described herein, manganese is present in the catalyst in an amount in the range of 1 to 20 wt%, e.g., in the range of 1 to 15 wt%, or 1 to 12 wt% or 1 to 10 wt%, based on the total weight of the catalyst. In various embodiments of the present disclosure as described herein, manganese is present in an amount in the range of 2 to 20 wt%, e.g., in the range of 2 to 15 wt%, or 2 to 12 wt%, or 2 to 10 wt%, based on the total weight of the catalyst. In various embodiments of the present disclosure as described herein, manganese is present in an amount in the range of 4 to 20 wt%, e.g., in the range of 4 to 15 wt%, or 4 to 12 wt%, or 4 to 10 wt%, based on the total weight of the catalyst.

[0030] The nickel and the manganese can be provided in a variety of weight ratios. For example, in some embodiments of the present disclosure as described herein, the weight ratio of nickel to manganese present in the catalyst is at least 0.05:1. For example, in various embodiments, the weight ratio of nickel to manganese is at least 0.1:1. In various embodiments of the present disclosure as described herein, the weight ratio of nickel to manganese present in the catalyst is at most 5:1. For example, the weight ratio of nickel to manganese is at most 2:1, or 1:1, or 0.5:1. For example, in various embodiments, the weight ratio of nickel to manganese present in the catalyst is in the range of 0.05:1 to 5:1. For example, the weight ratio of nickel to manganese is in the range of 0.05:1 to 2:1, or 0.05:1 to 1:1, or 0.05:1 to 0.5:1, or 0.05:1 to 0.3:1, or 0.07:1 to 5:1, or 0.07:1 to 2:1, or 0.07:1 to 1:1, or 0.07:1 to 0.5:1, or 0.07:1 to 0.3:1, or 0.1:1 to 5:1, or 0.1:1 to 2:1, or 0.1:1 to 1:1, or 0.1:1 to 0.5:1, or 0.1:1 to 0.3:1.

[0031] The present inventors have determined that suitable reverse water-gas shift catalysts can be formed of one or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide as a support, with nickel in combination with manganese included in/on the catalyst. As would be understood by the person of ordinary skill in the art, the amount of cerium, titanium, aluminum, zirconium, nickel, and manganese can be quantified on a metallic basis regardless of the form in which these metals may be present. For example, the amount of these metals can be calculated as a weight percentage based on the total weight of metals in the catalysts (i.e., on a metallic basis), i.e., without the inclusion of oxygen or non-metallic counterions in the calculation. Accordingly, in various embodiments of the present disclosure as described herein, the total amount of cerium, titanium, aluminum, zirconium, manganese, and nickel in the catalyst is at least 90 wt%, e.g., at least 95 wt%, or at least 98 wt% of the catalyst, on a metallic basis. For example, in some particular embodiments, the total amount of cerium, manganese, and nickel in the catalyst is at least 90 wt%, e.g., at least 95 wt%, or at least 98 wt% of the catalyst, on a metallic basis. In other embodiments, the total amount of titanium, manganese, and nickel in the catalyst is at least 90 wt%, e.g., at least 95 wt%, or at least 98 wt% of the catalyst, on a metallic basis. In other embodiments, the total amount of aluminum, manganese, and nickel in the catalyst is at least 90 wt%, e.g., at least 95 wt%, or at least 98 wt% of the catalyst, on a metallic basis. In other embodiments, the total amount of zirconium, manganese, and nickel in the catalyst is at least 90 wt%, e.g., at least 95 wt%, or at least 98 wt% of the catalyst, on a metallic basis.

[0032] As described above, the supported catalyst includes manganese and nickel. Depending on the method of synthesis, these species, which will typically be principally present in metallic form and/or oxide form, can be disposed at a variety of different places on the support. For example, they can be found in pores of the support and on the outer surface of the support. They may be found substantially throughout the support, e.g., as when a large volume of impregnation liquid is used, or only in a surface layer of the support, e.g., when impregnation liquid does not infiltrate into the entirety of the support, such as when using an incipient wetness technique.

[0033] Without intending to be bound by theory, it is believed that the active form of nickel is typically a substantially metallic form. As described below, as nickel may be present substantially in an oxide form after catalyst preparation and during shipment and storage, it is typically desirable to activate the catalyst by contacting it with a reductant, e.g., hydrogen gas, to convert a substantial fraction of such oxide to metallic form. However, the person of ordinary skill in the art will appreciate that the present disclosure contemplates the usefulness of a wide variety of nickel forms in its catalysts, as these can be active or can be conveniently transformed to active forms.

[0034] The manganese will typically be provided in oxide form after catalyst preparation and during shipment and storage. Without intending to be bound by theory, the present inventors believe that the manganese acts to improve the catalytic activity of the supported nickel catalysts by reducing CO methanation that can occur over the typical reverse water-gas shift reaction temperature range, which impacts CO selectivity. The present inventors believe that the improved activity can be attributed to the manganese interfacing with both the nickel and the support (e.g., cerium oxide, titanium oxide, aluminum oxide, zirconium oxide, or a mixed oxide).The present inventors contemplate that it is possible that some manganese oxide is converted to metallic form during the activation of the nickel species. However, the person of ordinary skill in the art will appreciate that the present disclosure contemplates the usefulness of a wide variety of manganese forms in its catalysts, as these can provide a promoting effect or can be conveniently transformed to forms that will.

[0035] The person of ordinary skill in the art will appreciate that the catalysts of the disclosure can be provided in many forms, depending especially on the particular form of the reactor system in which they are to be used, e.g., in a fixed bed or as a fluid bed. The supports themselves can be provided as discrete bodies of material, e.g., as porous particles, pellets or shaped extrudates, with nickel; and manganese provided thereon to provide the catalyst. However, in other embodiments, a catalyst of the disclosure can itself be formed as a layer on an underlying substrate. The underlying substrate is not particularly limited. It can be formed of, e.g., a metal or metal oxide, and can itself be provided in a number of forms, such as particles, pellets, shaped extrudates, or monoliths. Of course, as would be understood by the person of ordinary skill in the art, other embodiments may be possible.

[0036] Another aspect of the present disclosure provides for a method of making the catalyst as described herein. As described above, the method includes providing a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support including a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide; contacting the support with one or more liquids each including one or more nickel-containing compounds and/or one or more manganese-containing compounds dispersed in a solvent; allowing the solvent(s) to evaporate to provide a catalyst precursor; and calcining the catalyst precursor. The person of ordinary skill in the art will appreciate, of course, that other methods can be used to make the catalysts described herein.

[0037] In some embodiments of the present disclosure as described herein, contacting the support with the liquid includes adding the liquid in an amount about equal to (i.e., within 25% of, or within 10% of) the pore volume of the support. In other embodiments, contacting the support with the liquid includes adding the liquid in an amount greater than the pore volume of the support. For example, in some embodiments, the ratio of the amount of liquid to the amount of support on a mass basis is in the range of 0.75:1 to 5:1, e.g., in the range of 0.9:1 to 3:1. In some embodiments, contacting the support with the liquid provides a slurry.

[0038] In various embodiments of the present disclosure as described herein, allowing the solvent to evaporate is conducted at ambient temperature. In various embodiments, allowing the solvent to evaporate is conducted at an elevated temperature for a drying time. The person of ordinary skill in the art would be able to select appropriate apparatuses or instruments to allow the solvent to evaporate, and such apparatuses or instruments are not particularly limited. Additionally, the person of ordinary skill in the art would understand that the elevated temperature that will allow the solvent to evaporate depends on the boiling point of the solvent. As such, the person of ordinary skill in the art would be able to select an appropriate elevated temperature. For example, in some embodiments, the elevated temperature is in the range of 50-150 °C, e.g., in the range of 50-120 °C, or 50-100 °C, or 100-150 °C, or 100-120 °C. In some embodiments, the drying time is in the range of 1 to 48 hours, e.g., in the range of 10 to 36 hours, or 12 to 24 hours. For example, in particular embodiments, the drying time is about 24 hours. In some embodiments, allowing the solvent to evaporate is conducted under vacuum and at an elevated temperature for a drying time, as described herein. In some embodiments, allowing the solvent to evaporate is conducted in a stirring drybath at an elevated temperature, for example, in the range of 30-100 °C.

[0039] In some embodiments of the present disclosure as described herein, calcining the catalyst precursor is conducted in a furnace for a calcining time and at a calcining temperature. For example, in some embodiments, the calcining time is in the range of 0.5 to 24 hours, or 0.5 to 15 hours, or 0.5 to 10 hours, or 0.5 to 5 hours. In some embodiments, the calcining temperature is in the range of 100-600 °C, e.g., in the range of 120-500 °C.

[0040] As described above, the method of making the catalyst as described herein includes contacting the support with one or more liquids each including one or more nickel-containing compounds and/or one or more manganese-containing compounds dispersed in a solvent. The nickel- and manganese-containing compounds are not particularly limited and the person of ordinary skill in the art would be able to choose appropriate compounds that are soluble in the solvent. For example, in some embodiments of the disclosure as described herein, the nickel- and manganese-containing compounds may be selected from metal salts (e.g., nitrates and acetates). The solvent is also not particularly limited and the person of ordinary skill in the art would be able to choose an appropriate solvent that can be absorbed by the support. For example, in some embodiments of the disclosure as described herein, the solvent is water. As the person of ordinary skill in the art will appreciate, these metal species are conveniently provided in the same liquid, so that only one step of contacting the support with liquid is required. However, other schemes are possible.

[0041] In another aspect, the present disclosure provides a catalyst as described herein made by the methods as described herein.

[0042] Another aspect of the present disclosure provides a process for performing an integrated Fischer-Tropsch process (i.e., integrated with an rWGS process). The process includes providing a first feed stream comprising H_2 and CO_2; contacting at a first temperature in the range of 500-900 °C and at a first pressure a reverse water-gas shift catalyst, as described herein, with the first feed stream to perform a reverse water-gas shift reaction to provide a first product stream comprising CO and H_2, the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first stream feed stream. An example of such a process is shown schematically in FIG. 1. In FIG. 1, the process 100 includes performing a reverse water-gas shift reaction by providing a first feed stream 111 comprising H_2 and CO_2, here, to a first reaction zone, e.g., a reactor 110. A reverse water-gas shift catalyst 113, as described herein, is contacted at a first temperature in the range of 500-900 °C and at a first pressure with the feed stream 111 to provide a first product stream 112 comprising CO and H_2. The first product stream has a lower concentration of CO_2 and a higher concentration of CO than the first feed stream. The process of this aspect of the disclosure also includes contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream comprising H_2 and at least a portion of CO of the first product stream to provide a second product stream comprising C_{5+} hydrocarbons, In the process 100 of FIG. 1, at least a portion of CO of the first product stream 112 is included in second feed stream 121, which is contacted with Fischer-Tropsch catalyst 123, here, in a second reaction zone (e.g., a reactor 120). This provides a second product stream 122, which includes C_{5+} hydrocarbons.

[0043] As used herein, a “feed stream” is used to mean the total material input to a process step, e.g., reverse water-gas shift or Fischer-Tropsch reaction, regardless of whether provided in a single physical stream or multiple physical streams, and whether through a single inlet or multiple inlets. For example, H_2 and CO of the first feed stream can be provided to the reverse water-gas shift catalyst in a single physical stream (e.g., in a single pipe to reactor 110), or in multiple physical streams (e.g., separate inlets for CO and H_2, or one inlet for fresh CO and H2 and another for recycled CO and/or H2). Similarly, a “product stream” is used to mean the total material output from a process step, e.g., reverse water-gas shift or Fischer-Tropsch reaction, regardless of whether provided in a single physical stream or multiple physical streams, and whether through a single outlet or multiple outlets.

[0044] As described above, the first feed stream contains both H_2 and CO_2 (e.g., provided to a reaction zone in a single physical stream or multiple physical streams). In various embodiments as otherwise described herein, the molar ratio of H_2 to CO_2 in the first feed stream is at least 0.1:1, e.g., at least 0.5:1. In some embodiments, the molar ratio of H_2 to CO_2 in the first feed stream is at least 0.9:1, e.g., at least 1:1 or at least 1.5:1. In some embodiments, the molar ratio of H_2 to CO_2 in the first feed stream is at least 2:1, e.g., at least 2.5:1. In some embodiments, the molar ratio of H_2 to CO_2 in the first feed stream is no more than 100:1, e.g., no more than 75:1 or no more than 50:1. In some embodiments, the molar ratio of H_2 to CO_2 in the first feed stream is no more than 20:1, e.g., no more than 15:1 or no more than10:1. For example, in some embodiments, the molar ratio of H_2 to CO_2 in the first feed stream is in the range of 0.5:1 to 10:1. The person of ordinary skill in the art will provide a desired ratio of H_2:CO_2 in the first feed stream, based on the disclosure herein, that provides a desirable conversion and selectivity; excess H_2 can, if consistent with a desirable conversion and selectivity, be provided to flow through the system and provide a first product stream with a desirable ratio of H_2 to CO for a downstream process, e.g., a Fischer-Tropsch process.

[0045] Other gases may also be included in the first feed stream. For example, in some embodiments, the first feed stream further comprises CO. In some embodiments of the disclosure as otherwise described herein, the first feed stream further comprises one or more inert gases. For example, in some embodiments, the first feed stream further comprises nitrogen and/or methane.

[0046] The process as described herein includes contacting a rWGS catalyst with the first feed stream to perform the rWGS reaction. Notably, the present inventors have determined that the rWGS catalysts described herein can provide desirably high CO selectivities. For example, in various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a CO selectivity of at least 50%, e.g., of at least 60%, or 70%, or 80%, or 90%. As used herein, a “selectivity” for a given reaction product is the molar fraction of the relevant component of the feed (here, CO_2) that is converted to the product (for “CO selectivity,” CO). The present inventors have determined that the present rWGS catalysts as described herein, even when operating at lower temperatures than many conventional reverse water-gas shift catalysts, can provide excellent selectivity for CO, despite the potential for competition by the Sabatier reaction and the methanation of CO. For example, in various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a CO selectivity in the range of 50-99 wt%. For example, in various embodiments, the reverse water-gas shift reaction has a CO selectivity in the range of 50-90 wt%, or 50-80 wt%, or 50-70 wt%, or 50-60 wt%, or 60-99 wt%, or 60-90 wt%, or 60-80 wt%, or 60-70 wt%, or 70-99 wt%, or 70-90 wt%, or 70-80 wt%.

[0047] Notably, the catalysts described herein can be operated to provide carbon monoxide with only a very minor degree of methane formation. For example, in various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a methane selectivity of no more than 40%, e.g., no more than 35%, or 30%, or 25%, or 20%. For example, in various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a methane selectivity of no more than 10%, e.g., no more than 8%. For example, in various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a methane selectivity of no more than 5%, e.g., no more than 4%. For example, in some embodiments, the reverse water-gas shift reaction has a methane selectivity of no more than 2%, e.g., no more than 1%. In some embodiments, the reverse water-gas shift reaction has a methane selectivity of no more than 0.5%, e.g., no more than 0.4%.

[0048] The present inventors have determined that the rWGS catalysts described here can provide desirably high CO selectivity and desirably low methane selectivity at commercially relevant conversion rates. As used herein, a “conversion” is a molar fraction of a relevant component feed that is reacted (be it to desirable products or undesirable species). In various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a CO_2 conversion of at least 5%, e.g., at least 10%, or at least 20%. For example, in some embodiments, the reverse water-gas shift reaction has a CO_2 conversion of at least 30%, e.g., at least 40%, or at least 50%, or at least 60%. In various embodiments of the present disclosure as described herein, the reverse water-gas shift reaction has a CO_2 conversion of no more than 80%, e.g., no more than 70%. For example, in some embodiments, the reverse water-gas shift reaction has a CO_2 conversion of no more than 65%, e.g., no more than 60%. For example, in various embodiments as otherwise described herein, the CO_2 conversion is in the range of 10-80%, e.g., 10-70%, or 10-60%, or 10-65%, or 20-80%, or 20-70%, or 20-60%, or 20-65%, or 30-80%, or 30-70%, or 30-60%, or 30-65%, or 40-80%, or 40-70%, or 40-60%, or 40-65%. The person of ordinary skill in the art will, based on the disclosure herein, operate at a degree of conversion that provides a desirable product. And of course, in other embodiments, e.g., when in a stacked-bed or mixed-bed system, the effective CO_2 conversion may be even higher than described here.

[0049] Advantageously, the processes described herein can be performed at temperatures that are lower than temperatures used in many conventional reverse water-gas shift processes. As described above, various processes of the disclosure can be performed in a temperature range of 500-900°C. For example, in various embodiments of the disclosure as described herein, the process for performing the reverse water-gas shift reaction is conducted at a first temperature in the range of 500-850 °C, e.g., in the range of 500-800 °C, or 500-750 °C, or 500-700 °C, or 500-650 °C, or 500-600 °C. In some embodiments, the process for performing the reverse water-gas shift reaction is conducted at a first temperature in the range of 550-900 °C, e.g., in the range of 550-850 °C, or 550-800 °C, or 550-750 °C, or 550-700 °C, or 550-650 °C, or 550-600 °C. In some embodiments, the process for performing the reverse water-gas shift reaction is conducted at a first temperature in the range of 600-900 °C, e.g., in the range of 600-850 °C, or 600-800 °C, or 600-750 °C, or 600-700 °C, or 600-650 °C. In some embodiments, the process for performing the reverse water-gas shift reaction is conducted at a first temperature in the range of 650-900 °C, e.g., in the range of 650-850 °C, or 650-800 °C, or 650-750 °C, or 650-700 °C. In some embodiments, the process for performing the reverse water-gas shift reaction is conducted at a first temperature in the range of 700-900 °C, e.g., in the range of 700-850 °C, or 700-800 °C, or 700-750 °C.

[0050] In some embodiments, the reverse water-gas shift reaction is conducted at a first temperature in the range of 200-500 °C, e.g., 200-450 °C, or 200-400 °C, or 200-350 °C, or 250-500 °C, or 250-450 °C, or 250-400 °C, or 250-350 °C. The present inventors have noted that operation at these temperatures can provide for lower energy demand, as well as for facile integration with a subsequent Fischer-Tropsch process step.

[0051] Additionally, the rWGS processes described herein can be performed at a variety of pressures, as would be appreciated by the person of ordinary skill in the art. In various embodiments of the present disclosure, the process for performing the reverse water-gas shift reaction is conducted at a first pressure in the range of 1 to 100 barg. For example, the rWGS process is conducted at a first pressure in the range of 1 to 70 barg, or 1 to 50 barg, or 1 to 40 barg, or 1 to 35 barg, or 5 to 70 barg, or 5 to 50 barg, or 5 to 40 barg, or 5 to 35 barg, or 10 to 70 barg, 10 to 50 barg, or 10 to 40 barg, or 10 to 35 barg, or 20 to 70 barg, 20 to 50 barg, or 20 to 40 barg, or 20 to 35 barg, or 25 to 70 barg, 25 to 50 barg, or 25 to 40 barg, or 25 to 35 barg.

[0052] The rWGS processes described herein can be performed at a variety of GHSV (gas hourly space velocity), as would be appreciated by the person of ordinary skill in the art. As such, the GHSV for performing the reverse water-gas shift reaction is not particularly limited. For example, in some embodiments of the present disclosure, the method for performing the reverse water-gas shift reaction is conducted at a GHSV in the range of 1,000 to 2,000,000 h^{-1}. In various embodiments, the method for performing the reverse water-gas shift reaction is conducted at a GHSV in the range of 1,000 to 1,200,000 h^{-1}, or 1,000 to 500,000 h^{-1}, or 1,000 to 100,000 h^{-1}, or 5,000 to 1,200,000 h^{-1}, or 5,000 to 500,000 h^{-1}, or 5,000 to 100,000 h^{-1}, or 10,000 to 1,200,000 h^{-1}, or 10,000 to 500,000 h^{-1}, or 10,000 to 100,000 h^{-1}. In various embodiments of the present disclose, the method for performing the reverse water-gas shift reaction is conducted at a GHSV in the range of 1,000 to 50,000 h^{-1}, or 2,000 to 50,000 h^{-1}, or 5,000 to 50,000 h^{-1}, or 10,000 to 50,000, or 1,000 to 40,000 h^{-1}, or 2,000 to 40,000 h^{-1}, or 5,000 to 40,000 h^{-1}, or 10,000 to 40,000 h^{-1}, or 1,000 to 30,000 h^{-1}, or 2,000 to 30,000 h^{-1}, or 5,000 to 30,000 h^{-1}, or 10,000 to 30,000 h^{-1}.

