

(43) International Publication Date
26 February 2015 (26.02.2015)(51) International Patent Classification:
C07C 1/04 (2006.01)(21) International Application Number:
PCT/US2014/052052(22) International Filing Date:
21 August 2014 (21.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

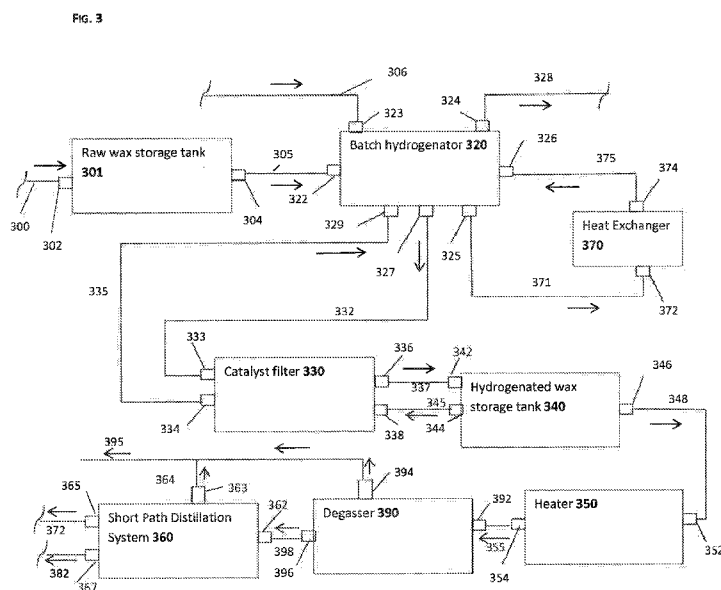
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: METHODS, SYSTEMS, AND APPARATUSES FOR LOW-TEMPERATURE FISCHER-TROPSCH WAX HYDROGENATION



(57) Abstract: A process for hydrogenating a Fischer-Tropsch ("FT") wax includes placing hydrogenation catalyst particles within a low-temperature hydrogenation reactor having a mixing sub-system and a vent at the top for excess hydrogen, placing the FT wax at a low temperature up to a predetermined level within the low-temperature, hydrogenation reactor, leaving a vapor space above the predetermined level, adding hydrogen under a desired pressure into the low-temperature hydrogenation reactor, mixing the input FT wax, the hydrogen gas and the hydrogenating catalyst particles together to create a mixture using the mixing subsystem and continuing the mixing until the FT wax has hydrogenated, stopping the mixing to allow the hydrogenation catalyst particles to settle, and removing an hydrogenated FT wax with residual hydrogenating catalyst particles from the low-temperature hydrogenation reactor. The hydrogenated FT wax may be filtered and subjected to vacuum distillation. Other embodiments are also disclosed.

**METHODS, SYSTEMS, AND APPARATUSES FOR LOW-TEMPERATURE
FISCHER-TROPSCH WAX HYDROGENATION****STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT**

[0001] Not applicable.

BACKGROUND**Field of the Invention**

[0002] This invention relates to a system and method for treating hydrocarbon waxes; specifically it relates to a system and method for improving the color of waxes produced by a Fischer-Tropsch process.

Background of the Invention

[0003] The Fischer-Tropsch (or “Fischer Tropsch,” “F-T” or “FT”) process (or synthesis or conversion) involves a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen (known as reformed gas, synthesis gas, or “syngas”) into liquid hydrocarbons (called “liquid FT hydrocarbons” herein). The process was first developed by German chemists Franz Fischer and Hans Tropsch in the 1920’s. The FT conversion is a catalytic and exothermic process. The FT process is utilized to produce petroleum substitutes, typically from carbon-containing energy sources such as coal, natural gas, biomass, or carbonaceous waste streams (such as municipal solid waste) that are suitable for use as synthetic fuels, waxes and/or lubrication oils. The carbon-containing energy source is first converted into a reformed gas (or synthetic gas or syngas), using a syngas preparation unit in what may be called a syngas conversion. Once the syngas is created, the syngas is used as an input to an FT reactor having an FT catalyst to make the liquid FT hydrocarbons in a Fischer-Tropsch synthesis (or FT synthesis or FT conversion). Depending on the type of FT reactor, the FT conversion of the syngas to liquid FT hydrocarbons takes place under appropriate operating conditions.