[0053] The rWGS catalyst described herein is based in part on nickel. It will typically be desirable to activate the rWGS catalyst, e.g., before contacting with the first feed stream. Thus in some embodiments of the present disclosure as described herein, the process comprises activating the rWGS catalyst prior to contacting the catalyst with the feed stream. For example, in some embodiments, activating the catalyst comprises contacting the catalyst with a reducing stream comprising a reductive gas, e.g., hydrogen. In various embodiments of the present disclose, the reducing stream comprises hydrogen in an amount of at least 25 mol%, e.g., at least 50 mol%, or 75 mol%, or 90 mol%. The person of ordinary skill in the art will determine suitable conditions for reducing activation of the rWGS catalyst. As such, the person or ordinary skill in the art would be able to choose an appropriate temperature, pressure, and time for activating the rWGS catalyst. For example, in various embodiments activating the rWGS catalyst is conducted at a temperature in the range of 200 °C to 800 °C. For example, in various embodiment, activating the rWGS catalyst is conducted at a temperature in the range of 250 °C to 800 °C, or 300 °C to 800 °C, or 200 °C to 700 °C, or 250 °C to 800 °C, or 300 °C to 700 °C. In some embodiments of the present disclosure as described herein, activating the rWGS catalyst provides a rWGS catalyst that is at least 10% reduced (e.g., at least 25%, or at least 50% reduced).

[0054] The present inventors have found that contacting the rWGS catalysts as described herein with a first feed stream can provide a first product stream with advantageously high CO selectivity and low methane selectivity. The amount of CO in the first product stream can be further controlled by the rWGS reaction conditions, as described above. But in general, the processes for performing the rWGS reaction as described herein, provide a first product stream comprising H_2 and CO, with the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first feed stream, as is consistent with the degrees of conversion and selectivities described herein. For example, in various embodiments, the first product stream includes no more than 95 mol% CO_2, or no more than 90 mol% CO_2. In some embodiments, the first product stream includes no more than 85 mol% CO_2, or no more than 80 mol% CO_2. In other examples, the first product stream includes no more than 75 mol%, or no more than 70 mol% CO_2.

[0055] However, as described above, the present inventors have determined that it can be desirable to perform the processes at intermediate degrees of conversion to provide desirably high CO selectivities and desirably low methane selectivities. Moreover, the present inventors have noted that it can be advantageous to perform the downstream Fischer-Tropsch process with a relatively high level of inerts, and thus contemplate that passing a significant amount of CO_2 to the Fischer-Tropsch process step can be beneficial. Accordingly, in various embodiments as otherwise described herein, the first product stream includes an amount of CO_2 together with the CO. In various embodiments, the first product stream comprises in the range of 5-95 mol% CO_2, e.g., 5-90 mol%, or 5-85 mol%, or 5-80 mol%, or 5-75 mol%, or 5-70 mol%, or 10-95 mol%, or 10-90 mol%, or 10-85 mol%, or 10-80 mol%, or 10-75 mol%, or 10-70 mol%, or 20-95 mol%, or 20-90 mol%, or 20-85 mol%, or 20-80 mol%, or 20-75 mol%, or 20-70 mol%, or 30-95 mol%, or 30-90 mol%, or 30-85 mol%, or 30-80 mol%, or 30-75 mol%, or 30-70 mol% CO_2.

[0056] Other gases may also be included in the first product stream. In some embodiments of the disclosure as otherwise described herein, the first product stream further comprises one or more inert gases. These inert gases may be included from the first feed stream or provided from a source other than the first feed stream. For example, in some embodiments, the first product stream further comprises nitrogen and/or methane.

[0057] Depending on, inter alia, the degree of conversion, the CO selectivity, the relative amounts of H_2 and CO_2 in the first feed stream, and the reaction conditions, the first product stream can include H_2 in combination with CO, in a variety of ratios. For example, in some embodiments, the ratio of H_2:CO in the first product stream is in the range of 0.1:1 to 100:1 (e.g., in the range of 0.1:1 to 50:1, or 0.1:1 to 25:1, or 0.1:1 to 10:1, or 0.1:1 to 5:1, or 1:1 to 100:1, or 1:1 to 50:1, or 1:1 to 25:1, or 1:1 to 10:1, or 1:1 to 5:1).

[0058] The person of ordinary skill in the art would appreciate that, based on the processes as described herein, the first product stream may include H_2, CO, and CO_2 and other components in various amounts. Components of the first product stream may be separated and used for various purposes in the integrated process.

[0059] For example, in various embodiments of the present disclosure as described herein, the process further comprises separating the first product stream to recycle at least a portion (e.g., at least 5 mol%, at least 10 mol%, at least 25 mol%, at least 50 mol%, at least 75 mol%, or at least 90 mol%) of one or more components of the first product stream to the first feed stream. For example, when the first product stream includes CO_2, the process can include recycling at least a portion (e.g., at least 5 mol%, at least 10 mol%, at least 25 mol%, at least 50 mol%, at least 75 mol%, or at least 90 mol%) of the CO_2 of the first product stream to the first feed stream. The first product stream may also include H_2; in some embodiments, the process further includes recycling at least a portion of H_2 of the first product stream (e.g., at least 5 mol%, at least 10 mol%, at least 25 mol%, at least 50 mol%, at least 75 mol%, or at least 90 mol%) to the first feed stream.

[0060] Such recycling is shown in the process 100 of FIG. 1. Here, the process 100 includes separating from the first product stream 112 at least a portion of CO_2 (stream 114) to recycle to the first feed stream 111. Similarly, the process 100 includes separating from the first product stream 112 at least a portion of H_2 (stream 115) to recycle to the first product stream 111. While stream 115 is depicted as entering reactor 110 through a different inlet than the rest of the first feed stream 111, it is considered to be part of the first feed stream, as it is part of the material input to the process step.

[0061] Moreover, as described below, Fischer-Tropsch catalysts typically require activation by a reducing gas. As would be understood by the person of skill in the art, different Fischer-Tropsch catalysts required different activation conditions (e.g., gas composition, temperature, pressure, time). For example, iron based Fischer-Tropsch catalysts require activation with both H_2 and CO, while cobalt based Fischer-Tropsch catalysts require activation with just H_2. As such, H_2 and CO or just H_2 from the first product stream can be used to perform this activation. Accordingly, in various embodiments as otherwise described herein, the process includes separating at least a portion of H_2 and CO (desirably in a ratio of at least 1:1 or at least 3:1) from the first product stream and contacting it with the Fischer-Tropsch catalyst to activate the Fischer-Tropsch catalyst. In various other embodiments as otherwise described herein, the process includes separating at least a portion of H_2 from the first product stream and contacting it with the Fischer-Tropsch catalyst to activate the Fischer-Tropsch catalyst. For example, in the process of FIG. 1, stream 125 separates H_2 or H_2 and CO and conducts it to reactor 120. This separation need not be continuous; rather, it need only be performed for a time desirable to provide reducing gas to the Fischer-Tropsch catalyst for activation. Of course, as would be understood by the person of skill in the art, other sources of H_2 or CO may be used to provide reducing gas to the Fischer-Tropsch catalyst for activation.

[0062] As shown above, water is a product of the reverse water-gas shift reaction. Accordingly, the first product stream will generally contain water. In many cases it can be desirable to reduce the amount of water that is provided to the Fischer-Tropsch process step. Accordingly, in various embodiments as otherwise described herein, the process further includes removing at least a portion (e.g., at least 25%, at least 50%, or at least 75%) of water from the first product stream. In the embodiment of FIG. 1, a water removal zone 116 is used to remove water and provide a water-containing stream 117. The person of ordinary skill in the art will appreciate that a variety of processes can be used to remove water from the first product stream. For example, the first product stream can be contacted with a water scavenger to remove water therefrom. For example, a molecular sieve guard bed can be used to remove water from the first product stream; water can be recovered from the molecular sieves of the guard bed, e.g., by heating and vacuum. In other embodiments, a knockout vessel can be used. However, use of a knockout vessel can in some cases cool the first product stream enough so that it is desirably reheated for introduction to the Fischer-Tropsch process step.

[0063] As noted above, one competing reaction in the reverse water-gas shift reaction is the Sabatier reaction, which makes methane. While in various embodiments the reverse water-gas shift processes described herein can be performed without forming large amounts of methane, in some embodiments there can be some methane formed. Accordingly, in various embodiments of the method as described herein, the first product stream comprises one or more light hydrocarbons. For example, in some embodiments, the first product stream may include one or more of methane, ethane, propane, or combinations thereof. As would be understood by the person of ordinary skill in the art, it may be desirable to operate the reverse water-gas shift reaction to provide higher amounts of light hydrocarbons in the first product feed. For example, such light hydrocarbons may be inert in further processing of the first product stream and so may be acceptable at higher amounts. The person of ordinary skill in the art would be able to select appropriate reaction conditions (e.g., temperature, pressure, feed stream composition) to provide a first product stream that includes methane at a desired amount. Accordingly, in various embodiments as otherwise described herein, the first product stream includes no more than 40 mol%, or 35 mol%, or 30 mol%, or 25 mol%, or 20 mol%, or 15 mol%, or 10 mol% methane. As noted above, when lower amounts of methane are desired in the product stream, the catalysts of the disclosure can provide very low methane selectivity. For example, in various embodiments, the first product stream includes no more than 5 mol%, or 1 mol%, or no more than 0.5 mol% methane.

[0064] These light hydrocarbons can be separated and used for other purposes. For example, in various embodiments, the process further includes separating at least a portion of one or more light hydrocarbons from the first product stream to provide a light hydrocarbon stream. For example, in process 100 of FIG. 1, at least a portion of one or more light hydrocarbons are separated from the first product stream 112 to provide a light hydrocarbon stream 118. The light hydrocarbon stream, for example, can be used to provide other products, can be partially oxidized to form CO, can be steam reformed to provide hydrogen, and/or can be burned to provide heat or other energy (e.g., electricity for electrolysis) for use in the integrated process or otherwise. Of course, as would be understood by the person of ordinary skill in the art, the light hydrocarbon stream may be used in other processes as well.

[0065] As noted above, the reverse water-gas shift process can be provided at a wide variety of temperatures. In some cases, those temperatures can be relatively close to the temperature of the subsequent Fischer-Tropsch process step (often 150-400 °C, e.g., 200-

350 °C, or other temperatures as described below). In other cases, the reverse water-gas shift process can be performed at temperatures significantly higher than the temperature of the Fischer-Tropsch step. The present inventors have noted that it can be desirable to provide for heat exchange with a relatively hot first product stream to cool the first product stream to a temperature more appropriate for the Fischer Tropsch step and to provide heat elsewhere to the integrated process. For example, in various embodiments of the processes as otherwise described herein, the process further comprises exchanging heat between at least a portion of the first product stream and at least a portion of the first feed stream, thereby cooling at least a portion of the first product stream and heating at least a portion of the first feed stream. An example of such a process is shown schematically in FIG. 2. In FIG. 2, the process 200, first reactor 210, first feed stream 211, first product stream 212, reverse water-gas shift catalyst 213, second reactor 220, second feed stream 221, second product stream 222 and Fischer-Tropsch catalyst 223 are generally as described above. Here, the process 200 includes exchanging heat between at least a portion of the first product stream 212 and a least a portion of the first feed stream 211 in a first heat exchange zone 230, thereby cooling at least a portion of the first product stream 212 and heating at least a portion of the first feed stream 211. The person of ordinary skill in the art will appreciate that a wide variety of heat exchangers can be used for this purpose.

[0066] Of course, any excess heat in the first product stream can be additionally or alternatively used for other purposes. For example, in various embodiments the process further comprises exchanging heat between at least a portion of the first product stream and a steam generation zone, thereby cooling at least a portion of the first product stream and providing heat to the steam generation zone. This is shown in FIG. 2. Here, after heat exchange with the first feed stream 211, the first product stream 212 is conducted to steam generation zone 232, to cool the first product stream 212 and provide heat to the steam generation zone 232. Steam can be generated from the heat provided, and electricity can be generated from the steam. For example, in the embodiment of FIG. 2, electricity stream 264 is provided by the generation of electricity using steam generated in the steam generation zone 232. Of course, as would be understood to the person of ordinary skill in the art, the steam generated in the steam generation zone may be used in other processes. In various embodiments, the steam may be used to heat the first feed stream. For example, in the embodiment of FIG. 2, the steam stream 266 generated in the steam generation zone 232 is conducted to the heat exchange zone 290 to heat the first feed stream 211.

[0067] As noted above, at least a portion of the CO of the first product stream is included in the second feed stream, for reaction in a Fischer-Tropsch process. For example, in various embodiments as otherwise described herein, at least 25% of the CO of the first product stream, e.g., at least 50% of the CO, at least 75% of the CO, or at least 90% of the CO of the first product stream is included in the second feed stream. Of course, as noted above, some of the CO of the first product stream can be used for other purposes, e.g., catalyst activation as described herein.

[0068] In some embodiments, substantially all of the CO of the second feed stream comes from the first product stream. However, in other embodiments, CO can be provided to the second feed stream from other sources. For example, in various embodiments, CO is provided to the second feed stream from a CO source other than the first product stream. In FIG. 2, a stream of CO 226a from some other source is included in the second feed stream 221. The person of ordinary skill in the art will appreciate that CO can be provided from a variety of sources, e.g., gasification, reforming, or electrochemical CO_2 reduction. Moreover, as described in more detail below, CO can be recycled to the second feed stream from the second product stream.

[0069] As noted above, the second feed stream includes H_2. Notably, the first product stream will often include H_2, e.g., unreacted from the first feed stream. In various embodiments, the first product stream includes H_2 wherein the second feed stream includes at least a portion of the H_2 of the first product stream. For example, in various embodiments as otherwise described herein, at least 25% of the H_2 of the first product stream, e.g., at least 50% of the H_2, at least 75% of the H_2, or at least 90% of the H_2 of the first product stream is included in the second feed stream. Of course, as noted above, some of the H_2 of the first product stream can be used for other purposes, e.g., catalyst activation as described herein.

[0070] In some embodiments, substantially all of the H_2 of the second feed stream comes from the first product stream. In fact, the person of ordinary skill in the art can provide more H_2 than necessary for the reverse water-gas shift reaction in the first feed stream, to provide excess H_2 in the first product stream that can then provide a desired amount of H_2 to the second feed stream for the Fischer-Tropsch process step. However, in other embodiments, H_2 can be provided to the second feed stream from other sources. For example, in various embodiments, H_2 is provided to the second feed stream from a H_2 source other than the first product stream. In FIG. 2, a stream of H_2 226b from some other source is included in the second feed stream 221. The person of ordinary skill in the art will appreciate that H_2 can be provided from a variety of sources, e.g., gasification, reforming, or H_2O electrolysis. Moreover, as described in more detail below, H_2 can be recycled to the second feed stream from the second product stream.

[0071] As noted above, it can be desirable to perform the Fischer-Tropsch process step in the presence of a significant level of inerts. One such inert, CO_2, can come from the reverse water-gas shift, e.g., via the first product stream. Accordingly, in various embodiments as otherwise described herein, the second feed stream includes at least a portion of CO_2 of the first product stream. For example, in various embodiments, at least 10% of the CO_2 of the first product stream, e.g., at least 25% of the CO_2, at least 50% of the CO_2, at least 75% of the CO_2, or at least 90% of the CO_2 of the first product stream is included in the second feed stream. Of course, in other embodiments, the second feed stream may not include any substantial amount of CO_2 of the first product stream. Accordingly, in various embodiments, the second feed stream does not include a substantial amount of CO_2 of the first product stream. While it can be desirable generally to recycle CO_2 to the first feed stream for use in the reverse water-gas shift reaction, as described in more detail below, unreacted CO_2 can be recycled from the second product stream to the first feed stream.

[0072] But it can additionally or alternatively be desirable to include additional inert content to the second feed stream, be it CO_2 or other inerts such as nitrogen and methane. For example, in various embodiments, one or more inerts (e.g., CO_2, nitrogen and/or methane) are provided to the second feed stream from a source other than the first product stream. In FIG. 2, a stream of inert(s) 226c from some other source is included in the second feed stream 221. The person of ordinary skill in the art will appreciate that inerts can be provided from a variety of sources. Moreover, as described in more detail below, inerts can be recycled to the second feed stream from the second product stream.

[0073] As noted above, it can be desirable to perform the Fischer-Tropsch process step in the presence of inerts. Accordingly, in various embodiments as otherwise described herein, the portion of the first product stream that is included in the second feed stream has a CO_2 content in the range of 10-95 mol% CO_2, e.g., 10-90 mol%, or 10-85 mol%, or 10-80 mol%, or 10-75 mol%, or 10-70 mol%, or 20-95 mol%, or 20-90 mol%, or 20-85 mol%, or 20-80 mol%, or 20-75 mol%, or 20-70 mol%, or 30-95 mol%, or 30-90 mol%, or 30-85 mol%, or 30-80 mol%, or 30-75 mol%, or 30-70 mol% CO_2.

[0074] Other gases may also be included in the second feed stream, as described above. For example, as noted above, it can be desirable to perform the Fischer-Tropsch process step in the presence of a significant amount of inerts (i.e., components that are not H_2 or CO). For example, in various embodiments, the second feed stream includes up to 80 mol% of one or more inerts, e.g., in the range of 3-80 mol%, or 5-80 mol%, or 10-80 mol%, or 15-80 mol%, or 30-80 mol% of one or more inerts. In various embodiments, the second feed stream includes up to 70 mol% inerts, up to 60 mol% inerts, or up to 50 mol% inerts, e.g., 3-70 mol%, or 5-70 mol%, or 10-70 mol%. or 15-70 mol%, or 30-70 mol%, or 3-60 mol%, or 5-60 mol%, or 10-60 mol%, or 15-60 mol%, or 30-60 mol%, or 3-50 mol%, or 5-50 mol%, or 10-50 mol%, or 15-50 mol%, or 30-50 mol% inerts. In various embodiments, the second feed stream includes up to 80% of one or more inerts selected from CO_2, methane and nitrogen, e.g., up to 70 mol%, up to 60 mol%, or up to 50 mol%, or 15-70 mol%, or 30-70 mol%, or 15-60 mol%, or 30-60 mol%, or 15-50 mol%, or 30-50 mol%. In various embodiments, the second feed stream includes up to 80 mol% of CO_2, e.g., up to 70 mol%, up to 60 mol%, or up to 50 mol%, or 15-70 mol%, or 30-70 mol%, or 15-60 mol%, or 30-60 mol%, or 15-50 mol%, or 30-50 mol%.

[0075] The person of ordinary skill in the art can tune the portion of the first product stream that is included in the second feed stream to provide a desirable H_2:CO ratio. For example in various embodiments, the portion of the first product stream that is included in the second feed stream has a H_2:CO ratio in the range of 0.5:1 to 10:1, e.g., in the range of 1:1 to 2.5:1. Of course, whatever the H_2:CO ratio of the portion of the first product stream that is included in the second feed stream, the person of ordinary skill in the art can add H_2 or CO as described above as necessary to provide the desired ratio overall in the second feed stream.

[0076] As described above, the second feed stream contains both H_2 and CO and the second feed stream includes all feeds to the Fischer Tropsch reactor, regardless of whether the second feed stream is provided as a mixture of feeds or as feeds provided individually to a reaction zone. In various embodiments of the present disclosure as described herein, the second feed stream has a H_2:CO ratio in the range of 0.5:1 to 6:1. In some embodiments, the second feed stream has a H_2:CO ratio in the range of 1:1 to 3:1, or 1:1 to 2.5:1. In some embodiments, the second feed stream has a H_2:CO ratio of at least 1.4:1. For example, in some embodiments, the second feed stream has a H_2:CO ratio in the range of 1.4:1 to 3:1, or 1.4:1 to 2:1. The person of ordinary skill in the art will provide a desired ratio of H_2:CO in the second feed stream, based on the disclosure herein that provides a desirable conversion and selectivity in the Fischer-Tropsch process.

[0077] As noted above it can be desirable to reduce the amount of water that is conducted to the Fischer-Tropsch process step. Accordingly, in various embodiments as otherwise described herein, the portion of the first product stream that is included in the second feed stream has a water content of no more than 10 mol%, e.g., or no more than 2 mol%, or no more than 0.5 mol%.

[0078] And as noted above, it can be desirable to perform the Fischer-Tropsch process with a relatively small amount of water present. Accordingly, in various embodiments, the second feed stream has a water content of no more than 10 mol%, e.g., or no more than 2 mol%, or no more than 0.5 mol%.

[0079] The processes as described here include contacting a Fischer-Tropsch catalyst with the second feed stream as described herein. The Fischer-Tropsch catalyst for use in the processes as described herein is not particularly limited and the person of ordinary skill in the art would be able to choose a catalyst as appropriate for their desired Fischer-Tropsch product. In some embodiments, the Fischer-Tropsch catalyst includes cobalt, iron, rhodium, ruthenium, or a combination thereof.

[0080] For example, in some embodiments of the present disclosure as described herein, the Fischer-Tropsch catalyst comprises cobalt, e.g., in an amount in the range of 5-25 wt%, calculated as Co(0). “Calculated as Co(0)” and analogous terms mean that the weight of cobalt atoms/ions themselves are used in the calculation, and not the total amount of any compound or polynuclear ion in which those cobalt atoms/ions might be bound. For example, in various embodiments, the Fischer-Tropsch catalyst comprises cobalt in an amount in the range of 7-25 wt%, or 10-25 wt%, or 5-20 wt%, or 7-20 wt%, or 10-20 wt%, calculated as Co(0). As the person of ordinary skill in the art will appreciate, cobalt-based catalysts are often provided to the reaction zone in the form of cobalt oxide on a support; the cobalt can be reductively activated (e.g., with H_2) in situ to provide an active catalyst species with a significant concentration of Co(0).

[0081] In some embodiments, the Fischer-Tropsch catalyst comprises iron, e.g., in an amount in the range of 5-95 wt%, calculated as Fe(0). For example, in various embodiments, the Fischer-Tropsch catalyst comprises iron in the range of 10-95 wt%, or 25-95 wt%, or 50-95 wt%, or 5-75 wt%, or 10-75 wt%, or 25-75 wt%, or 5-50 wt%, or 10-50 wt%, or 25-50 wt%, calculated as Fe(0). As the person of ordinary skill in the art will appreciate, iron-based catalysts are often provided to the reaction zone in the form of metallic iron or iron oxide, optionally on a support; the iron can be activated (e.g., by reaction with H_2 and CO) to provide an active catalyst species with a significant concentration of iron carbide.

[0082] In various embodiments of the disclosure as described herein, especially when the catalyst is a cobalt-based catalyst, the Fischer-Tropsch catalyst further includes manganese. For example, in various embodiments, the Fischer-Tropsch catalyst includes manganese in an amount up to 15 wt%, e.g., up to 12 wt%, or up to 10 wt%, or up to 7 wt%, calculated as Mn(0). In certain such embodiments, a catalyst material includes manganese in an amount in the range of 0.1-15 wt%, e.g., 0.1-10 wt%, or 0.1-5 wt%, 0.5-15 wt%, or 0.5-10 wt%, or 0.5-5 wt%, or calculated as Mn(0). Of course, in other embodiments substantially no manganese is present (e.g., less than 0.1 wt% or less than 0.5 wt% manganese is present).

[0083] The Fischer-Tropsch catalysts suitable for use in the process as described herein can be a variety of forms and are not particularly limited. For example, the Fischer-Tropsch catalyst may be a supported or unsupported catalyst. While the form of the catalyst is not particularly limited, in various desirable embodiments, the Fischer-Tropsch catalyst is a supported catalyst, wherein the support comprises at least one of titanium oxide, zirconium oxide, cerium oxide, aluminum oxide, silicon oxide and zinc oxide. For example, in various embodiments, the support comprises at least one or titanium oxide, aluminum oxide, and silicon oxide. In some embodiments of the present disclosure as described herein, the support is a titanium dioxide support.

[0084] The person of ordinary skill in the art will appreciate that the Fischer-Tropsch catalysts of the disclosure can be provided in many forms, depending especially on the particular form of the reactor system in which they are to be used, e.g., in a fixed bed or as a fluidized bed. The supports of the Fischer-Tropsch catalysts can be provided themselves as discrete bodies of material, e.g., as porous particles, pellets or shaped extrudates, with the metals provided thereon to provide the Fischer-Tropsch catalyst. However, in other embodiments, a Fischer-Tropsch catalyst of the disclosure can itself be formed as a layer on an underlying substrate. The underlying substrate is not particularly limited. It can be formed of, e.g., a metal or metal oxide, and can itself be provided in a number of forms, such as particles, pellets, shaped extrudates, or monoliths. The person of ordinary skill in the art will select an appropriate Fischer-Tropsch catalyst for the particular reactor system.

[0085] As with the rWGS catalyst, Fischer-Tropsch catalysts are typically activated before use, e.g., to provide cobalt(0) species on a cobalt-based catalyst, or iron carbide species on an iron-based catalyst. Such activation can be performed prior to contacting the Fischer-Tropsch catalyst with a second feed stream.

[0086] For example, in some embodiments, the Fischer-Tropsch catalyst is activated by contact with a reducing gas. For example, hydrogen can be an especially suitable gas for activating Fischer-Tropsch catalyst, e.g., when the activation is a reduction to metal(0) species, e.g., as for many cobalt-based catalysts. In various embodiments of the present disclosure as otherwise described herein, the reducing gas comprises at least a portion of H_2 from the first product stream. For example, in some embodiments, the process further comprises separating at least a portion of H_2 of the first product stream and contacting it with the Fischer-Tropsch catalyst to activate Fischer-Tropsch catalyst. In the process 100 shown schematically in FIG. 1, at least a portion of hydrogen stream 125 is separated from the first product stream 112 and contacted with the Fischer-Tropsch catalyst 123 to activate it. In other embodiments, H_2 present in the second feed stream can be used to activate the catalyst. As would be understood by the person of ordinary skill in the art, activation temperatures can vary depending on the Fischer-Tropsch catalyst used. As such, the person of ordinary skill in the art would be able to select an appropriate temperature for activating the catalyst, e.g., in the range of 200-400 °C.

[0087] In various embodiments, the Fischer-Tropsch catalyst is activated by contact with H_2 and CO. This can be especially suitable when the activation provides conversion to carbide, e.g., as for many iron-based catalysts. In various embodiments of the present disclosure as otherwise described herein, the reducing gas comprises at least a portion of H_2 and CO from the first product stream. For example, in some embodiments, the process further comprises separating at least a portion of H_2 and at least a portion of CO of the first product stream and contacting it with the Fischer-Tropsch catalyst to activate Fischer-Tropsch catalyst. In the process 200 shown schematically in FIG. 2, at least a portion of H_2 and CO stream 227 is separated from the first product stream 212 and contacted with the Fischer-Tropsch catalyst 223 to activate it. In other embodiments, H_2 and CO present in the second feed stream can be used to activate the catalyst. Activation temperatures can vary, e.g., in the range of 200-400 °C.

[0088] As described above, the process includes contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream. The person of ordinary skill in the art will select appropriate reaction conditions in conjunction with the particular feed and catalyst used to provide desired Fischer-Tropsch processes. In some embodiments of the disclosure as described herein, the second temperature is in the range of 150-400 °C. For example, in various embodiments, the second temperature is in the range of 150-350 °C, or 150-300 °C, or 150-250°C, or 150-200°C, or 200-400 °C, or 200-350 °C, or 200-300°C, or 200-250 °C, or 250-400 °C, or 250-350 °C, or 250-300 °C, or 300-400 °C. In some particular embodiments, the second temperature is in the range of 200-350 °C.

[0089] Notably, in many embodiments, the first temperature and the second temperature can be relatively close to one another. The present inventors have noted that the reverse water-gas shift catalysts described herein can provide suitable activity and CO selectivity even at relatively low temperatures. Accordingly, the first product stream can be provided with a temperature that is suitable for, or at least close to suitable for, the Fischer-Tropsch reaction step. This can desirably provide for increased process integration. For example, in various embodiments, the first temperature is within 100 °C of the second temperature, e.g., within 50 °C of the second temperature, or within 25 °C of the second temperature.

[0090] However, in other embodiments, the first temperature and the second temperature are less close to one another. The present inventors have noted that in many cases a desirable reverse water-gas shift process temperature will be significantly greater than a desirable Fischer-Tropsch process temperature. For example, in various embodiments, the first temperature is at least 100 °C greater than the second temperature, e.g., at least 150 °C greater than the second temperature, or at least 200 °C greater than the second temperature. The excess heat in the first product stream can be used for a number of purposes, for example, to preheat at least part of the first feed stream or to generate steam for use in generating electricity, as described above.

[0091] In some embodiments of the disclosure as described herein, the second pressure is in the range of 10-50 barg. For example, in various embodiments, the second pressure is in the range of 20-50 barg, or 25-50 barg, or 10-40 barg, or 20-40 barg, or 25-40 barg or 10-35 barg, or 20-35 barg, or 25-35 barg. In some embodiments, the second pressure is in the range of 20-50 barg.

[0092] The Fischer-Tropsch processes described herein can be performed at a variety of GHSV (gas hourly space velocity) values, as would be appreciated by the person of ordinary skill in the art. As such, the GHSV for performing the Fischer-Tropsch reaction is not particularly limited. For example, in some embodiments of the present disclosure, the method for performing the Fischer-Tropsch reaction is conducted at a GHSV in the range of 1,000 to 2,000,000 h^{-1}. In various embodiments, the method for performing the reverse water-gas shift reaction is conducted at a GHSV in the range of 1,000 to 1,200,000 h^{-1}, or 1,000 to 500,000 h^{-1}, or 1,000 to 100,000 h^{-1}, or 5,000 to 1,200,000 h^{-1}, or 5,000 to 500,000 h^{-1}, or 5,000 to 100,000 h^{-1}, or 10,000 to 1,200,000 h^{-1}, or 10,000 to 500,000 h^{-1}, or 10,000 to 100,000 h^{-1}. In various embodiments of the present disclose, the method for performing the Fischer-Tropsch reaction is conducted at a GHSV in the range of 1,000 to 50,000 h^{-1}, or 2,000 to 50,000 h^{-1}, or 5,000 to 50,000 h^{-1}, or 10,000 to 50,000, or 1,000 to 40,000 h^{-1}, or 2,000 to 40,000 h^{-1}, or 5,000 to 40,000 h^{-1}, or 10,000 to 40,000 h^{-1}, or 1,000 to 30,000 h^{-1}, or 2,000 to 30,000 h^{-1}, or 5,000 to 30,000 h^{-1}, or 10,000 to 30,000 h^{-1}.

[0093] The Fischer-Tropsch process is typically used to make C_{5+} hydrocarbons, for example, unsubstituted C_{5+} hydrocarbons (e.g., alkanes and alkenes) and oxygenated C_{5+} hydrocarbons (e.g., C_{5+} alcohols, aldehydes, ketones, carboxylic acids). In various embodiments of the disclosure as described herein, contacting the Fischer-Tropsch catalyst with the second feed stream to provide the second product stream is performed with a C_{5+} selectivity (i.e., for all C_{5+} species) of at least 30%, e.g., at least 50%, or at least 70%. For example, in some embodiments, the selectivity for C_{5+} alkanes is at least 30%, e.g., at least

50%, or at least 70%. In some embodiments, the selectivity for C_{5+} alkanes and C_{5+} alcohols is at least 30%, e.g., at least 50%, or at least 70%.

[0094] Additional components may be in present in the second product stream. For example, in some embodiments, the second product stream includes water, which is another product of the Fischer-Tropsch reaction. Also present can be one or more light hydrocarbons (i.e., C_1-C_4) as a side product. CO and/or H_2 can be present, e.g., unreacted from the second feed stream. CO_2 or other inerts as described herein can also be present. Such components of the second product stream can be separated and/or recycled in various manners.

[0095] For example, in various embodiments, the process further comprises separating at least a portion of water from the second process stream. This is shown schematically in FIG. 3. In the embodiment of FIG. 3, the reverse water-gas shift catalyst 313 and the Fischer-Tropsch catalyst 323 are provided in separate beds in the same reactor. Thus, the first reaction zone 310 is a volume of the reactor 305 that includes the bed 314 containing the reverse water-gas shift catalyst 313, and the second reaction zone 320 is a volume of the reactor 305 that includes the bed 324 containing the Fischer-Tropsch catalyst 323. First feed stream 311 is contacted with the reverse water-gas shift catalyst 313 to provide first product stream 312, which is passed directly as the second feed stream 321 to the Fischer-Tropsch catalyst 323 to provide second product stream 322. Here, the process also optionally includes separating at least a portion of water (e.g., at least 50%, at least 75%, or at least 90%) from the second product stream 322 to provide water-containing stream 334.

[0096] Light hydrocarbons, while often not a desired portion of a Fischer-Tropsch product to be used as a fuel or a lubricant, can themselves be useful for a number of purposes. Accordingly, in various embodiments, the process further includes separating at least a portion of C_1-C_4 hydrocarbons from the second product stream to provide a light hydrocarbon stream. The light hydrocarbon stream can, for example, be recycled to the first feed stream or the second feed stream. For example, in the process 200 of FIG. 2, light hydrocarbons can be provided as part of the recycle stream 236, which becomes part of the second feed stream 221. In the process 300 of FIG. 3, light hydrocarbons can be provided as part of the recycle stream 336, which becomes part of the first feed stream 311. In the process 400 of FIG. 4, light hydrocarbons are recycled via recycle stream 442 to first feed stream 411.

[0097] There are other uses for the light hydrocarbon stream. For example, in some embodiments, the process further comprises oxidizing at least a portion of the light hydrocarbon stream to provide a CO- and/or CO_2-containing partial oxidation (pOX) stream, and including at least a portion of the pOX stream in the first feed stream and/or the second feed stream. An example of such a process is shown schematically in FIG. 4, in which the process 400, the first feed stream 411, the first product stream 412, the reverse water-gas shift catalyst 413, the second feed stream 421, the second product stream 422 and the Fischer-Tropsch catalyst 423 can be as otherwise described herein. Here, the process includes oxidizing at least a portion of the light hydrocarbon stream 450) in a partial oxidation reaction zone 452 to provide a CO- and/or CO_2 containing pOX stream, and including at least a portion of the pOX stream 454 stream in the first feed stream 411 and/or the second feed stream 421.

[0098] Moreover, the light hydrocarbon stream can be burned to provide heat energy, which can be used to heat various process streams, or to generate electricity. Accordingly, in various embodiments, the process includes burning at least a portion of the light hydrocarbon stream to provide energy, e.g., heat energy or electrical energy. For example, in the process 400 of FIG. 4, a portion of light hydrocarbon stream 450 is burned in a power generation zone (here, in an electrical generator 470), to generate electricity stream 472. In various embodiments, the heat energy may be used to provide the needed heat duty for the reverse water-gas shift process. For example, in the process 400 of FIG. 4, a portion of the light hydrocarbon stream 450 is burned in a power generation zone (here, in a heat generator 480), to generate heat stream 482. The heat stream 482 is conducted to a heat exchange zone 490 to heat the first feed stream 411.

[0099] As with the first product stream, heat can be exchanged from the second product stream to provide heat to, for example, a feed stream or a steam generation zone. For example, in various embodiments, the process further comprises exchanging heat between at least a portion of the second product stream and at least a portion of the first feed stream, thereby cooling at least a portion of the second product stream and heating at least a portion of the first feed stream. In process 300 of FIG. 3, heat is exchanged between at least a portion of the second product stream 322 and first feed stream 311 in a second heat exchange zone 330, thereby cooling the second product stream 322 and heating the first feed stream 311. Of course, heat can also be exchanged from the second product stream to the second feed stream. For example, in various embodiments, the process further comprises exchanging heat between at least a portion of the second product stream and at least a portion of the second feed stream, thereby cooling at least a portion of the second product stream and heating at least a portion of the second feed stream. In process 400 of FIG. 4, heat is exchanged between at least a portion of the second product stream 422 and second feed stream 421 in a second heat exchange zone 430, thereby cooling the second product stream 422 and heating the second feed stream 421. The person of ordinary skill in the art will appreciate that a wide variety of heat exchangers can be used for this purpose.

[00100] Of course, any excess heat in the second product stream can be additionally or alternatively used for other purposes. For example, in various embodiments the process further comprises exchanging heat between at least a portion of the second product stream and a steam generation zone, thereby cooling at least a portion of the second product stream and providing heat to the steam generation zone. This is shown in FIG. 3. Here, after heat exchange with the first feed stream 311, the second product stream 322 is conducted to steam generation zone 332, to cool the second product stream 322 and provide heat to the steam generation zone 332. Steam can be generated from the heat provided, and electricity can be generated from the steam (not shown here).

[00101] It can be desirable to recycle hydrogen from the second product stream, for example, to the first feed stream and/or the second feed stream. For example, in various embodiments, the process includes recycling at least a portion of H_2 of the second product stream to the second feed stream. For example, in the process of FIG. 2, at least a portion of H_2 of the second product stream (e.g., at least 25%, at least 50%, or at least 75%) can be recycled to the second feed stream 221 via recycle stream 236. In various embodiments, the process includes recycling at least a portion of H_2 of the second product stream to the first feed stream. For example, in the process of FIG. 3, at least a portion of H_2 of the second product stream (e.g., at least 25%, at least 50%, or at least 75%) can be recycled to the first feed stream 311 via recycle stream 336. In various embodiments, at least 25%, e.g., at least 50% of H_2 of the second product stream is recycled to the first feed stream or the second feed stream. In various embodiments, at least 75%, e.g., at least 90% of H_2 of the second product stream is recycled to the first feed stream or the second feed stream.

[00102] In some cases, e.g., when H_2 is provided to the second feed stream from an H_2 source other than the first product stream, H_2 from the second product stream can make up most of the H_2 of the first feed stream, e.g., at least 90%, at least 95%, or at least 98% of the H_2 of the first feed stream. This is shown, e.g., in FIG. 4. Here, the primary H_2 input to the process is through stream 440, which becomes part of the second feed stream 421. H_2 of the second product stream is included in recycle stream 442, which becomes part of first feed stream 411.

[00103] Similarly, it can be desirable to recycle CO of the second product stream, for example, to the first feed stream and/or the second feed stream. For example, in various embodiments, the process includes recycling at least a portion of CO of the second product stream to the second feed stream. For example, in the process of FIG. 2, at least a portion of CO of the second product stream (e.g., at least 25%, at least 50%, or at least 75%) can be recycled to the second feed stream 221 via recycle stream 236. In various embodiments, the process includes recycling at least a portion of CO of the second product stream to the first feed stream. For example, in the process of FIG. 3, at least a portion of CO of the second product stream (e.g., at least 25%, at least 50%, or at least 75%) can be recycled to the first feed stream 311 via recycle stream 336. In various embodiments, at least 25%, e.g., at least 50% of CO of the second product stream is recycled to the first feed stream or the second feed stream. In various embodiments, at least 75%, e.g., at least 90% of CO of the second product stream is recycled to the first feed stream or the second feed stream.

[00104] In many cases, both CO and H_2 of the second product stream will be recycled.