[0004] Depending on the physical form of the carbon-containing energy source, syngas preparation may involve technologies such as steam methane reforming, gasification, carbon monoxide shift conversion, acid gas removal gas cleaning and conditioning. These steps convert the carbon-containing energy source to simple molecules, predominantly carbon monoxide and hydrogen, which are the active ingredients of synthesis gas. The synthesis gas will also inevitably contain carbon dioxide, water vapor, methane, nitrogen. Impurities

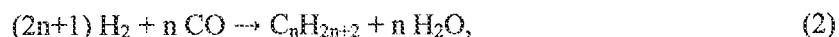
deleterious to catalyst operation such as sulfur and nitrogen compounds are often present in trace amounts and are removed to very low concentrations as part of synthesis gas conditioning.

[0005] Turning to the syngas conversion step, to create the syngas from natural gas, for example, methane in the natural gas reacts with steam and oxygen in a syngas preparation unit to create syngas. The syngas comprises principally carbon monoxide, hydrogen, carbon dioxide, water vapor and unconverted methane. When partial oxidation is used to produce the synthesis gas, typically, the syngas contains more carbon monoxide and less hydrogen than is optimal and consequently, steam is added to the react with some of the carbon monoxide in a water-gas shift reaction. The water gas shift reaction can be described as:



[0007] Thermodynamically, there is an equilibrium between the forward and the backward reactions. That equilibrium is determined by the concentration of the gases present.

[0008] Once the syngas is created and conditioned, the syngas is used as an input to an FT reactor having an FT catalyst to make the liquid FT hydrocarbons in a Fischer-Tropsch synthesis (or FT synthesis or FT conversion). Depending on the type of FT reactor, the FT conversion of the syngas to liquid FT hydrocarbons takes place under appropriate operating conditions. The Fischer-Tropsch (FT) reactions for the FT conversion of the syngas to the liquid FT hydrocarbons may be simplistically expressed as:



where 'n' is a positive integer.

[0009] In addition to liquid FT hydrocarbons, the Fischer-Tropsch synthesis also commonly produces gases (called "FT tail gases" herein) and water (called "FT water" herein). The FT tail gases typically contain CO (carbon monoxide), CO₂ (carbon dioxide), H₂ (hydrogen), light hydrocarbon molecules, both saturated and unsaturated, typically having carbon values ranging from C₁ to C₄, and a small amount of light oxygenated hydrocarbon molecules such as methanol. Typically, FT tail gases are mixed in a facility's fuel gas system for use as fuel. The FT water will typically include dissolved oxygenated species, such as alcohols, and light hydrocarbons, which are typically removed prior to disposal of the FT water.

[0010] The FT reaction is performed in the presence of a catalyst, called a Fischer-Tropsch catalyst ("FT catalyst"). Unlike reagents, a catalyst does not participate in the chemical reaction and is not consumed by the reaction itself. In addition, a catalyst may participate in

multiple chemical transformations. Catalytic reactions have a lower rate-limiting free energy of activation than the corresponding un-catalyzed reaction, resulting in higher reaction rate at the same temperature. However, the mechanistic explanation of catalysis is complex. Catalysts may affect the reaction environment favorably, or bind to the reagents to polarize bonds, e.g. acid catalysts for reactions of carbonyl compounds, or form specific intermediates that are not produced naturally, such as osmate esters in osmium tetroxide-catalyzed dihydroxylation of alkenes, or cause lysis of reagents to reactive forms, such as atomic hydrogen in catalytic hydrogenation. In addition to FT catalysts, other catalysts may also be used in other steps of an FT process.

[0011] The FT process results in longer-chain hydrocarbons than the feedstock, mainly n-paraffins, but with small amounts of impurities, such as branched chain material (for example, 2-methyl and 3-methyl derivatives), alpha olefins and oxygenates. The n-paraffins have a full range of carbon numbers from C_1 to well above C_{100} . Lighter materials C_1 through C_4 are typically not condensed in the process and remain in a gaseous phase. The lighter materials contain substantial amounts of alpha olefins (i.e. ethylene, propylene and 1-butene). Products of a typical FT process may include FT naphtha (which may have carbon numbers C_5 to C_{12}), FT diesel (which may have carbon numbers C_9 to C_{25}) and FT wax (mostly C_{20+} material). It is possible to cut narrower distillation range products such as kerosene ($C_8 - C_{16}$), drilling fluid, distillate and the various single carbon number materials (such as heptane).