[00105] Moreover, when one or more inerts are used in the Fischer-Tropsch process step, it can be desirable to recycle these. For example, in various embodiments, the process includes recycling at least a portion of inerts of the second product stream to the second feed stream. For example, in the process of FIG. 2, at least a portion of inerts of the second product stream (e.g., at least 25%, at least 50%, or at least 75%) can be recycled to the second feed stream 221 via recycle stream 236. In various embodiments, the process includes recycling at least a portion of inerts of the second product stream to the first feed stream. For example, in the process of FIG. 3, at least a portion of inerts of the second product stream (e.g., at least 25%, at least 50%, or at least 75%) can be recycled to the first feed stream 311 via recycle stream 336. In various embodiments, at least 25%, e.g., at least 50% of inerts of the second product stream is recycled to the first feed stream or the second feed stream. In various embodiments, at least 75%, e.g., at least 90% of inerts of the second product stream is recycled to the first feed stream or the second feed stream. In various embodiments, a purge stream can be incorporated with the recycle stream to prevent uncontrolled accumulation of inerts in the recycle stream (not shown here).

[00106] Specifically, as CO_2 is the carbon source for the reverse water-gas shift process step, it can be especially desirable to recycle CO_2 to the first feed stream. Accordingly, in various embodiments, the process includes recycling at least a portion (e.g., at least 50%, at least 75%, or at least 90%) of CO_2 of the second product stream to the first feed stream. For example, in the process of FIG. 3, at least a portion of CO_2 of the second product stream (e.g., at least 50%, at least 75%, or at least 90%) can be recycled to the first feed stream 311 via recycle stream 336.

[00107] In some cases, e.g., when CO_2 is provided to the second feed stream from a CO_2 source other than the first product stream, CO_2 from the second product stream can make up most of the CO_2 of the first feed stream, e.g., at least 90%, at least 95%, or at least 98%

of the CO_2 of the first feed stream. This is shown, e.g., in FIG. 4. Here, the primary CO_2 input to the process is through stream 440, which becomes part of the second feed stream 421. CO_2 of the second product stream is included in recycle stream 442, which becomes part of first feed stream 411.

[00108] As noted above, the Fischer-Tropsch process step provides a second product stream that includes C_{5+} hydrocarbons (e.g., unsubstituted hydrocarbons like alkanes and alkenes, and/or oxygenated hydrocarbons such as alcohols). Accordingly, in various embodiments, one or more products are provided from at least a portion of C_{5+} hydrocarbons of the second product stream. The C_{5+} hydrocarbons can be used as the basis of a variety of fuels, e.g., gasoline, diesel, aviation fuel. Other products, like waxes and lubricants, can also be made. And alkenes and oxygenates can be used as feedstocks in a variety of other processes.

[00109] The person of ordinary skill in the art will use conventional post-processing techniques to convert the C_{5+} hydrocarbon-containing product to desirable products such as desirable fuels. For example, in various embodiments, the process further includes hydroprocessing at least a portion of C_{5+} hydrocarbons of the second product stream. As the person of ordinary skill in the art will appreciate, hydroprocessing is a treatment of the hydrocarbon stream with hydrogen in the presence of a suitable catalyst. A wide variety of hydroprocessing techniques are known, and the person of ordinary skill in the art will apply them here. For example, in the process 300 of FIG. 3, second product stream 322 is hydroprocessed in hydroprocessing reactor 350, to provide a hydroprocessed product stream 352.

[00110] As described above, CO_2 and H_2 are substantial inputs to the claimed processes. Advantageously, the present inventors have recognized that each of these can come from renewable or otherwise environmentally responsible sources.

[00111] CO_2 can be captured from the environment generally, or more directly from processes that form CO_2 (especially in difficult-to-abate sectors). This can make the eventual hydrocarbon product substantially carbon-neutral or of lower carbon intensity. Accordingly, in some embodiments of the disclosure as described herein, at least a part of the CO_2 of the first feed stream and/or the second feed stream is from a renewable source. In some embodiments, at least part (e.g., at least 25%, at least 50%, or at least 75%) of the CO_2 of the first feed stream and/or the second feed stream is from direct air capture. In some embodiments, at least part (e.g., at least 25%, at least 50%, or at least 75%) of the CO_2 of the first feed stream and/or the second feed stream is from a manufacturing plant such as a bioethanol plant (e.g., CO_2 produced fermentation), a steel plant, or a cement plant. Accordingly, the rWGS-Fischer Tropsch integrated processes of the disclosure as described herein can be not only carbon neutral, but in some cases a net consumer of carbon dioxide. These benefits in particular make the integrated processes highly attractive for decarbonizing transportation fuels, for both automotive and aviation sectors, since the carbon monoxide produced in the rWGS reaction can be readily utilized by well-established technologies to synthesize liquid hydrocarbon fuels by Fischer-Tropsch processes.

[00112] Similarly, H_2 can be provided from environmentally-responsible sources. In some embodiments, at least a part of the H_2 of the first feed stream and/or the second feed stream is from a renewable source. For example, in various embodiments, at least part (e.g., at least 25%, at least 50%, or at least 75%) of the H_2 of the first feed stream and/or the second feed stream can be so-called “green” hydrogen, e.g., produced from the electrolysis of water operated using renewable electricity (such as wind, solar, or hydro-electric power). In some embodiments, at least part (e.g., at least 25%, at least 50%, or at least 75%) of the H_2 of the first feed stream and/or the second feed stream may be from a so-called “blue” source, e.g., from a natural gas reforming process with carbon capture. Of course, other sources of H_2 can be used in part or in full. For example, in some embodiments, at least part (e.g., at least 25%, at least 50%, or at least 75%) of the H_2 of the first feed stream and/or the second feed stream is grey hydrogen, black hydrogen, brown hydrogen, pink hydrogen, turquoise hydrogen, yellow hydrogen, and/or white hydrogen.

[00113] The present inventors have noted that electrolysis of water is a desirable way to provide hydrogen to the claimed processes. Accordingly, in some embodiments, the process includes providing at least a portion of H_2 to the first feed stream and/or the second feed stream by electrolysis of water. In some embodiments, the electrolysis of water is performed using at least partially electricity from a renewable source, e.g., to provide so-called “green hydrogen.” However, the present inventors have noted that electricity can be generated as part of the claimed process, e.g., using heat exchange from the first or second product stream, or by burning light hydrocarbons as described above. In some embodiments, the electrolysis of water is performed using at least partially electricity generated according to the processes as described herein. For example, in the process 200 of FIG. 2, water 262 separated from the first product stream is electrolyzed in electrolyzer 260, using electricity 264 generated from steam made in the steam generation zone 232 by heat exchange from the first product stream. H_2 generated in the electrolysis is provided via stream 265 to the first feed stream. In some embodiments, at least a portion of O_2 generated in the electrolysis is provided to a partial oxidation reaction zone as described herein and as shown in the embodiment of FIG. 6.

[00114] The processes described herein can be operated in a wide variety of reactor systems. In some embodiments, the first reaction zone (i.e., in which the reverse water-gas shift process step is performed) comprises a first reactor in which a reverse water-gas shift catalyst is disposed, and the second reaction zone (i.e., in which the Fischer-Tropsch process step is performed) comprises a second reactor in which the Fischer-Tropsch catalyst is disposed. Examples of such processes are shown schematically in FIGS. 1, 2, and 4. In these examples, the process (100, 200, 400) is performed in a reactor system that includes a first reactor (110, 210, 410) in which a reverse water-gas shift catalyst (113, 213, 413) is disposed, and a second reactor (120, 220, 420) in which the Fischer-Tropsch catalyst (123, 223, 423) is disposed. The reactors used for the integrated process of the present disclosure as described herein are not particularly limited, and the person of ordinary skill in the art will be able to select an appropriate reactor.

[00115] But other embodiments are possible. For example, in some embodiments, the process is performed in a reactor system comprising first catalyst bed in which the reverse water-gas shift catalyst is disposed, and wherein the second reaction zone comprises a second catalyst bed in which the Fischer-Tropsch catalyst is disposed. In some embodiments, the first reactor bed and the second reactor bed are disposed within the same reactor. Such a configuration is shown in FIG. 3, in which the reverse water-gas shift catalyst 313 is disposed in a first catalyst bed 314, and the Fischer-Tropsch catalyst 323 is disposed in a second catalyst bed 324. Here, the catalyst beds 314 and 324 are in the same reactor, with process gases flowing between them. Such a configuration can be especially desirable when the first temperature and the second temperature are relatively close to one another.

[00116] In various embodiments, the process is performed in a reactor system comprising one or more first catalyst containers in which the reverse water-gas shift catalyst is disposed, and wherein the second reaction zone comprises one or more second catalyst containers in which the Fischer-Tropsch catalyst is disposed. These can be provided in the same reactor, such as described above with respect to catalyst beds.

[00117] As noted above, the reverse water-gas shift process step using the nickel catalysts described herein and the Fischer-Tropsch process step can be performed under similar conditions. Accordingly, in various embodiments, the reverse water-gas shift catalyst and the Fischer-Tropsch catalyst can be provided together in the same catalyst bed, e.g., mixed together. Such an embodiment is shown in FIG. 5. Here, the process 500 is performed in a reactor system that includes a reactor 505 in which the reverse water-gas shift catalyst 513 and the Fischer-Tropsch catalyst 523 are mixed together in a single catalyst bed 524. Here, first feed stream 511 and second product stream 522 can be substantially as described herein. The first product stream and the second feed stream are understood to be the mixture of process gases within the mixed catalysts.

[00118] In the embodiments particularly-described above, separate rWGS and Fischer-Tropsch catalysts are used, e.g., in separate reactors, in separate regions of the same reactor, or even comingled in the same region of a reactor.

[00119] However, the present inventors also note that there are certain commonalities between the rWGS catalysts described herein and certain Fischer-Tropsch catalysts. For example, as the person of ordrinary skill in the art would appreciate, magnesium is a common modifier used in Fischer-Tropsch catalysts, especially those based on cobalt. The present inventors also note that similar supports can be used for each.

[00120] Accordingly, in addition to the configurations described above, the present inventors contemplate the provision of a single bifunctional catalyst with both reverse water-gas shift activity and Fischer-Tropsch activity. Such a bifunctional catalyst includes both rWGS-active catalyst metal and the Fischer-Tropsch active catalyst metal in the same body. The person or ordinary skill in the art will appreciate that both the rWGS catalysts and the Fischer-Tropsch catalysts are supported catalyst, e.g., metal oxide supported catalyst. As such, in various embodiments of the present disclosure, the rWGS-active catalyst metals and Fischer-Tropsch active catalyst metals can be provided together on the same support to provide a bifunctional catalyst. For example, in some embodiments, the supports of bifunctional catalyst are provided themselves as discrete body of material, e.g., as porous particles, pellets, or shaped extrudates, with the rWGS-active catalyst metals and the FT-active catalyst metals provided thereon to provide a bifunctional catalyst. The rWGS-active catalyst metals and the FT-active catalyst metals may be homogenous distributed throughout the support or may be distributed in discrete areas throughout the support. However, in other embodiments, the bifunctional catalyst of the disclosure can itself be formed as a layer on an underlying substrate. For example, in some embodiments, the bifunctional catalyst is formed from a layer of rWGS-active catalyst metals and a layer of FT-active catalyst metals on an underlying substrate. The rWGS-active catalyst metals and the FT-active catalyst metals may be homogeneously distributed on the underlying substrate. In other embodiments, the rWGS-active catalyst metals and the FT-active catalyst metals may be in discrete areas on the underlying substrate. The underlying substrate is not particularly limited. It can be formed of, e.g., a metal or metal oxide, and can itself be provided in a number of forms, such as particles, pellets, shaped extrudates, or monoliths.

[00121] The bifunctional catalyst includes a support material, the rWGS-active catalyst metals as described herein, and the Fischer-Tropsch active catalyst metals as described herein. For example, the bifunctional catalyst includes a support that is a metal oxide support as described herein, nickel, manganese, and at least one of cobalt, iron, rhodium, and ruthenium. In some embodiments of present disclosure, the bifunctional catalyst includes a support that is a metal oxide support as described herein, nickel, manganese, and cobalt. In some embodiments of the present disclosure, the bifunctional catalyst includes a support comprising at least one of titanium oxide, zirconium oxide, cerium oxide, or aluminum oxide, nickel, manganese, and cobalt. In some embodiments, the bifunctional catalyst includes a titanium oxide support, nickel, manganese, and cobalt. For example, in some embodiments, the bifunctional catalyst includes a titanium oxide support, nickel, present in an amount in the range of 0.05 to 10 wt%, manganese, present in an amount in the range of 0.5 to 20 wt%, and cobalt, present in an amount in the range of 7-25 wt%. The ratio of rWGS-active catalyst metals to FT-active catalyst metals in the bifunctional catalyst is not particularly limited and the person of ordinary skill in the art would be able to select an appropriate ratio. For example, in some embodiments, the ratio of rWGS-active catalyst metals to FT-active catalyst metals in the bifunctional catalyst is at least 0.1:1. In various embodiments, the ratio of rWGS-active catalyst metals to FT-active catalyst metals in the bifunctional catalyst is at least 0.2:1, or 0.5, or 1:1.

[00122] Such catalysts can be used in embodiments like those described with respect to FIG. 5. The person of ordinary skill in the art will select reaction conditions that provide the appropriate balance of reverse water-gas shift activity and Fischer-Tropsch activity.

[00123] FIG. 6 is a schematic depiction of another integrated process according to the disclosure. Here, the reverse water-gas shift and Fischer-Tropsch process steps are integrated together with partial oxidation of light hydrocarbons to provide CO and H_2 to the Fischer-Tropsch process step; electrolysis to provide H_2 for the reverse water-gas shift process step and O_2 for the partial oxidation; and various recycles and optional feeds, as described throughout the present specification.

[00124] The person of ordinary skill in the art will provide the materials and perform the processes described herein based on the general disclosure above, and with reference to the Examples below.

EXAMPLES

[00125] The Examples that follow are illustrative of specific embodiments of the catalysts and processes of the disclosure, and various uses thereof. They are set forth for explanatory purposes only, and are not to be taken as limiting the scope of the disclosure.

[00126] Example 1. Modelling

[00127] The present inventors performed modelling of various equilibrium conditions of the reverse water-gas shift reaction. The predicted carbon dioxide conversion and product composition of the rWGS reaction (Equation 1) in competition with the Sabatier reaction (Equation 3) and the CO methanation reaction (Equation 4) was calculated over the temperature range of 400-800 °C, based on thermodynamic equilibrium. From the modeling, the carbon monoxide selectivity increased at temperatures greater than 600 °C, while methane selectivity decreased at higher temperatures.

[00128] From these results, it is clear that the Sabatier reaction (Equation (3)) and CO methanation (Equation (4)) side reactions are exothermic and favored at lower temperatures, while the rWGS reaction (Equation (1)) is endothermic and favored at higher temperatures. However, other carbon-producing side reactions, not accounted for in this example, can occur at high temperatures. As such, the present inventors have investigated catalysts that operate at middle to high temperatures. These catalysts are discussed in more detail below.

[00129] Example 2. Catalyst Preparation

[00130] A conventional impregnation method was used to prepare catalysts before testing their viability for reverse water-gas shift reactions. The supports used are described in Table 1.

[00131] Table 1.

Chemical	Supplier	Pore Volume
Cerium(IV) oxide	Sigma-Aldrich	0.1 mL/g
ɣ-Alumina	Saint Gobain	0.83 mL/g
Titania P-25 Aeroxide	Evonik	0.5 mL/g
Zirconia SZ 6	Saint Gobain	0.38 mL/g

[00132] To prepare the catalyst, a solution of nickel (II) nitrate hexahydrate (purity 99.9985%, VWR) and manganese acetate tetrahydrate (purity 99.9%, Fisher Chemicals) was prepared in deionized water. The solution of nickel and manganese was added to the support powder. The amount of support added is based on the amount of the water on a mass basis so that the ratio of water:support is 3:1. The slurry was then stirred at room temperature for 4 hours. Excess water was then evaporated using a stirring drybath at a temperature of 60 °C. The resulting catalyst precursor powder was then dried for 24 hours at 90 °C in a drying oven.

[00133] That catalyst precursor powder was then subjected to calcination by evenly spreading out the powder in a crucible. The crucible is placed in a calcination furnace and the temperature is increased from ambient to 120°C at a rate of 10°C per minute. The temperature was then held at 120°C for 1 hour, and then increased from 120°C to 500°C at a rate of 2°C per minute. The temperature was held at 500°C for 4 hours, and then cooled to ambient temperature. The resulting catalysts were then tested for its viability for reverse water-gas shift reactions.

[00134] Example 3. Performance of Nickel Catalysts

[00135] Catalysts prepared as explained in Example 2 were then tested for their catalytic performance for reverse water-gas shift reactions. The catalysts tested were titania supported catalysts that include nickel at 5 wt% with manganese at 0 wt% or 5 wt%. To test the catalytic performance of these catalysts, 20 μL of the catalyst diluted with SiC F100 to provide a ratio of 1:10 was loaded into a 3mm ID ceramic tube reactor, resulting in a 0.22 mL catalyst bed with a zone height of 31.1 mm. Prior to performing the rWGS reaction, the catalysts were activated at 590 °C for 5 hours in a 97% hydrogen and 3% argon atmosphere. Then, the catalysst were contacted at two different temperatures with a feed stream comprising H_2 and CO_2 at two different ratios. The total pressure was kept at 10 barg. The GHSV for trials 1 and 2 was 100,000 h^{-1} and for trials 3-6 was 120,000 h^{-1}. The catalytic performance was analyzed by detecting the gas composition of the reactor outlet feed using a multi-detector gas chromatograph. The catalytic performance of these catalysts are shown in Table 2. In Table 2, and Tables 3-8 below, the amount of nickel and/or manganese present in the catalyst are shown in parenthesis. These numbers are in weight percent and based on the total weight of the catalyst. For example, CeO_2Ni(5)Mn(5) corresponds to a catalyst with 5 wt% Ni, 5 wt% Mn, and 90 wt% CeO_2.

[00136] Table 2.

Trial No.	Catalyst	H_2:CO_2	Temperature (°C)	CH_4 STY (kg $l^{-1}h^{-1}$)	CO Selectivity (%)	CO_2 conversion (%)
1	TiO_2Ni(5)	3:1	750	4.0	62.4	66.7
2	TiO_2Ni(5)Mn(5)	3:1	750	0.8	91.7	62.5
3	TiO_2Ni(5)	2:1	750	3.6	75.9	57.4
4	TiO_2Ni(5)Mn(5)	2:1	750	0.5	95.5	45.1
5	TiO_2Ni(5)	2:1	600	1.9	82.2	40.8
6	TiO_2Ni(5)Mn(5)	2:1	600	0.4	94.8	26.2

[00137] The addition of 5 wt% manganese to the 5 wt% nickel supported on titania resulted in an increase in CO selectivity, albeit with a loss in catalyst activity, as shown by the decrease in CO_2 conversion.

[00138] Catalysts with nickel present in 0.5 wt%, 1 wt%, or 5 wt%, and manganese present in 5 wt% on either titania or ceria supports were tested at 600°C, a H_2:CO_2 ratio of 2:1, a pressure of 30 barg, and a GHSV of 1,200,000 h^{-1}. These results are reported in Table 3.

[00139] Table 3.

Trial No.	Catalyst	CH_4 STY (kg $l^{-1}h^{-1}$)	CO Selectivity (%)	CO_2 conversion (%)
7	TiO_2Ni(0.5)Mn(5)	6.4	88.5	21.6
8	TiO_2Ni(1)Mn(5)	11	84.6	28.1
9	TiO_2Ni(5)Mn(5)	32	71.1	42.9
10	CeO_2Ni(5)Mn(5)	22	80.4	42.5

[00140] The results of Table 3 indicate that while increasing the nickel content does not improve the selectivity of CO, the CO_2 conversion is improved.

[00141] Example 4. Impact of Support on Catalyst Performance

[00142] The impact of the support was also investigated by evaluating nickel and manganese supported catalyst on a variety of catalytic supports (ceria, alumina, titania, and zirconia). The catalysts contained 5 wt% nickel and 5 wt% manganese. These catalysts were prepared by the method as described in Example 2 and the reactor setup and catalyst activation was used as described in Example 3. These catalysts were contacted at two different temperatures at a pressure of 10 barg, a GHSV of 800,000 h^{-1}, and two different H_2:CO_2 ratios. The catalytic performance was analyzed by detecting the gas composition of the reactor outlet feed using a multi-detector gas chromatograph. The results are shown in Table 4.

[00143] Table 4.

Trial No.	Catalyst	Temperature (°C)	H_2:CO_2	CO Selectivity (%)	CO_2 conversion (%)
11	Al_2O_3Ni(5)Mn(5)	760	1:1	93.7	42.5
12	CeO_2Ni(5)Mn(5)	760	1:1	95.8	43.0
13	ZrO_2Ni(5)Mn(5)	760	1:1	96.4	41.8
14	TiO_2Ni(5)Mn(5)	760	1:1	97.6	37.8
15	Al_2O_3Ni(5)Mn(5)	700	2:1	79.4	53.8
16	CeO_2Ni(5)Mn(5)	700	2:1	87.8	53.7
17	ZrO_2Ni(5)Mn(5)	700	2:1	87.6	51.6
18	TiO_2Ni(5)Mn(5)	700	2:1	94.9	46.6

[00144] Additionally, these catalysts were contacted at temperature of 700 °C with a feed stream having a H_2 to CO_2 ratio of 2:1, at a pressure of 20 barg, and a GHSV of 800,000 h^{-1}. The results are shown in Table 5.

[00145] Table 5.

Trial No.	Catalyst	CO Selectivity (%)	CO_2 conversion (%)
19	Al_2O_3Ni(5)Mn(5)	55.6	51.0
20	CeO_2Ni(5)Mn(5)	75.4	53.5
21	ZrO_2Ni(5)Mn(5)	67.9	52.4
22	TiO_2Ni(5)Mn(5)	84.8	53.5

[00146] Tables 4 and 5 shows that the performance of nickel manganese supported catalysts are reproduced with a variety of support materials with greater CO selectivity observed at 10 barg and a H_2:CO_2 ratio of 1:1. Methane selectivity increased as the temperature was lowered from 760 °C to 700 °C. A further increase in methane selectivity was observed when the reaction pressure was doubled to 20 barg at 700 °C. Of all supports tested in this work, titania supported nickel manganese catalyst showed the highest CO selectivity at conditions tested, even though it showed the lowest activity out of all supports.

[00147] The high selectivity of nickel manganese supported catalysts make them desirable as candidates for middle to high temperature reverse water-gas shift. The high yield and selectivity to CO demonstrated in the trials above provide an effluent stream suitable for integration with other processes.

[00148] Example 6. Impact of Catalyst Activation on Catalyst Performance

[00149] Catalysts prepared as explained in Example 2 were evaluated for the impact of catalyst activation on catalyst performance. The catalysts used in the study were titania supported catalysts with 5 wt% nickel and 5 wt% manganese, alumina supported catalysts with 5 wt% nickel and 5 wt% manganese, and ceria supported catalysts with 5 wt% nickel and 5 wt% manganese. These supported catalysts were activated in a hydrogen atmosphere at three different temperature (400 °C, 590 °C, and 760 °C) and then used in a rWGS process. To a 3mm ID ceramic tube reactor, 20 µL of the catalyst diluted with SiC F100 to provide a ratio of 1:10 was loaded, resulting in a 0.22 mL catalyst bed with a zone height of 31.1 mm. Activation of the catalyst was carried out using pure H_2 at a GHSV of 200,000 h^{-1}. The reactor pressure was set to 10 barg, followed by heating the reactor to the desired activation temperature at a rate of 1K/min and holding at that temperature for 5 hours. After activation, the reactors were cooled to the temperature for the rWGS process. Four rWGS reaction temperatures, 400 °C, 500 °C, 600 °C, and 700 °C, were evaluated. As the rWGS reaction temperature was reached, the feed stream was introduced followed by setting the reaction pressure. The activated catalysts were contacted with a feed stream of H_2 and CO_2, present at a mole ratio of 2:1, at a pressure of 30 barg and a GHSV of 1,200,000 h^{-1}. The catalytic performance was analyzed by detecting the gas composition of the reactor outlet feed using a multi-detector gas chromatograph. The results are shown in Tables 6, 7 and 8.

[00150] Table 6.

Trial No.	Catalyst	Activation Temperature (°C)	Reaction Temperature (°C)	CO Selectivity (%)	CO_2 Conversion (%)
23	TiO_2Ni(5)Mn(5)	400	400	16.3	10.4
24	TiO_2Ni(5)Mn(5)	400	500	75.2	8.6
25	TiO_2Ni(5)Mn(5)	400	600	65.5	43.6
26	TiO_2Ni(5)Mn(5)	400	700	63.3	52.4
27	TiO_2Ni(5)Mn(5)	590	400	43.7	3.8
28	TiO_2Ni(5)Mn(5)	590	500	74.4	11.6
29	TiO_2Ni(5)Mn(5)	590	600	68.9	45.3
30	TiO_2Ni(5)Mn(5)	590	700	68.3	53.1
31	TiO_2Ni(5)Mn(5)	760	400	78.5	2.6
32	TiO_2Ni(5)Mn(5)	760	500	79.3	13.8
33	TiO_2Ni(5)Mn(5)	760	600	65.7	46.1
34	TiO_2Ni(5)Mn(5)	760	700	68.6	53.7

[00151] Table 7.

Trial No.	Catalyst	Activation Temperature (°C)	Reaction Temperature (°C)	CO Selectivity (%)	CO_2 Conversion (%)
35	Al_2O_3Ni(5)Mn(5)	400	400	30.8	7.7
36	Al_2O_3Ni(5)Mn(5)	400	500	66.1	11.2
37	Al_2O_3Ni(5)Mn(5)	400	600	42.6	47.3
38	Al_2O_3Ni(5)Mn(5)	400	700	48.3	50
39	Al_2O_3Ni(5)Mn(5)	590	400	34.2	7.8
40	Al_2O_3Ni(5)Mn(5)	590	500	63.6	12.3
41	Al_2O_3Ni(5)Mn(5)	590	600	44.6	46.5
42	Al_2O_3Ni(5)Mn(5)	590	700	46.4	50
43	Al_2O_3Ni(5)Mn(5)	760	400	40.7	7
44	Al_2O_3Ni(5)Mn(5)	760	500	59.5	13.9
45	Al_2O_3Ni(5)Mn(5)	760	600	40.6	46.6
46	Al_2O_3Ni(5)Mn(5)	760	700	50.2	50.6

[00152] Table 8.

Trial No.	Catalyst	Activation Temperature (°C)	Reaction Temperature (°C)	CO Selectivity (%)	CO_2 Conversion (%)
47	CeO_2Ni(5)Mn(5)	400	400	17.5	17.4
48	CeO_2Ni(5)Mn(5)	400	500	61.6	22.9
49	CeO_2Ni(5)Mn(5)	400	600	74.2	44
50	CeO_2Ni(5)Mn(5)	400	700	51.8	50.6
51	CeO_2Ni(5)Mn(5)	590	400	30.2	9.4
52	CeO_2Ni(5)Mn(5)	590	500	72.1	18.5
53	CeO_2Ni(5)Mn(5)	590	600	76.1	42.9
54	CeO_2Ni(5)Mn(5)	590	700	52	50.9
55	CeO_2Ni(5)Mn(5)	760	400	52.3	3.8
56	CeO_2Ni(5)Mn(5)	760	500	82.3	12.6
57	CeO_2Ni(5)Mn(5)	760	600	78.5	38.6
58	CeO_2Ni(5)Mn(5)	760	700	73	53.2

[00153] For the titania supported nickel and manganese catalysts, alumina supported nickel and manganese catalysts, and the ceria supported nickel and manganese catalysts, the CO_2 conversion increases as the reaction temperature increases and is consistent across all activation temperature.

[00154] The results of Tables 6-8 show that the activation temperature, reaction temperature, and support type influence the CO selectivity. The CO selectivity of the titania supported nickel and manganese catalysts increases with higher reaction temperatures for activation at both 400 °C and 560 °C. However, when activated at 760 °C, the CO selectivity generally decreases as reaction temperature increases. For the alumina supported nickel and manganese catalysts, the CO selectivity peaks at a reaction temperature of 500 °C for all activation temperatures, with a higher activation temperature having a higher CO selectivity over all reaction temperatures measured. Similarly, for the ceria supported nickel and manganese catalysts, the CO selectivity peaks at reaction temperatures between 500-600 °C for all activation temperatures, with a higher activation temperature having a higher CO selectivity over all reaction temperatures measured. Overall, the results of Tables 6-8 show that the activation temperature is another variable to adjust the resulting product stream.

[00155] Additional aspects of the disclosure are provided by the following enumerated embodiments, which may be combined in any number and in any combination that is not logically or technically inconsistent.

Embodiment 1. A process for performing an integrated Fischer-Tropsch process, the process comprising:

providing a first feed stream comprising H_2 and CO_2;

contacting at a first temperature in the range of 500-900 °C and at a first pressure a reverse water-gas shift catalyst with the first feed stream to perform a reverse water-gas shift reaction to provide a first product stream comprising CO and H_2, the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first feed stream;

contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream comprising H_2 and at least a portion of CO of the first product stream to provide a second product stream comprising C_{5+} hydrocarbons,

wherein the reverse water-gas shift catalyst is a supported reverse water-gas shift catalyst comprising:

a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support comprising a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide;

nickel, present in an amount in the range of 0.05 to 10 wt% of the catalyst, based on the total weight of the catalyst; and

manganese, present in an amount in the range of 0.5 to 20 wt% of the catalyst, based on the total weight of the catalyst.

Embodiment 2. The process of embodiment 1, wherein the support makes up at least 70 wt% (e.g., at least 75 wt%, or 80 wt%, or 85 wt%, or 90 wt%) of the catalyst, on an oxide basis.

Embodiment 3. The process of embodiment 1 or embodiment 2, wherein the support is a cerium oxide support.

Embodiment 4. The process of embodiment 3, wherein at least a surface layer of the cerium oxide support comprises at least 60 wt% cerium oxide, e.g., at least 70 wt% cerium oxide or at least 80 wt% cerium oxide, on an oxide basis.

Embodiment 5. The process of embodiment 3, wherein at least a surface layer of the cerium oxide support comprises at least 90 wt% cerium oxide, e.g., at least 95 wt% cerium oxide, or at least 98 wt% cerium oxide, on an oxide basis.

Embodiment 6. The process of any of embodiments 3-5, wherein the cerium oxide support comprises at least 50 wt% cerium oxide, e.g., at least 60 wt% cerium oxide, or at least 70 wt% cerium oxide, or at least 80 wt% cerium oxide, on an oxide basis.

Embodiment 7. The process of any of embodiments 3-5, wherein the cerium oxide support comprises at least 90 wt% cerium oxide, e.g., at least 95 wt% cerium oxide, or at least 98 wt% cerium oxide, on an oxide basis.

Embodiment 8. The process of embodiment 1 or embodiment 2, wherein the support is a titanium oxide support.

Embodiment 9. The process of embodiment 8, wherein at least a surface layer of the titanium oxide support comprises at least 60 wt% titanium oxide, e.g., at least 70 wt% titanium oxide, or at least 80 wt% titanium oxide, on an oxide basis.

Embodiment 10. The process of embodiment 8, wherein at least a surface layer of the titanium oxide support comprises at least 90 wt% titanium oxide, e.g., at least 95 wt% titanium oxide, or at least 98 wt% titanium oxide.

Embodiment 11. The process of any of embodiments 8-10, wherein the titanium oxide support comprises at least 50 wt% titanium oxide, e.g., at least 60 wt% titanium oxide, or at least 70 wt% titanium oxide, or at least 80 wt% titanium oxide, on an oxide basis.

Embodiment 12. The process of any of embodiments 8-10, wherein the titanium oxide support comprises at least 90 wt% titanium oxide, e.g., at least 95 wt% titanium oxide, or at least 98 wt% titanium oxide, on an oxide basis.

Embodiment 13. The process of embodiment 1 or embodiment 2, wherein the support is an aluminum oxide support.

Embodiment 14. The process of embodiment 13, wherein at least a surface layer of the aluminum oxide support comprises at least 60 wt% aluminum oxide, e.g., at least 70 wt% aluminum oxide or at least 80 wt% aluminum oxide, on an oxide basis.

Embodiment 15. The process of embodiment 13, wherein at least a surface layer of the aluminum oxide support comprises at least 90 wt% aluminum oxide, e.g., at least 95 wt% aluminum oxide, or at least 98 wt% aluminum oxide, on an oxide basis.

Embodiment 16. The process of any of embodiments 13-15, wherein the aluminum oxide support comprises at least 50 wt% aluminum oxide, e.g., at least 60 wt% aluminum oxide, or at least 70 wt% aluminum oxide, or at least 80 wt% aluminum oxide, on an oxide basis.

Embodiment 17. The process of any of embodiments 13-15, wherein the aluminum oxide support comprises at least 90 wt% aluminum oxide, e.g., at least 95 wt% aluminum oxide, or at least 98 wt% aluminum oxide, on an oxide basis.

Embodiment 18. The process of embodiment 1 or embodiment 2, wherein the support is a zirconium oxide support.

Embodiment 19. The process of embodiment 18, wherein at least a surface layer of the zirconium oxide support comprises at least 60 wt% zirconium oxide, e.g., at least 70 wt% zirconium oxide or at least 80 wt% zirconium oxide, on an oxide basis.

Embodiment 20. The process of embodiment 18, wherein at least a surface layer of the zirconium oxide support comprises at least 90 wt% zirconium oxide, e.g., at least 95 wt% zirconium oxide, or at least 98 wt% zirconium oxide, on an oxide basis.

Embodiment 21. The process of any of embodiments 18-20, wherein the zirconium oxide support comprises at least 50 wt% zirconium oxide, e.g., at least 60 wt% zirconium oxide, or at least 70 wt% zirconium oxide, or at least 80 wt% zirconium oxide, on an oxide basis.

Embodiment 22. The process of any of embodiments 18-20, wherein the zirconium oxide support comprises at least 90 wt% zirconium oxide, e.g., at least 95 wt% zirconium oxide, or at least 98 wt% zirconium oxide, on an oxide basis.

Embodiment 23. The process of embodiment 1 or embodiment 2, wherein the support is a mixed oxide support having at least a surface layer comprising at least 50 wt% of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide, on an oxide basis.

Embodiment 24. The process of any of embodiments 1-23, wherein the support does not include additional metals in a total amount of additional metals in excess of 2 wt%, e.g., in excess of 1 wt% or in excess of 0.5 wt%, on an oxide basis.

Embodiment 25. The process of any of embodiments 1-23, wherein the support includes at least one additional metal.

Embodiment 26. The process of embodiment 25, wherein the total amount of the at least one additional metal is in the range of 0.5-20 wt%, e.g., 1-20 wt%, or 2-20 wt%, or 0.5-15 wt%, or 1-15 wt%, or 2-15 wt%, or 0.5-10 wt%, or 1-10 wt%, or 2-10 wt%, or 0.5-5 wt%, or 1-5 wt%, on an oxide basis.

Embodiment 27. The process of any of embodiments 1-26, wherein the support has a pore volume of at least 0.05 mL/g.

Embodiment 28. The process of any of embodiments 1-27, wherein the support has a pore volume of at most 1.5 mL/g.

Embodiment 29. The process of any of embodiments 1-28, wherein the support has a pore volume in the range of 0.05-1.5 mL/g.

Embodiment 30. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in the range of 0.1 to 10 wt%, e.g., in the range of 0.5 to 10 wt%, or 1 to 10 wt%, or 2 to 10 wt%, or 5 to 10 wt%, based on the total weight of the catalyst.

Embodiment 31. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in the range of 0.05 to 7 wt%, e.g., in the range of 0.1 to 7 wt%, or 0.5 to 7 wt%, or 1 to 7 wt%, or 2 to 7 wt%, based on the total weight of the catalyst.

Embodiment 32. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in the range of 0.05 to 5 wt%, e.g., in the range of 0.1 to 5 wt%, or 0.5 to 5 wt%, or 1 to 5 wt%, or 2 to 5 wt%, based on the total weight of the catalyst.

Embodiment 33. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in a range of 0.05 to 2 wt%, e.g., in the range of 0.1 to 2 wt%, or 0.3 to 2 wt%, or 0.5 to 2 wt%, or 1 to 2 wt%, based on the total weight of the catalyst.

Embodiment 34. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in a range of 0.05 to 1.5 wt%, e.g., in the range of 0.1 to 1.5 wt%, or 0.3 to 1.5 wt%, or 0.5 to 1.5 wt%, based on the total weight of the catalyst.

Embodiment 35. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in the range of 0.05 to 1 wt%, e.g., in the range of 0.1 to 1 wt%, or 0.3 to 1 wt%, or 0.5 to 1 wt%, based on the total weight of the catalyst.

Embodiment 36. The process of any of embodiments 1-29, wherein nickel is present in the catalyst in an amount in the range of 0.05 to 0.8 wt%, e.g., in the range of 0.1 to 0.8 wt%, or 0.3 to 0.8 wt%, or 0.5 to 0.8 wt%, based on the total weight of the catalyst.

Embodiment 37. The process of any of embodiments 1-36, wherein manganese is present in the catalyst in an amount in the range of 0.5 to 15 wt%, e.g., in the range of 0.5 to 12 wt% or 0.5 to 10 wt%, based on the total weight of the catalyst.

Embodiment 38. The process of any of embodiments 1-36, wherein manganese is present in the catalyst in an amount in the range of 1 to 20 wt%, e.g., in the range of 1 to15 wt%, or 1 to 12 wt%, or 1 to 10 wt%, based on the total weight of the catalyst.

Embodiment 39. The process of any of embodiments 1-36, wherein manganese is present in the catalyst in an amount in the range of 2 to 20 wt%, e.g., in the range of 2 to15 wt%, or 2 to 12 wt%, or 2 to 10 wt%, based on the total weight of the catalyst.

Embodiment 40. The process of any of embodiments 1-36, wherein manganese is present in the catalyst in an amount in the range of 4 to 20 wt%, e.g., in the range of 4 to 15 wt%, or 4 to 12 wt%, or 4 to 10 wt%, based on the total weight of the catalyst.

Embodiment 41. The process of any of embodiments 1-40, wherein a weight ratio of nickel to manganese is at least 0.05:1, e.g., at least 0.1:1.

Embodiment 42. The process of any of embodiments 1-41, wherein a weight ratio of nickel to manganese is at most 5:1, e.g., at most 2:1, or 1:1, or 0.5:1.

Embodiment 43. The process of any of embodiments 1-42, wherein a ratio of nickel to manganese is in the range of 0.05:1 to 5:1 (e.g., in the range of 0.05:1 to 2:1, or 0.05:1 to 1:1, or 0.05:1 to 0.5:1, or 0.05:1 to 0.3:1, or 0.07:1 to 5:1, or 0.07:1 to 2:1, or 0.07:1 to 1:1, or 0.07:1 to 0.5:1, or 0.07:1 to 0.3:1, or 0.1:1 to 5:1, or 0.1:1 to 2:1, or 0.1:1 to 1:1, or 0.1:1 to 0.5:1, or 0.1:1 to 0.3:1).

Embodiment 44. The process of any of embodiments 1-43, wherein the total amount of cerium, titanium, aluminum, zirconium, manganese, and nickel in the catalyst is at least 90 wt%, e.g., at least 95 wt% or at least 98 wt% of the catalyst, on a metallic basis.

Embodiment 45. The process of any of embodiments 1-44, wherein the molar ratio of H_2 to CO_2 in the first feed stream is at least 0.1:1, e.g., at least 0.5:1.

Embodiment 46. The process of any of embodiments 1-44, wherein the molar ratio of H_2 to CO_2 in the first feed stream is at least 0.9:1, e.g., at least 1:1 or at least 1.5:1.