[0012] The production of olefins and oxygenates decline relative to the paraffins as the molecular weight increases. Nevertheless, there may be sufficient impurities in FT wax, including olefins and oxygenates, that may cause problems with the FT wax product. An olefin is an unsaturated hydrocarbon with a carbon-carbon double bond. Oxygenates, as used herein, mean compounds such as alcohols, aldehydes, ketones and carboxylic acids that have an oxygen-containing group as a termination group (in the case of alcohols, carboxylic acids and aldehydes), or contained within (in the case of ketones) a predominantly paraffinic carbon/hydrogen chain. The olefins may react with oxygen via a process that leads to the production of aldehydes and ketones associated with an undesirable odor. Pure paraffin hydrocarbons are transparent and colorless as a liquid and colorless to white (Saybolt 30) as a solid. Untreated FT wax tends to be colorless to light yellow (liquid), white to off-white (solid) and the color tends to deteriorate in storage.

[0013] Olefins in FT waxes are unstable with respect to oxygen. If an olefin becomes an oxygenated compound, it may become rancid and may cause problems with color or odor in the FT wax.

[0014] If a fixed bed FT reactor is used with a synthetic gas ("syngas") made from a feedstock, the amount of impurities, such as olefins and oxygenates, contained in the untreated FT wax may depend on the catalyst used. For example, use of an iron-based catalyst with a syngas in a fixed bed FT reactor may result in the an FT wax having up to about 20% olefins and oxygenates, while use of the same elements, except with a typical cobalt-based catalyst, may result in the FT wax having up to only about less than 3% olefins and about less than 0.1% oxygenates. Hydrogenation can be used to remove impurities such as olefins and oxygenates from FT wax.

[0015] Typically, trickle bed reactors, packed with catalyst, have been used for FT wax hydrogenation. Hydrogen and wax are generally added as inputs at the top of the reactor and products are collected at or near the bottom of the reactor. These systems work with a constant flow of FT wax and they work well when the FT wax is heavily contaminated, such as in the case of when a fixed bed FT reactor is used with iron-based catalysts to produce FT products. The trickle bed reactors operate at high temperatures and high pressures and are, accordingly, expensive. The size of the catalyst particles used in beds with trickle bed hydrogenation reactors is generally larger than one millimeter in diameter, to avoid a high pressure drop through the reactor. The trickle bed reactors often require between 20 and 50 molecules of hydrogen for every one molecule of hydrogen consumed during the process. Hydrogen is generally collected, compressed and recycled.

[0016] Batch hydrogenation is extensively applied in fine chemicals and pharmaceutical industries. Other industries have used also batch processes for hydrogenation, for example, for perfume oils and edible products like margarine. Hydrogenation reactors used with such processes operate at relatively low temperatures and pressures. For example, use of a low pressure, low temperature hydrogenation reactor having an eductor was pioneered by Buss ChemTech, based in Switzerland, in the 1950's. *See*, for example, the Buss ChemTech web sites:

http://www.buss-ct.com/reaction_technology.html

http://www.buss-ct.com/buss_loop_reactor.html

[0017] However, oils of plant or animal origin differ considerably from FT waxes. Hydrogenation is sometimes used for plant or animal oils to address other issues not presented with FT waxes, such as adding a desired texture. Moreover, the concerns in the

edible oil industry are different from concerns with respect to an FT wax. As an example, in edible oils, trans-olefins can be a concern. Trans-olefins are not present in FT waxes. In FT waxes, the concerns focus on alpha olefins.