Embodiment 47. The process of any of embodiments 1-44, wherein the molar ratio of H_2 to CO_2 in the first feed stream is at least 2:1, e.g., at least 2.5:1.

Embodiment 48. The process of any of embodiments 1-47, wherein the molar ratio of H_2 to CO_2 in the first feed stream is no more than 100:1, e.g., no more than 75:1, or 50:1.

Embodiment 49. The process of any of embodiments 1-47, wherein the molar ratio of H_2 to CO_2 in the first feed stream is no more than 20:1, e.g., no more than 15:1, or 10:1.

Embodiment 50. The process of any of embodiments 1-49, wherein the molar ratio of H_2 to CO_2 in the first feed stream is in the range of 0.5:1 to 10:1.

Embodiment 51. The process according to any of embodiments 1-50, wherein the first feed stream further comprises CO.

Embodiment 52. The process according to any of embodiments 1-51 wherein the first feed stream further comprises one or more inert gases (e.g., nitrogen and/or methane).

Embodiment 53. The process of any of embodiments 1-52, wherein the reverse water-gas shift reaction has a CO selectivity of at least 50%, e.g., of at least 60%, or 70%, or 80%, or 90%.

Embodiment 54. The process of any of embodiments 1-52, wherein the reverse water-gas shift reaction has a CO selectivity of in the range of 50-99 w% (e.g., in the range of 50-90 wt%, or 50-80 wt%, or 50-70 wt%, or 50-60 wt%, or 60-99 wt%, or 60-90 wt%, or 60-80 wt%, or 60-70 wt%, or 70-99 wt%, or 70-90 wt%, or 70-80 wt%).

Embodiment 55. The process of any of embodiments 1-54, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 40%, e.g., no more than 35%, or 30%, or 25% or 20%.

Embodiment 56. The process of any of embodiments 1-54, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 10%, e.g., no more than 8%.

Embodiment 57. The process of any of embodiments 1-54, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 5%, e.g., no more than 4%.

Embodiment 58. The process of any of embodiments 1-54, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 2%, e.g., no more than 1%.

Embodiment 59. The process of any of embodiments 1-54, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 0.5%, e.g., no more than 0.2%.

Embodiment 60. The process of any of embodiments 1-59, wherein the reverse water-gas shift reaction has a CO_2 conversion of at least 5%, e.g., at least 10%, or 20%.

Embodiment 61. The process of any of embodiments 1-59, wherein the reverse water-gas shift reaction has a CO_2 conversion of at least 30%, e.g., at least 40%.

Embodiment 62. The process of any of embodiments 1-61, wherein the reverse water-gas shift reaction has a CO_2 conversion of no more than 80%, e.g., no more than 70%.

Embodiment 63. The process of any of embodiments 1-61, wherein the reverse water-gas shift reaction has a CO_2 conversion of no more than 65%, e.g., no more than 60%.

Embodiment 64. The process of any of embodiments 1-63, conducted at a first temperature in the range of 500-850 °C, e.g., in the range of 500-800 °C, or 500-750 °C , or 500-700 °C, or 500-650 °C, or 500-600 °C.

Embodiment 65. The process of any of embodiments 1-63, conducted at a first temperature in the range of 550-900 °C, e.g., in the range of 550-850 °C, or 550-800 °C, or 550-750°C, or 550-700 °C, or 550-650 °C, or 550-600 °C.

Embodiment 66. The process of any of embodiments 1-63, conducted at a first temperature in the range of 600-900 °C, e.g., in the range of 600-850 °C, or 600-800 °C, or 600-750°C, or 600-700 °C, or 600-650 °C.

Embodiment 67. The process of any of embodiments 1-63, conducted at a first temperature in the range of 650-900 °C, e.g., in the range of 650-850 °C, or 650-800 °C, or 650-750°C, or 650-700 °C.

Embodiment 68. The process of any of embodiments 1-63, conducted at a first temperature in the range of 700-900 °C, e.g., in the range of 700-850 °C, or 700-800 °C, or 700-750°C.

Embodiment 69. The process of any of embodiments 1-68, wherein the reverse water-gas shift reaction is conducted at a pressure in the range of 1 to 100 barg (e.g., in the range of 1 to 70 barg, or 1 to 50 barg, or 1 to 40 barg, or 1 to 35 barg, or 5 to 80 barg, or 5 to 50 barg, or 5 to 40 barg, or 5 to 35 barg, or 10 to 70 barg, 10 to 50 barg, or 10 to 40 barg, or 10 to 35 barg, or 20 to 70 barg, 20 to 50 barg, or 20 to 40 barg, or 20 to 35 barg, or 25 to 70 barg, 25 to 50 barg, or 25 to 40 barg, or 25 to 35 barg).

Embodiment 70. The process of any of embodiments 1-69, wherein the reverse water-gas shift reaction is conducted at a GHSV in the range of 1,000 to 2,000,000 h^{-1} (e.g., in the range of 1,000 to 1,200,000 h^{-1}, or 1,000 to 500,000 h^{-1}, or 1,000 to 100,000 h^{-1}, or 5,000 to 1,200,000 h^{-1}, or 5,000 to 500,000 h^{-1}, or 5,000 to 100,000 h^{-1}, or 10,000 to 1,200,000 h^{-1}, or 10,000 to 500,000 h^{-1}, or 10,000 to 100,000 h^{-1}).

Embodiment 71. The process of any of embodiments 1-70, wherein the process comprises activating the reverse water-gas shift catalyst, e.g., prior to contacting the reverse water-gas shift catalyst with the first feed stream.

Embodiment 72. The process of embodiment 71, wherein activating the rWGS catalyst comprises contacting the rWGS catalyst with a reducing stream comprising a reductive gas (e.g., hydrogen).

Embodiment 73. The process of embodiment 71 or embodiment 72, wherein the reducing stream comprises hydrogen in an amount of at least 25 mol% (e.g., at least 50 mol%, or 75 mol%, or 90 mol%).

Embodiment 74. The process of any of embodiments 71-73, wherein activating the rWGS catalyst is conducted at a temperature in the range of 200 °C to 800 °C. (e.g., in the range of 250 °C to 800 °C, or 300 °C to 800 °C, or 200 °C to 700 °C, or 250 °C to 700 °C, or 300 °C to 700 °C).

Embodiment 75. The process of any of embodiments 71-74, wherein activating the rWGS catalyst provides a catalyst that is at least 10% reduced (e.g., at least 25%, or 50%).

Embodiment 76. The process of any of embodiments 1-75, wherein the first product stream comprises no more than 95 mol% CO_2 (e.g., no more than 90 mol% CO_2).

Embodiment 77. The process of any of embodiments 1-75, wherein the first product stream comprises no more than 85 mol% CO_2 (e.g., no more than 80 mol% CO_2).

Embodiment 78. The process of any of embodiments 1-75, wherein the first product stream comprises no more than 75 mol% CO_2 (e.g., no more than 70 mol% CO_2).

Embodiment 79. The process of any of embodiments 1-75, wherein the first product stream comprises in the range of 5-95 mol% CO_2, e.g., 5-90 mol%, or 5-85 mol%, or 5-80 mol%, or 5-75 mol%, or 5-70 mol%, or 10-95 mol%, or 10-90 mol%, or 10-85 mol%, or 10-80 mol%, or 10-75 mol%, or 10-70 mol%, or 20-95 mol%, or 20-90 mol%, or 20-85 mol%, or 20-80 mol%, or 20-75 mol%, or 20-70 mol%, or 30-95 mol%, or 30-90 mol%, or 30-85 mol%, or 30-80 mol%, or 30-75 mol%, or 30-70 mol% CO_2.

Embodiment 80. The process of any of embodiments 1-79, wherein the first product stream comprises no more than 40 mol% methane, e.g., no more than 35 mol%, or 30 mol%, or 25 mol%, or 20 mol%, or 15 mol%, or 10 mol% methane.

Embodiment 81. The process of any of embodiments 1-79, wherein the first product stream comprises no more than 10 mol% methane, e.g., no more than 5 mol% or 1 mol%, or 0.5 mol%, or 0.1 mol% methane.

Embodiment 82. The process of any of embodiments 1-81, wherein a ratio of H_2:CO in the first product stream is up to 100:1, e.g., up to 50:1, or up to 25:1, or up to 10:1.

Embodiment 83. The process of any of embodiments 1-81, wherein a ratio of H_2:CO in the first product stream is in the range of 0.1:1 to 100:1 (e.g., in the range of 0.1:1 to 50:1, or 0.1:1 to 25:1, or 0.1:1 to 10:1, or 0.1:1 to 5:1, or 1:1 to 100:1, or 1:1 to 50:1, or 1:1 to 25:1, or 1:1 to 10:1, or 1:1 to 5:1).

Embodiment 84. The process of any of embodiments 1-83, wherein the process further comprises separating the first product stream to recycle at least a portion of one or more components of the first product stream to the first feed stream.

Embodiment 85. The process of any of embodiments 1-84, wherein the process further comprises separating the first product stream to recycle at least a portion (e.g., at least 5 mol%, at least 10 mol%, at least 25 mol%, at least 50 mol%, at least 75 mol%, or at least 90 mol%) of CO_2 of the first product stream to the first feed stream.

Embodiment 86. The process of any of embodiments 1-85, wherein the process further comprises separating the first product stream to recycle at least a portion of H_2 (e.g., at least 5 mol%, at leat10 mol%, at least 25 mol%, at least 50 mol%, at least 75 mol%, or at least 90 mol%) to the first feed stream.

Embodiment 87. The process of any of embodiments 1-86, wherein the process further comprises separating at least a portion of H_2 and/or CO from the first product stream and contacting it with the Fischer-Tropsch catalyst to activate the Fischer-Tropsch catalyst.

Embodiment 88. The process of any of embodiments 1-87, wherein the process further comprises removing at least a portion (e.g., at least 25%, at least 50%, or at least 75%) of water from the first product stream.

Embodiment 89. The process according to any of embodiments 1-88, wherein the first product stream comprises one or more light hydrocarbons (e.g., methane, ethane, propane).

Embodiment 90. The process according to embodiment 89, further comprising separating at least a portion of the one or more light hydrocarbons from the first product stream to provide a light hydrocarbon stream.

Embodiment 91. The process of any of embodiments 1-90, wherein the process further comprises exchanging heat between at least a portion of the first product stream and at least a portion of the first feed stream, thereby cooling at least a portion of the first product stream and heating at least a portion of the first feed stream.

Embodiment 92. The process of any of embodiments 1-91, wherein the process further comprises exchanging heat between at least a portion of the first product stream and a steam generation zone, thereby cooling at least a portion of the first product stream and providing heat to the steam generation zone.

Embodiment 93. The process of embodiment 92, further comprising generating steam from the heat provided to the steam generation zone, and generating electricity from the steam.

Embodiment 94. The process of embodiment 92 or 93, wherein steam is used to heat the first feed stream and/or the second feed stream.

Embodiment 95. The process of any of embodiments 1-94, wherein at least 25% of the CO of the first product stream, e.g., at least 50% of the CO, at least 75% of the CO, or at least 90% of the CO of the first product stream is included in the second feed stream.

Embodiment 96. The process of any of embodiments 1-95, wherein CO is provided to the second feed stream from a CO source other than the first product stream.

Embodiment 97. The process of any of embodiments 1-96, wherein the first product stream includes H_2, and wherein the second feed stream includes at least a portion of the H_2 of the first product stream.

Embodiment 98. The process of any of embodiments 1-97, wherein at least 25% of the H_2 of the first product stream, e.g., at least 50% of the H_2, at least 75% of the H_2, or at least 90% of the H_2 of the first product stream is included in the second feed stream.

Embodiment 99. The process of any of embodiments 1-98, wherein H_2 is provided to the second feed stream from a hydrogen source other than the first product stream.

Embodiment 100. The process of any of embodiments 1-99, wherein the second feed stream includes at least a portion of CO_2 of the first product stream.

Embodiment 101. The process of any of embodiments 1-100, wherein at least 10% of the CO_2 of the first product stream, e.g., at least 25% of the CO_2, at least 50% of the CO_2, at least 75% of the CO_2, or at least 90% of the CO_2 of the first product stream is included in the second feed stream.

Embodiment 102. The process of any of embodiments 1-100, wherein the second feed stream does not include a substantial amount of CO_2 of the first product stream.

Embodiment 103. The process of any of embodiments 1-102, wherein the portion of the first product stream that is included in the second feed stream has a H_2:CO ratio in the range of 0.5:1 to 10:1, e.g., in the range of 1:1 to 3:1.

Embodiment 104. The process of any of embodiments 1-103, wherein the portion of the first product stream that is included in the second feed stream has a water content of no more than 10 mol%, e.g., or no more than 2 mol%, or no more than 0.5 mol%.

Embodiment 105. The process of any of embodiments 1-104, wherein the portion of the first product stream that is included in the second feed stream has a CO_2 content in the range of 10-95 mol% CO_2, e.g., 10-90 mol%, or 10-85 mol%, or 10-80 mol%, or 10-75 mol%, or 10-70 mol%, or 20-95 mol%, or 20-90 mol%, or 20-85 mol%, or 20-80 mol%, or 20-75 mol%, or 20-70 mol%, or 30-95 mol%, or 30-90 mol%, or 30-85 mol%, or 30-80 mol%, or 30-75 mol%, or 30-70 mol% CO_2.

Embodiment 106. The process of any of embodiments 1-105, wherein the second feed stream has a H_2:CO ratio in the range of 0.5:1 to 6:1.

Embodiment 107. The process of any of embodiments 1-105, wherein the second feed stream has a H_2:CO ratio in the range of 1:1 to 3:1, e.g., 1:1 to 2.5:1.

Embodiment 108. The process of any of embodiments 1-105, wherein the second feed stream has a H_2:CO ratio of at least 1.4:1, e.g., in the range of 1.4:1 to 3:1, or 1.4:1 to 2.5:1.

Embodiment 109. The process of any of embodiments 1-108, wherein the second feed stream includes up to 80% of one or more inerts, e.g., up to 70 mol%, up to 60 mol%, or up to 50 mol%, or 15-70 mol%, or 30-70 mol%, or 15-60 mol%, or 30-60 mol%, or 15-50 mol%, or 30-50 mol%.

Embodiment 110. The process of any of embodiments 1-108, wherein the second feed stream includes up to 80% of one or more inerts selected from CO_2, methane and nitrogen, e.g., up to 70 mol%, up to 60 mol%, or up to 50 mol%, or 15-70 mol%, or 30-70 mol%, or 15-60 mol%, or 30-60 mol%, or 15-50 mol%, or 30-50 mol%.

Embodiment 111. The process of any of embodiments 1-110, wherein the second feed stream includes up to 80% of CO_2, e.g., up to 70 mol%, up to 60 mol%, or up to 50 mol%, or 15-70 mol%, or 30-70 mol%, or 15-60 mol%, or 30-60 mol%, or 15-50 mol%, or 30-50 mol%.

Embodiment 112. The process of any of embodiments 1-111, wherein the second feed stream has a water content of no more than 10 mol%, e.g., or no more than 2 mol%, or no more than 0.5 mol%.

Embodiment 113. The process of any of embodiments 1-112, wherein the Fischer-Tropsch catalyst comprises cobalt, iron, rhodium, ruthenium, or a combination thereof.

Embodiment 114. The process of any of embodiments 1-112, wherein the Fischer-Tropsch catalyst comprises cobalt, for example, in an amount in the range of 5-25 wt%, e.g., 7-25 wt%, or 10-25 wt%, or 5-20 wt%, or 7-20 wt%, or 10-20 wt%, calculated as Co(0).

Embodiment 115. The process of any of embodiments 1-112, wherein the Fischer-Tropsch catalyst comprises iron, for example, in an amount in the range of 5-95 wt%, e.g., 10-95 wt%, or 25-95 wt%, or 50-95 wt%, or 5-75 wt%, or 10-75 wt%, or 25-75 wt%, or 5-50 wt%, or 10-50 wt%, or 25-50 wt%, calculated as Fe(0).

Embodiment 116. The process of any of embodiments 113-115, wherein the Fischer-Tropsch catalyst further comprises manganese.

Embodiment 117. The process of embodiment 116, wherein the manganese is present in an amount up to 15 wt%, e.g., up to 12 wt%, or up to 10 wt%, or up to 7 wt%, or in the range of 0.1-15 wt%, e.g., 0.1-10 wt%, or 0.1-5 wt%, 0.5-15 wt%, or 0.5-10 wt%, or 0.5-5 wt%, calculated as Mn(0).

Embodiment 118. The process of any of embodiments 1-117, wherein the Fischer-Tropsch catalyst is a supported catalyst, wherein the support comprises at least one of titanium oxide, zirconium oxide, cerium oxide, aluminum oxide, silicon oxide and zinc oxide.

Embodiment 119. The process of any of embodiments 1-117, wherein the Fischer-Tropsch catalyst is a supported catalyst, wherein the support comprises at least one of titanium oxide, aluminum oxide, and silicon oxide.

Embodiment 120. The process of any of embodiments 1-117, wherein the Fischer-Tropsch catalyst is a supported catalyst, wherein the support is a titanium dioxide support.

Embodiment 121. The process of any of embodiments 1-120, wherein the Fischer-Tropsch catalyst is activated by contact with a reducing gas, e.g., hydrogen.

Embodiment 122. The process of embodiment 119, wherein the reducing gas comprises at least a portion of hydrogen from the first product stream.

Embodiment 123. The process of any of embodiments 1-120, wherein the Fischer-Tropsch catalyst is activated by contact with H_2 and CO.

Embodiment 124. The process of embodiment 123, wherein the reducing gas comprises at least a portion of H_2 and CO from the first product stream.

Embodiment 125. The process of any of embodiments 121-123, wherein the activation is performed at a temperature in the range of 200-400 °C

Embodiment 126. The process of any of embodiments 1-125, wherein the second temperature is in the range of 150-400 °C (e.g., in the range of 150-350 °C, or 150-300 °C, or 150-250°C, or 150-200°C, or 200-400 °C, or 200-350 °C, or 200-300°C, or 200-250 °C, or 250-400 °C, or 250-350 °C, or 250-300 °C, or 300-400 °C).

Embodiment 127. The process of any of embodiments 1-126, wherein the second temperature is in the range of 200-350 °C.

Embodiment 128. The process of any of embodiments 1-127, wherein the first temperature is within 100 °C of the second temperature, e.g., within 50 °C of the second temperature, or within 25 °C of the second temperature.

Embodiment 129. The process of any of embodiments 1-127, wherein the first temperature is at least 100 °C greater than the second temperature, e.g., at least 150 °C greater than the second temperature, or at least 200 °C greater than the second temperature.

Embodiment 130. The process of any of embodiments 1-129, wherein the second pressure is in the range of 10-50 barg (e.g., 20-50 barg, or 25-50 barg, or 10-40 barg, or 20-40 barg, or 25-40 barg or 10-35 barg, or 20-35 barg, or 25-35 barg).

Embodiment 131. The process of any of embodiments 1-130, wherein the second pressure is in the range of 20-50 barg.

Embodiment 132. The process of any of embodiments 1-131, wherein the Fischer-Tropsch reaction is conducted at a GHSV in the range of 1,000 to 2,000,000 h^{-1} (e.g., in the range of 1,000 to 1,200,000 h^{-1}, or 1,000 to 500,000 h^{-1}, or 1,000 to 100,000 h^{-1}, or 5,000 to 1,200,000 h^{-1}, or 5,000 to 500,000 h^{-1}, or 5,000 to 100,000 h^{-1}, or 10,000 to 1,200,000 h^{-1}, or 10,000 to 500,000 h^{-1}, or 10,000 to 100,000 h^{-1}).

Embodiment 133. The process of any of embodiments 1-132, wherein the contacting of the Fischer-Tropsch catalyst with the second feed stream to provide the second product stream is performed with a C_{5+} selectivity of at least 30%, e.g., at least 50%, or at least 70%.

Embodiment 134. The process of any of embodiments 1-133, wherein the contacting of the Fischer-Tropsch catalyst with the second feed stream to provide the second product stream is performed with a selectivity for C_{5+} alkanes of at least 30%, e.g., at least 50%, or at least 70%.

Embodiment 135. The process of any of embodiments 1-134, wherein the contacting of the Fischer-Tropsch catalyst with the second feed stream to provide the second product stream is performed with a selectivity for C_{5+} alkanes and C_{5+} alcohols of at least 30%, e.g., at least 50%, or at least 70%.

Embodiment 136. The process of any of embodiments 1-135, further comprising separating at least a portion of water from the second product stream.

Embodiment 137. The process of any of embodiments 1-136, further comprising separating at least a portion of C_1-C_4 hydrocarbons from the second product stream to provide a light hydrocarbon stream.

Embodiment 138. The process of embodiment 137, further comprising including at least a portion of the light hydrocarbon stream in the first feed stream and/or the second feed stream.

Embodiment 139. The process of embodiment 137 or embodiment 138, further comprising oxidizing at least a portion of the light hydrocarbon stream to provide a CO- and/or CO_2-containing pOX stream, and including at least a portion of the pOX stream in the first feed stream and/or the second stream.

Embodiment 140. The process of any of embodiments 137-139, further comprising burning at least a portion of the light hydrocarbon stream to provide energy, e.g., heat energy or electrical energy.

Embodiment 141. The process of embodiment 140, wherein the heat energy is used to heat the first feed stream.

Embodiment 142. The process of any of embodiments 1-141, wherein the process further comprises exchanging heat between at least a portion of the second product stream and a steam generation zone, thereby cooling at least a portion of the first feed stream and providing heat to the steam generation zone.

Embodiment 143. The process of embodiment 142, further comprising generating steam from the heat provided to the steam generation zone, and generating electricity from the steam.

Embodiment 144. The process of embodiment 142 or 143, wherein steam is used to heat the first feed stream and/or the second feed stream.

Embodiment 145. The process of any of embodiments 1-144, wherein the process further comprises exchanging heat between at least a portion of the second product stream and at least a portion of the second feed stream, thereby cooling at least a portion of the second product stream and heating at least a portion of the second feed stream.

Embodiment 146. The process of any of embodiments 1-145, further comprising recycling at least a portion of H_2 of the second product stream to the second feed stream.

Embodiment 147. The process of any of embodiments 1-146, further comprising recycling at least a portion of H_2 of the second product stream to the first feed stream.

Embodiment 148. The process of embodiment 147, further comprising providing H_2 to the second feed stream from a H_2 source other than the first product stream.

Embodiment 149. The process of embodiment 148, when H_2 from the second product stream makes up most of the H_2 of the first feed stream, e.g., at least 90%, at least 95%, or at least 98% of the H_2 of the first feed stream.

Embodiment 150. The process of any of embodiments 1-149, further comprising recycling at least a portion of CO of the second product stream to the second feed stream.

Embodiment 151. The process of any of embodiments 1-150, further comprising recycling at least a portion of CO of the second product stream to the first feed stream.

Embodiment 152. The process of any of embodiments 1-151, further comprising recycling at least a portion of inerts of the second product stream to the second feed stream.

Embodiment 153. The process of any of embodiments 1-152, further comprising recycling at least a portion of inerts of the second product stream to the first feed stream.

Embodiment 154. The process of any of embodiments 1-153, further comprising recycling at least a portion of CO_2 of the second product stream to the first feed stream.

Embodiment 155. The process of embodiment 154, further comprising providing CO_2 to the second feed stream from a CO_2 source other than the first product stream.

Embodiment 156. The process of embodiment 155, when CO_2 from the second product stream makes up most of the CO_2 of the first feed stream, e.g., at least 90%, at least 95%, or at least 98% of the CO_2 of the first product stream.

Embodiment 157. The process of any of embodiments 1-156, wherein one or more products are provided from at least a portion of C5+ hydrocarbons of the second product stream.

Embodiment 158. The process of embodiment 157, wherein the one or more products include fuels (e.g., gasoline, diesel fuel, aviation fuel), lubricants and waxes.

Embodiment 159. The process of any of embodiments 1-158, further comprising hydroprocessing at least a portion of C5+ hydrocarbons of the second product stream.

Embodiment 160. The process of any of embodiments 1-159, wherein at least part of the CO_2 of the first feed stream and/or the second feed stream is from a renewable source.

Embodiment 161. The process of any of embodiments 1-160, wherein at least part of the CO_2 of the first feed stream and/or the second feed stream is from direct air capture.

Embodiment 162. The process of any of embodiments 1-161, wherein at least part of the CO_2 of the first feed stream and/or the second feed stream is captured from a manufacturing plant, e.g., a bioethanol plant, a steel plant, or a cement plant.

Embodiment 163. The process of any of embodiments 1-162, wherein at least part of the H_2 of the first feed stream or the second feed stream is from a renewable source.

Embodiment 164. The process of any of embodiment 1-163, wherein at least a portion of the hydrogen of the first feed stream or the second feed stream is green hydrogen.

Embodiment 165. The process of any of embodiment 1-164, wherein at least a portion of the hydrogen of the first feed stream or the second feed stream is blue hydrogen.

Embodiment 166. The process of any of embodiment 1-165, wherein at least a portion of the hydrogen of the first feed stream or the second feed stream is grey hydrogen, black hydrogen, brown hydrogen, pink hydrogen, turquoise hydrogen, yellow hydrogen, and/or white hydrogen.

Embodiment 167. The process of any of embodiments 1-166, further comprising providing at least a portion of H_2 to the first feed stream and/or the second feed stream by electrolysis of water.

Embodiment 168. The process of embodiment 167, wherein the electrolysis of water is performed using at least partially electricity from a renewable source.

Embodiment 169. The process of embodiment 167 or embodiment 168, wherein the electrolysis of water is performed using at least partially electricity generated from steam made by heat exchange from the first product stream and/or the second product stream, or by burning a light hydrocarbon stream.

Embodiment 170. The process of any of embodiments 168-169, further comprising providing at least a portion of O_2 generated in the electrolysis to a partial oxidation.

Embodiment 171. The process of any of embodiments 1-170, wherein the process is performed in a reactor system comprising a first reactor in which the reverse water-gas shift catalyst is disposed, and a second reactor in which the Fischer-Tropsch catalyst is disposed.

Embodiment 172. The process of any of embodiments 1-170, wherein the process is performed in a reactor system comprising first catalyst bed in which the reverse water-gas shift catalyst is disposed, and wherein the second reaction zone comprises a second catalyst bed in which the Fischer-Tropsch catalyst is disposed.

Embodiment 173. The process of embodiment 172, wherein the first reactor bed and the second reactor bed are disposed within the same reactor.

Embodiment 174. The process of any of embodiments 1-170, wherein the process is performed in a reactor system comprising one or more first catalyst containers in which the reverse water-gas shift catalyst is disposed, and wherein the second reaction zone comprises one or more second catalyst containers in which the Fischer-Tropsch catalyst is disposed.

Embodiment 175. The process of embodiment 174, wherein the one or more first catalyst containers and the one or more second catalyst containers are disposed within the same reactor.

Embodiment 176. The process of any of embodiments 1-175, wherein the process is performed in a reactor system comprising a reactor in which the reverse water-gas shift catalyst and the Fischer-Tropsch catalyst are disposed, e.g., in admixture.

Embodiment 177. A method for making a reverse water-gas shift catalyst, the method comprising:

providing a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support comprising a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide;
contacting the support with one or more liquids each comprising one or more nickel-containing compounds and/or one or more manganese-containing compounds dispersed in a solvent(s);
allowing the solvent(s) to evaporate to provide a catalyst precursor; and
calcining the catalyst precursor.

Embodiment 178. The method of embodiment 177, wherein contacting the support with the liquid comprises adding the liquid in an amount equal to the pore volume of the support.

Embodiment 179. The method of embodiment 177, wherein contacting the support with the liquid comprises adding the liquid in an amount greater than the pore volume of the support.

Embodiment 180. The method of any of embodiments 177-179, wherein ratio of the amount liquid to the amount of support on a mass basis is in the range of 1:1 to 5:1 (e.g., in the range of 1:1 to 3:1).

Embodiment 181. The method of any of embodiments 177-180, wherein contacting the support with the liquid provides a slurry.

Embodiment 182. The method of any of embodiments 177-181, wherein allowing the solvent to evaporate is conducted at ambient temperature.

Embodiment 183. The method of embodiments 177-181, wherein allowing the solvent to evaporate is conducted at an elevated temperature (e.g., in the range of 50-150 °C) for a drying time (e.g., 24 hours).

Embodiment 184. The method of embodiments 177-181, wherein allowing the solvent to evaporate is conducted under vacuum and at an elevated temperature (e.g., in the range of 50-150 °C) for a drying time (e.g., 24 hours).

Embodiment 185. The method of any of embodiments 177-181, wherein allowing the solvent to evaporate is conducted in a stirring drybath at an elevated temperature (e.g., in the range of 30-100 °C).

Embodiment 186. The method of any of embodiments 177-185, wherein calcining the catalyst precursor is conducted for a calcining time in the range of 0.5 to 24 hours (e.g., 0.5 to 15 hours, or 0.5 to 10 hours, or 0.5 to 5 hours).

Embodiment 187. The method of any of embodiments 177-186, wherein calcining the catalyst precursor is conducted for a calcining is in the range of 100-600 °C (e.g., in the range of 120-500 °C).

[00156] The particulars shown herein are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of various embodiments of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for the fundamental understanding of the invention, the description taken with the drawings and/or examples making apparent to those skilled in the art how the several forms of the invention may be embodied in practice. Thus, before the disclosed processes and devices are described, it is to be understood that the aspects described herein are not limited to specific embodiments, apparatuses, or configurations, and as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and, unless specifically defined herein, is not intended to be limiting.

[00157] The terms “a,” “an,” “the” and similar referents used in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value is incorporated into the specification as if it were individually recited herein. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[00158] All methods described herein can be performed in any suitable order of steps unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention otherwise claimed. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

[00159] Unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”. Words using the singular or plural number also include the plural and singular number, respectively. Additionally, the words “herein,” “above,” and “below” and words of similar import, when used in this application, shall refer to this application as a whole and not to any particular portions of the application.

[00160] As will be understood by one of ordinary skill in the art, each embodiment disclosed herein can comprise, consist essentially of or consist of its particular stated element, step, ingredient or component. As used herein, the transition term “comprise” or “comprises” means includes, but is not limited to, and allows for the inclusion of unspecified elements, steps, ingredients, or components, even in major amounts. The transitional phrase “consisting of” excludes any element, step, ingredient or component not specified. The transition phrase “consisting essentially of” limits the scope of the embodiment to the specified elements, steps, ingredients or components and to those that do not materially affect the embodiment.

[00161] Unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00162] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[00163] Groupings of alternative elements or embodiments of the invention disclosed herein are not to be construed as limitations. Each group member may be referred to and claimed individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability. When any such inclusion or deletion occurs, the specification is deemed to contain the group as modified thus fulfilling the written description of all Markush groups used in the appended claims.

[00164] Some embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations on these described embodiments will become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[00165] Furthermore, it is to be understood that the embodiments of the invention disclosed herein are illustrative of the principles of the present invention. Other modifications that may be employed are within the scope of the invention. Thus, by way of example, but not of limitation, alternative configurations of the present invention may be utilized in accordance with the teachings herein. Accordingly, the present invention is not limited to that precisely as shown and described.

We Claim:

1. A process for performing an integrated Fischer-Tropsch process, the process comprising:

    providing a first feed stream comprising H_2 and CO_2;

    contacting at a first temperature in the range of 500-900 °C and at a first pressure a reverse water-gas shift catalyst with the first feed stream to perform a reverse water-gas shift reaction to provide a first product stream comprising CO and H_2, the first product stream having a lower concentration of CO_2 and a higher concentration of CO than the first feed stream;

    contacting at a second temperature and at a second pressure a Fischer-Tropsch catalyst with a second feed stream comprising H_2 and at least a portion of CO of the first product stream to provide a second product stream comprising C_{5+} hydrocarbons,

wherein the reverse water-gas shift catalyst is a supported reverse water-gas shift catalyst comprising:

    a support that is a cerium oxide support, a titanium oxide support, an aluminum oxide support, a zirconium oxide support, or a mixed oxide support comprising a mixture of two or more of cerium oxide, titanium oxide, aluminum oxide, and zirconium oxide;

    nickel, present in an amount in the range of 0.05 to 10 wt% of the catalyst, based on the total weight of the catalyst; and

    manganese, present in an amount in the range of 0.5 to 20 wt% of the catalyst, based on the total weight of the catalyst.

2. The process of claim 1, wherein the support makes up at least 70 wt% of the catalyst, on an oxide basis.

3. The process of claim 1, wherein nickel is present in the catalyst in an amount in the range of 0.1 to 10 wt%.

4. The process of claim 1, wherein manganese is present in the catalyst in an amount in the range of 2 to 20 wt%.

5. The process of claim 1, wherein manganese is present in the catalyst in an amount in the range of 4 to 20 wt%, e.g., in the range of 4 to 15 wt%, or 4 to 12 wt%, or 4 to 10 wt%, based on the total weight of the catalyst.

6. The process of claim 1, wherein a ratio of nickel to manganese is in the range of 0.05:1 to 1:1.

7. The process of claim 1, wherein the molar ratio of H_2 to CO_2 in the first feed stream is in the range of 0.5:1 to 10:1.

8. The process of claim 1, wherein the reverse water-gas shift reaction has a CO selectivity of at least 50%.

9. The process of claim 1, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 40%.

10. The process of claim 1, wherein the reverse water-gas shift reaction has a methane selectivity of no more than 10%.

11. The process of claim 1, wherein the reverse water-gas shift reaction has a CO_2 conversion of at least 30%.

12. The process of claim 1, wherein the reverse water-gas shift reaction has a CO_2 conversion of no more than 80%.

13. The process of claim 1, conducted at a first temperature in the range of 600-800 °C.

14. The process of claim 1, wherein the process comprises activating the reverse water-gas shift catalyst with a reducing stream comprising a reductive gas.

15. The process of claim 1, wherein the first product stream comprises no more than 75 mol% CO_2.

16. The process of claim 1, wherein the first product stream comprises no more than 40 mol% methane.

17. The process of claim 1, wherein the process further comprises separating the first product stream to recycle at least a portion of CO_2 or H_2 of the first product stream to the first feed stream.

18. The process of claim 1, wherein at least 25% of the CO of the first product stream is included in the second feed stream.

19. The process of claim 1, wherein the first product stream includes H_2, and wherein at least 25% of the H_2 of the first product stream is included in the second feed stream.

20. The process of claim 1, wherein at least 10% of the CO_2 of the first product stream is included in the second feed stream.

21. The process of claim 1, wherein the second feed stream does not include a substantial amount of CO_2 of the first product stream.

22. The process of claim 1, wherein the second feed stream has a H_2:CO ratio in the range of 0.5:1 to 6:1.

23. The process of claim 1, wherein the Fischer-Tropsch catalyst comprises cobalt, iron, rhodium, ruthenium, or a combination thereof.

24. The process of claim 23, wherein the Fischer-Tropsch catalyst further comprises manganese.

25. The process of claim 1, wherein the second temperature is in the range of 200-350 °C.

26. The process of claim 1, wherein the first temperature is at least 100 °C greater than the second temperature than the second temperature.

27. The process of claim 1, wherein the contacting of the Fischer-Tropsch catalyst with the second feed stream to provide the second product stream is performed with a selectivity for C_{5+} alkanes of at least 30%.

28. The process of claim 1, further comprising separating at least a portion of C_1-C_4 hydrocarbons from the second product stream to provide a light hydrocarbon stream.

29. The process of claim 1, wherein the process further comprises exchanging heat between at least a portion of the second product stream and at least a portion of the second

feed stream, thereby cooling at least a portion of the second product stream and heating at least a portion of the second feed stream.

30. The process of claim 1, further comprising recycling at least a portion of H_2 of the second product stream to the second feed stream.

31. The process of claim 1, further comprising recycling at least a portion of H_2 of the second product stream to the first feed stream, wherein H2 from the second product stream makes up at least 90% of the H_2 of the first feed stream.

32. The process of claim 1, further comprising recycling at least a portion of CO of the second product stream to the second feed stream or the first feed stream.

33. The process of claim 1, further comprising recycling at least a portion of CO_2 of the second product stream to the first feed stream, wherein CO_2 from the second product stream makes up at least 90% of the CO_2 of the first feed stream.