[0018] Another difference between edible oil hydrogenation requirements and FT wax hydrogenation requirements concerns the difference in the starting hydrogen demands for each. A starting hydrogen demand is a ratio of the double bonds present to the total carbon present in an oil. For example, typically, edible oils are triglycerides of C_{10} to C_{20} fatty acids, each fatty acid having between zero and four double bonds. Therefore, a typical chemical hydrogen demand for an edible oil would likely be between 0.002 and 0.006 kg-mols/kg. By contrast, an FT wax might have a carbon number of 20 (C_{20}) or above and three percent of such molecules on average have a single double-bond, yielding a typical chemical hydrogen demand of 0.0001 kg-mols/kg. In edible oil hydrogenation, consequently, the chemical hydrogen demand is substantially higher than is the case for a Fischer Tropsch wax.

[0019] Furthermore, in edible oil process, it is typically not desirable to hydrogenate the edible oil completely; a certain amount of residual olefin can be desirable in these applications. By contrast, one wishes to hydrogenate an FT wax as completely as possible. In the edible oil industry, it is a typical practice to measure an Iodine number, which is linearly related to the hydrogen demand, rather to directly measure the hydrogen demand itself. For example, in a typical edible oil application, one may need to reduce the Iodine number from 70 – 110 down to 20 – 40. By contrast, for an FT wax, the starting Iodine number would be much lower (less than 10, more typically less than 2) and the objective would be to get the Iodine number as close to zero as practical. Accordingly, given these differences, such low pressure, low temperature reactors and processes have not been previously considered for use with FT wax hydrogenation.

[0020] Accordingly, there are needs in the art for novel systems and methods for treatment of FT wax having light contamination with impurities. Desirably, such systems and methods yield a high quality product at lower cost.

SUMMARY

[0021] Methods in one of more embodiments of the present disclosure for hydrogenating a Fischer-Tropsch ("FT") wax include placing the FT wax at a low temperature up to a predetermined level within a low-temperature hydrogenation reactor having a mixing sub-system and a vent at the top and containing hydrogenating catalyst particles, , leaving a vapor space above the predetermined level. The method also includes adding a hydrogen gas under

pressure into the low-temperature hydrogenation reactor, bringing the low-temperature hydrogenation reactor up to a pre-determined operating pressure. The method further includes mixing the input FT wax, the hydrogen gas and the hydrogenation catalyst particles together using the mixing subsystem under operating conditions including a low temperature and the pre-determined operating pressure to create a mixture, thus permitting the FT wax to become hydrogenated, and stopping the mixing to allow the hydrogenation catalyst particles to settle for a period of time, and removing the hydrogenated FT wax with residual hydrogenating catalyst particles from the low-temperature hydrogenation reactor.

[0022] In one or more embodiments of the present disclosure, a method for hydrogenating a Fischer-Tropsch ("FT") wax includes the steps of (1) placing an input FT wax, at a low temperature of below about 200° C, up to a predetermined level within a low-temperature, low-pressure hydrogenation reactor, having a mixing sub-system comprising a hollow shaft gas impeller system, having a vent at the top and containing hydrogenation catalyst particles, leaving a vapor space above the predetermined level; (2) adding hydrogen gas under pressure to the low-temperature low-pressure hydrogenation reactor, bringing the low-temperature low-pressure hydrogenation reactor up to a pre-determined low operating pressure of below about 100 psig; (3) mixing the input FT wax, the hydrogen gas and the hydrogenation catalyst particles together using the mixing subsystem under operating conditions including a low temperature and the pre-determined operating pressure to create a mixture, thus permitting the FT wax to become hydrogenated; (4) depressurizing the low-temperature low-pressure hydrogenation reactor; (5) flushing the hydrogen gas from the vapor space of the low-temperature low-pressure hydrogenation reactor using nitrogen at a low pressure; (6) stopping the mixing and allowing the hydrogenation catalyst particles to settle for a period of time, leaving at least one residual hydrogenation catalyst particle suspended in the hydrogenated FT wax; (7) removing the hydrogenated FT wax and the at least one residual hydrogenation catalyst particle from the low-temperature, low-pressure hydrogenation reactor through a dip tube by adding nitrogen under a low pressure to the low-temperature, low-pressure hydrogenation reactor; (8) sending the removed hydrogenated FT wax and the at least one residual hydrogenation catalyst particle through a catalyst filter to remove at least one residual hydrogenation catalyst particle and to create a filtered hydrogenated FT wax; (9) degassing the filtered hydrogenated FT wax; (10) subjecting the degassed, filtered hydrogenated FT wax to a vacuum distillation process in a short path distillation system to produce at least a first FT wax product having a congealing point between about 50° C and

about 70° C and a second FT wax product having a congealing point between about 85° C and about 100° C; and (11) sending the second FT wax product to the low-temperature, low-pressure hydrogenation reactor, for supplemental hydrogenation.