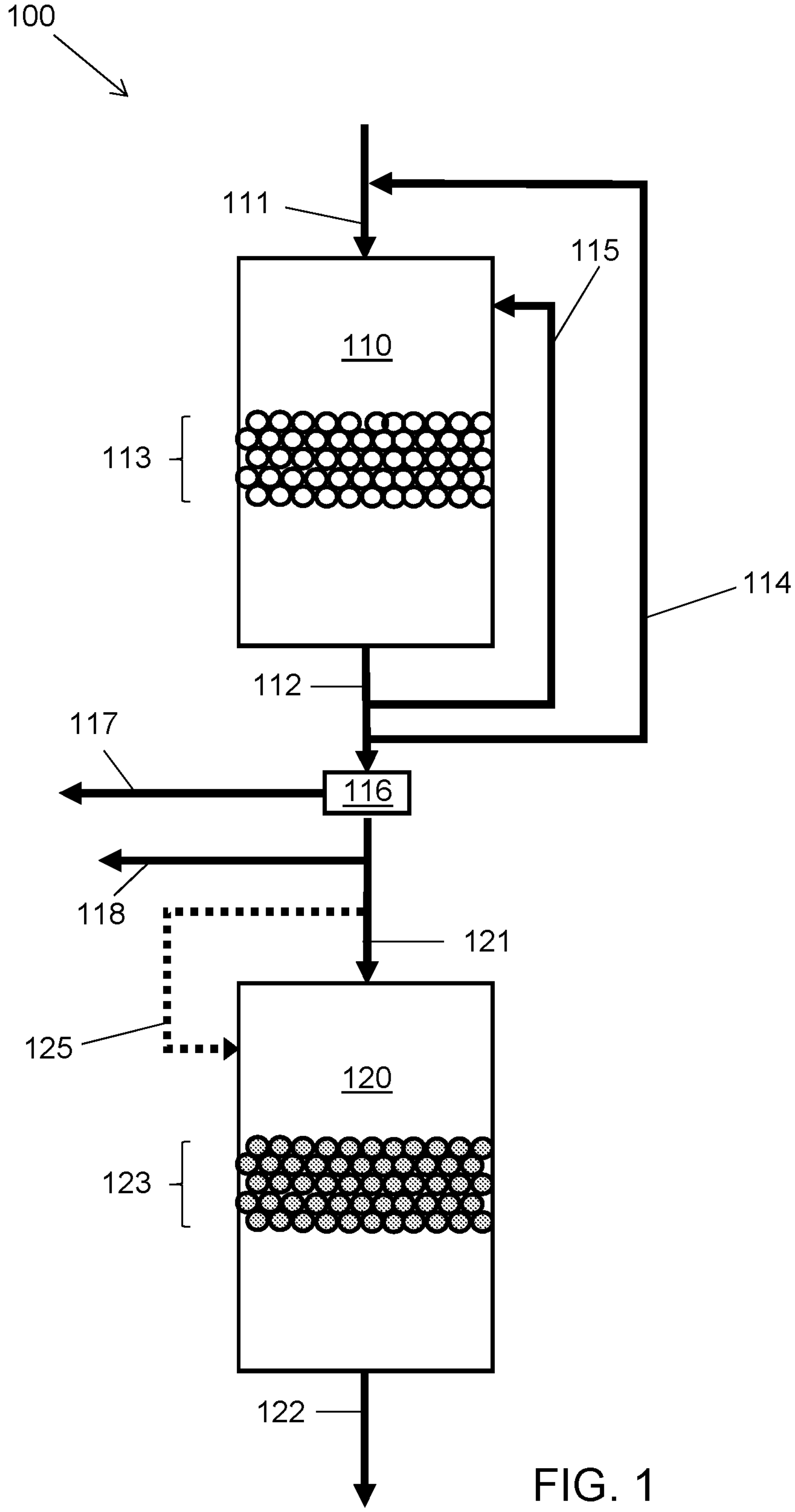

FIG. 1

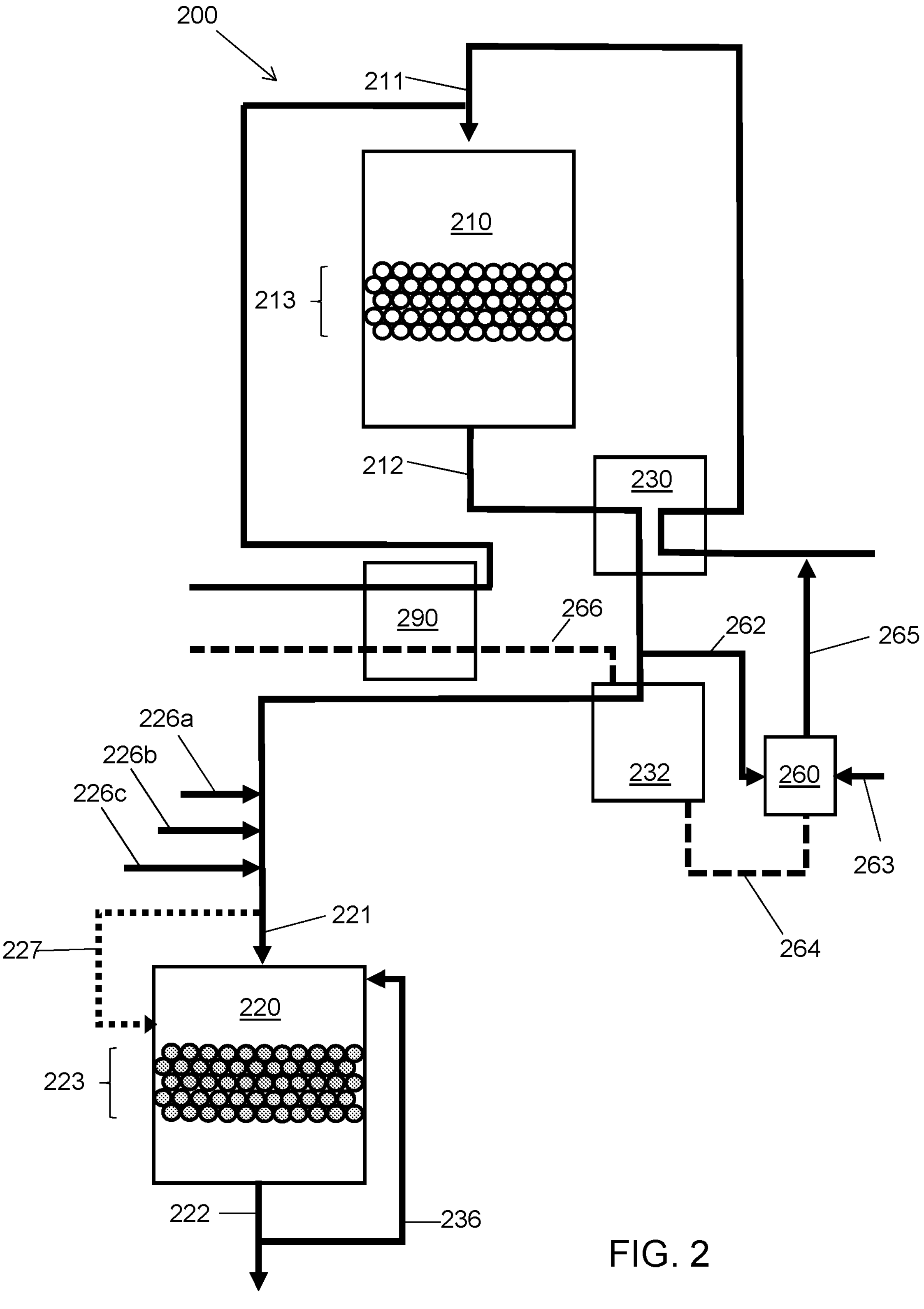
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FIG. 2

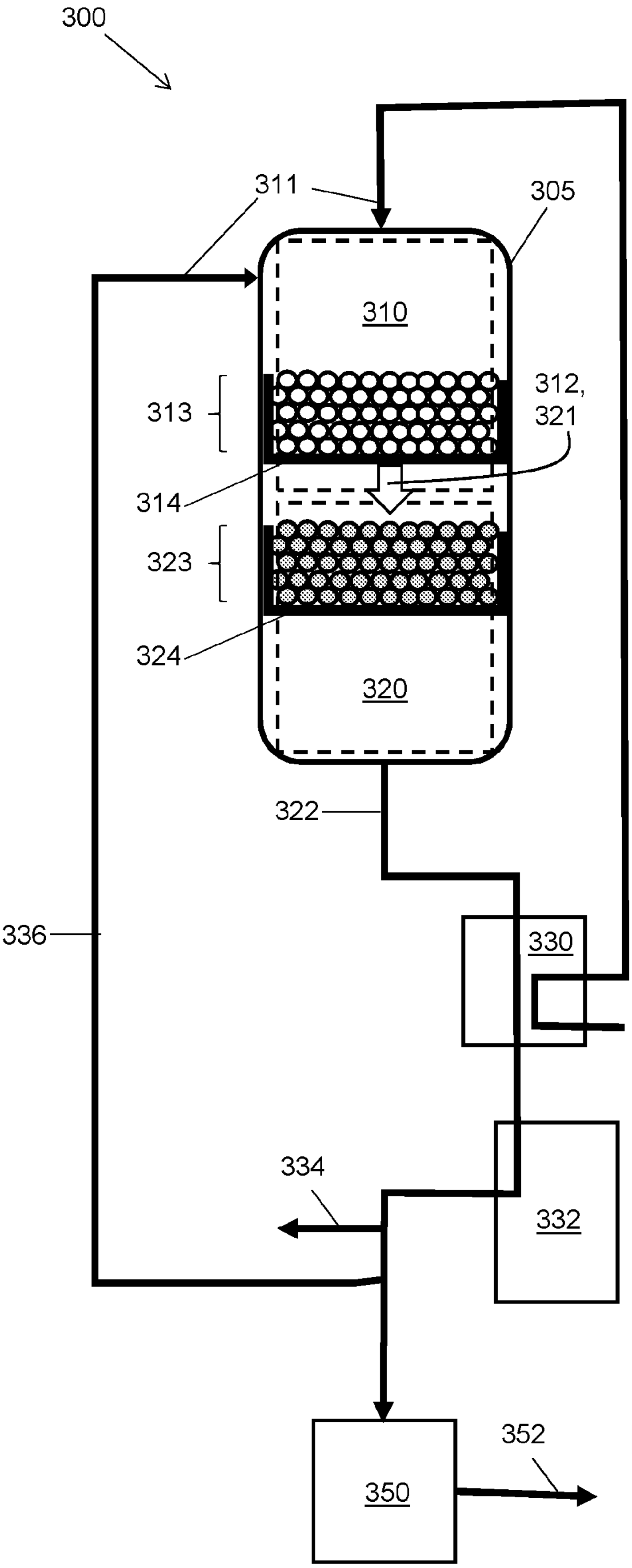
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FIG. 3

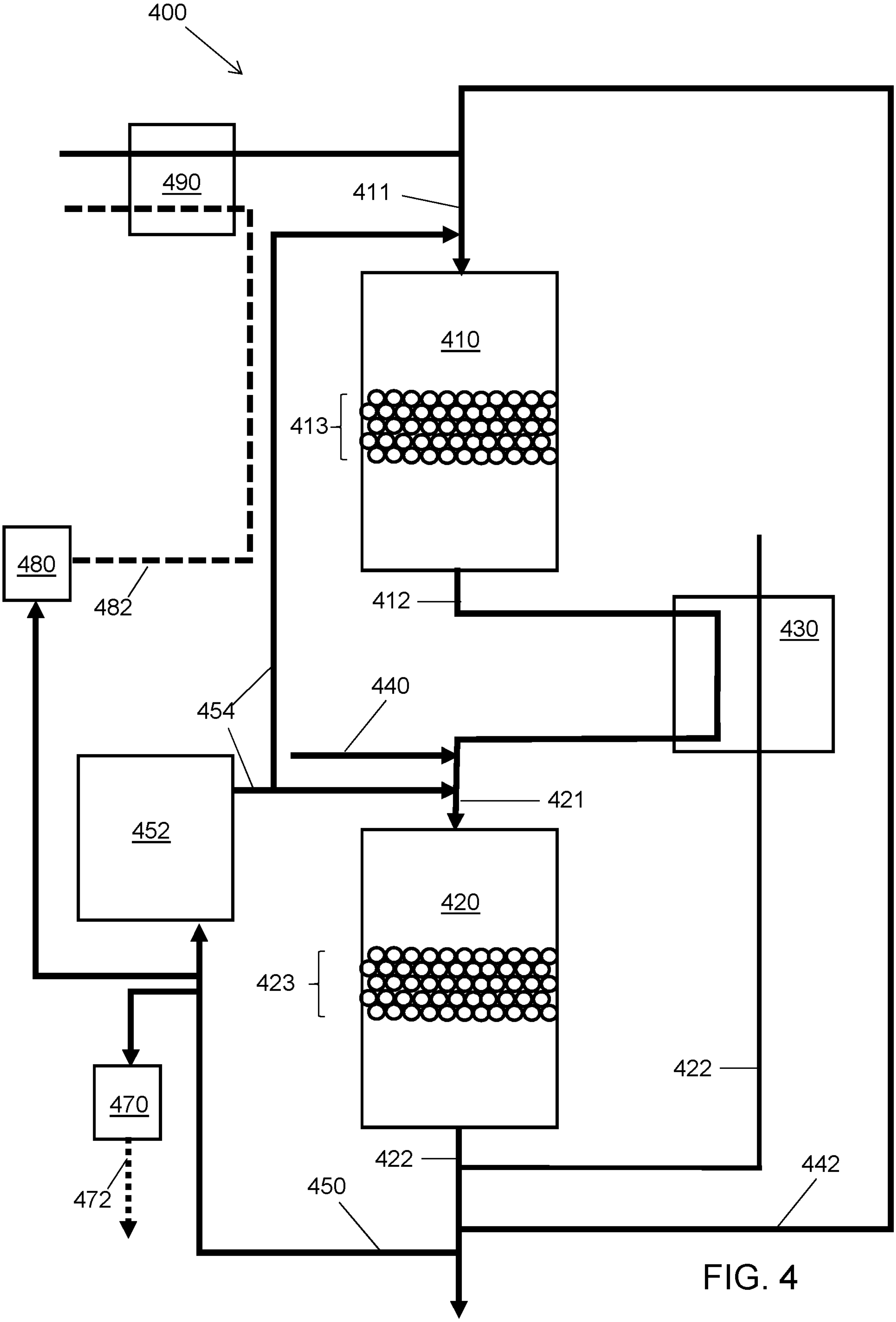
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FIG. 4

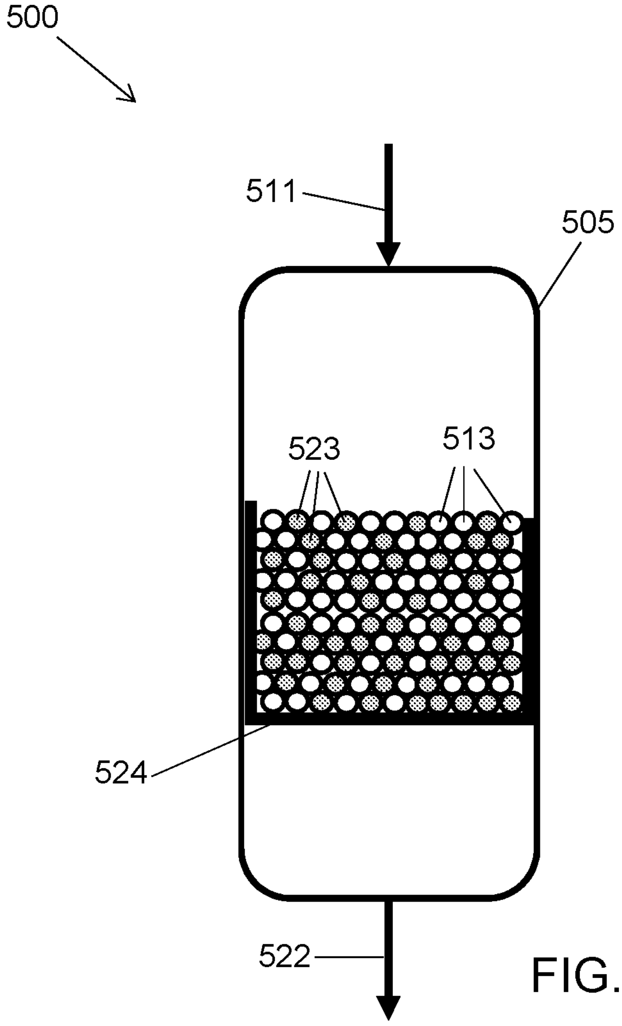

FIG. 5

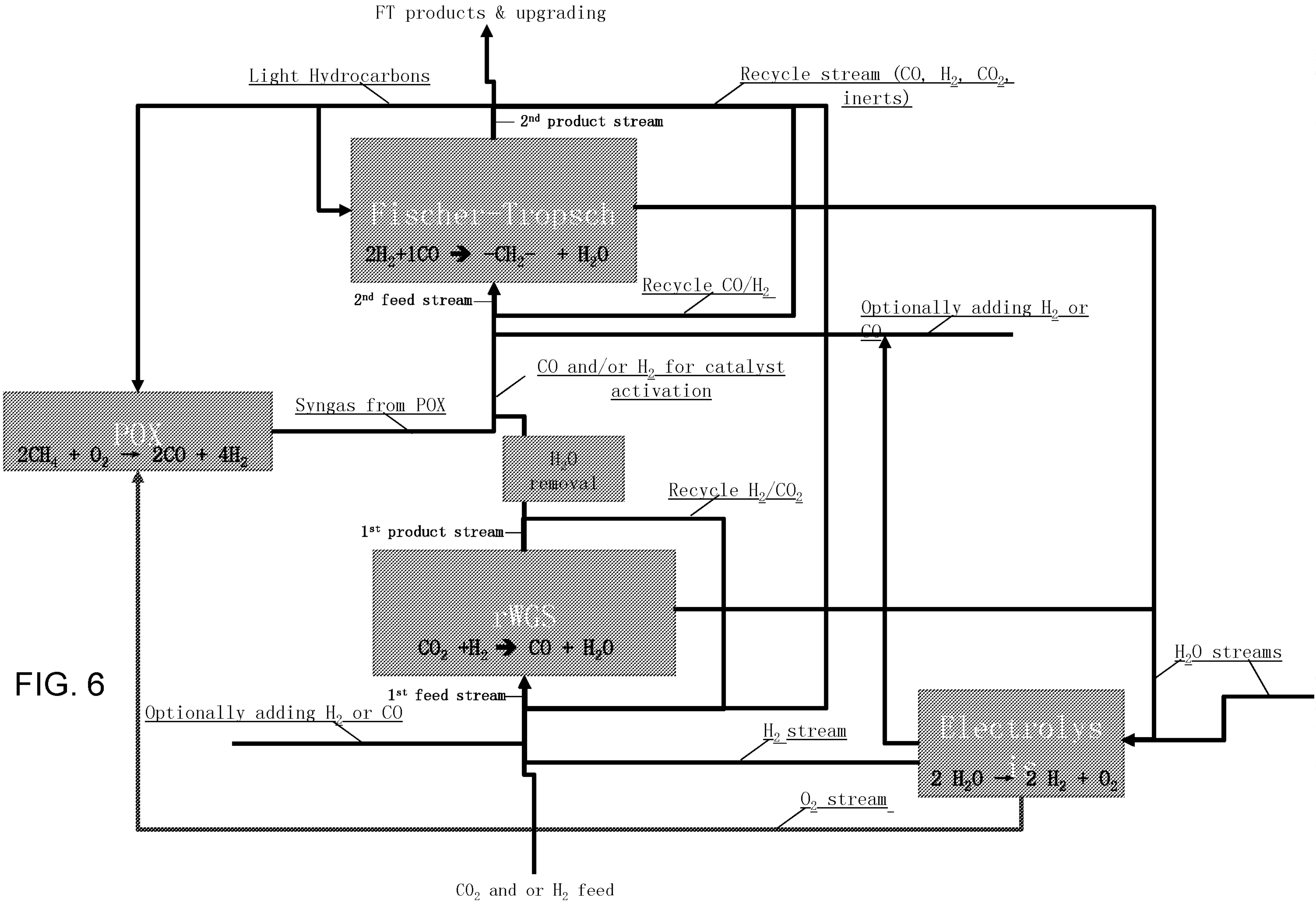
FT products & upgrading
Light Hydrocarbons
Recycle stream (CO, H_2, CO_2, inerts)
2nd product stream
Fischer-Tropsch
$2H_2 + 1CO \rightarrow -CH_2- + H_2O$
Recycle CO/H_2
2nd feed stream
Optionally adding H_2 or CO
CO and/or H_2 for catalyst activation
Syngas from POX
POX
$2CH_4 + O_2 \rightarrow 2CO + 4H_2$
H_2O removal
Recycle H_2/CO_2
1st product stream
rWGS
$CO_2 + H_2 \rightarrow CO + H_2O$
H_2O streams
1st feed stream
Optionally adding H_2 or CO
H_2 stream
Electrolysis
$2 H_2O \rightarrow 2 H_2 + O_2$
O_2 stream
CO_2 and or H_2 feed

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2022/102799

A. CLASSIFICATION OF SUBJECT MATTER

C07C 1/12(2006.01)i; C07C 11/10(2006.01)i; C07C 27/06(2006.01)i; B01J 12/00(2006.01)i; B01J 23/889(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C; 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)

CNTXT, ENTXT, ENTXTC, DWPI, SIPOABS, CNKI, ISI Web of Science:BP, ARMITAGE Gareth, SUNLEY Glen, DOSCKOCIL Eric, GUO Meiling, Mn, manganese, Ni, nickel, reverse water gas shift, RWGS, react+, F-T, FT, Fischer Tropsch, synthesis, process, cataly+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2017130081 A1 (SABIC GLOBAL TECHNOLOGIES B.V.) 03 August 2017 (2017-08-03) paragraphs [0009]-[0034]	1-33
Y	US 2005232833 A1 (HARDY Dennis R. et al.) 20 October 2005 (2005-10-20) paragraphs [0009]-[0013]	1-33
Y	US 2018093888 A1 (SABIC GLOBAL TECHNOLOGIES B.V. et al.) 05 April 2018 (2018-04-05) paragraphs [0009]-[0035]	1-33
Y	WO 2017074843 A1 (SABIC GLOBAL TECHNOLOGIES B.V. et al.) 04 May 2017 (2017-05-04) paragraphs [0008]-[0039]	1-33
Y	US 2016280618 A1 (SAUDI BASIC IND. CORP.) 29 September 2016 (2016-09-29) paragraphs [0026]-[0030], [0041]-[0057]	1-33
Y	US 2010190874 A1 (MAMEDOV Agaddin M.Kh. et al.) 29 July 2010 (2010-07-29) paragraphs [0015]-[0028]	1-33

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

*	Special categories of cited documents:	"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
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"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search **12 December 2022**	Date of mailing of the international search report **03 January 2023**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **JIN,Ting** Telephone No. **(86-10)53962751**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	LIU Yan et al. "STUDY ON PROPERTIES OF Mn BASED CATALYSTS FOR CO2 HYDROGENATION" 《*JOURNAL OF FUEL CHEMISTRY AND TECHNOLOGY*》, Vol. 26, No. 5, 31 October 1998 (1998-10-31), ISSN: 0253-2409, page 414	1-33

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2022/102799

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
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		EP 2152409 B1	29 June 2016