[0023] In one of more embodiments of the present disclosure, a system for hydrogenating an FT wax includes hydrogenation reactor for FT wax, designed for low temperature conditions and a pre-determined operating pressure. The hydrogenation reactor for FT wax has a mixing sub-system, a vent at the top for excess hydrogen, a first inlet to allow input of hydrogen gas under pressure, and a second inlet to allow input of the FT wax. The mixing subsystem is suitable for mixing the FT wax at a low temperature and the pre-determined operating pressure with a plurality of hydrogenation catalyst particle and hydrogen gas to produce a mixture. The hydrogenation reactor for FT wax also includes an outlet to allow egress of a fluid comprising the hydrogenated FT wax, after the mixing has stopped and the hydrogenation catalyst particles have been permitted to settle for a period of time. In one of more embodiments of the present disclosure, an apparatus for hydrogenating FT wax includes a hydrogenation reactor shell designed for low temperature and low pressure operating conditions and having a vent at the top for excess hydrogen, a first inlet in the hydrogenation reactor shell to allow hydrogen gas to enter the hydrogenation reactor shell under a low pressure, a second inlet suitable for an FT wax, a third inlet to allow input of hydrogen gas and an outlet to allow egress of a fluid including hydrogenated FT wax. The apparatus further includes a mixing mechanism inside the hydrogenation reactor shell, suitable for mixing a mixture comprised of hydrogenation catalyst particles with the FT wax and the hydrogen gas to facilitate hydrogenating the FT wax.

[0024] Other embodiments are also disclosed herein.

[0025] These and other embodiments, features and advantages will be apparent in the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] For a more detailed description of the present invention, reference will now be made to the accompanying drawings, wherein:

[0027] FIG. 1 is a block diagram, of a system in accordance with one or more embodiments of the present disclosure;

[0028] FIG. 2 is a more detailed representation of a low-temperature, low-pressure reactor and catalyst filter in accordance with one or more embodiments of the present disclosure;

[0029] FIG. 3 is a block diagram of a system in accordance with one or more embodiments of the present disclosure;

[0030] FIG. 4 is a flowchart for a process in accordance with one or more embodiments of the present disclosure, through a filtration step;

[0031] FIG. 5 is a flowchart for a process in accordance with one or more embodiments of the present disclosure, through a step separating the hydrogenated FT wax into two or more products.

[0032] None of the Figures are drawn to scale.

NOTATION AND NOMENCLATURE

[0033] As used herein, the term “low-pressure” with respect to a hydrogenation reactor means below about 350 psig. While pressures above this level are still in the scope of this disclosure, the pressure is typically limited to be below a pressure at which (given the anticipated temperatures and selected metallurgy) the flange rating jumps from ANSI Class 300 to ANSI Class 600, in order to keep costs low.

[0034] As used herein, the term “low-temperature” with respect to a hydrogenation reactor means under about 280° C. Ideally, in a “low temperature” hydrogenation reactor, the temperature of the FT wax within the hydrogenation reactor would be high enough so that the wax is liquid, but low enough that hydrocracking of the FT wax is not significant.

[0035] As used herein, the term “raw” with respect to a wax means a wax that has not been chemically treated.

[0036] As used herein, the term “sweet natural gas” means natural gas from which any excess sulfur or sulfur compounds such as H₂S has been previously removed.

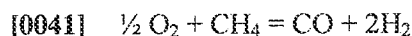
[0037] As used herein, the abbreviation “FT” stands for Fischer-Tropsch.

[0038] As used herein, the term “FT products” means hydrocarbon products produced from an FT reactor.

[0039] As used herein, the term “FT wax” means a wax made using a Fischer Tropsch process.

[0040] As used herein, the terms “reformed gas” or “syngas” means the effluent from a syngas conversion unit, such as (without limitation) a steam methane reformer, autothermal reformer, hybrid reformer, or partial oxidation reactor. Steam methane reformers do not use oxygen as part of the process; autothermal reformers do. Both use reformer catalysts. Hybrid reformers are a combination of steam methane reforming, as a first step, and an autothermal reforming with oxidation as a second step. Partial oxidation reactors are similar to autothermal

reformers, but do not include the use of a reformer catalyst. Partial oxidation reactors operate in accordance with the following equation:



(3) Steam reformers operate in accordance with the following equation:



[0043] Autothermal reformers perform both reforming and partial oxidation and so operate in accordance with both Equation (3) and Equation (4). This explanation is a bit simplified as some carbon dioxide may be made by SMR reactors and additional reactions take place in autothermal reformers and partial oxidation reactors.

[0044] As used herein, the term “hydrogenation” means a reduction reaction that results in an addition of hydrogen (usually as H_2). If an organic compound is hydrogenated, it becomes more “saturated.” Hydrogenation has many applications, but most people are familiar with the reaction as the one used to make liquid oils into semi-solid and solid fats. Hydrogenation is a form of hydrotreating, which also includes many other treatments. For example, hydrogenation may be done without hydrocracking, which is another form of hydrotreating, but hydrocracking includes hydrogenation.

DETAILED DESCRIPTION

[0045] FIG. 1 is a block diagram, of a Fischer-Tropsch (“FT”) wax hydrogenation system in accordance with one or more embodiments of the present disclosure. An input wax 10 and hydrogen gas (H_2) 15 are introduced into a low-temperature, low-pressure hydrogenation reactor 20 through first and second inlets 11, 16. The low-temperature, low-pressure hydrogenation reactor 20 contains hydrogenation catalyst particles 22. In one or more embodiments, the input wax 10 fills the low-temperature, low-pressure hydrogenation reactor 20 containing the hydrogenation catalyst particles 22 to a desired volume, leaving a vapor space 26 above the top 29 of the input wax 10 and the hydrogenation catalyst particles 22. The hydrogenation catalyst particles 22 may have been placed within the low-temperature, low-pressure hydrogenation reactor 20 through a catalyst inlet (not separately depicted in FIG. 1) of the low-temperature, low-pressure hydrogenation reactor 20. The input wax 10 comprises a Fischer-Tropsch (“FT”) wax, which may be raw, and preferably, an FT wax produced by using a synthetic gas (“syngas”) with a fixed bed FT reactor and a cobalt-based FT catalyst to turn the syngas into FT products. The input wax 10 may comprise in part olefins and oxygenates. The input wax 10 may be transported from an FT wax source, such as an FT plant, via, for example, a tanker truck

or a flowline. Preferably, the hydrogen gas 15 is added under pressure into the low-temperature, low-pressure hydrogenation reactor 20 after the input wax is in place. The addition of the hydrogen gas 15 pressurizes the interior of the low-temperature, low-pressure hydrogenation reactor 20 to the desired operating pressure. The hydrogen gas 15 may be delivered to the low-temperature, low-pressure hydrogenation reactor 20, for example, via tanker truck, tanks or via a flowline or from a hydrogen flowline. The first inlet 11 for the input wax 10 and a second inlet 16 for the hydrogen gas 15 may be placed anywhere on the low-temperature, low-pressure hydrogenation reactor 20, but it may be preferable to place both the first inlet 11 and the second inlet 16 in the lower half of the low-temperature, low-pressure hydrogenation reactor 20, to improve mixing. In other embodiments, the wax inlet and/or the hydrogen inlet may be placed at the top of the low-temperature, low-pressure hydrogenation reactor 20 or at other locations. (In one or more alternate embodiments, one inlet could be used for more than one inputs placed within the low-temperature, low-pressure hydrogenation reactor 20.) The low-temperature, low-pressure hydrogenation reactor 20 also includes a stirrer 24 or other type of mixing mechanism in its interior. The purpose of the stirrer is to keep the catalyst particles in suspension and to mix the hydrogen with the input wax 10. A more detailed view of a low-temperature, low-pressure hydrogenation reactor 20 that may be used in accordance with one or more embodiments of the present disclosure is depicted in FIG. 2.

[0046] The maximum size of the hydrogenation catalyst particles 22 used should generally be no greater than about 250 microns, so that the hydrogenation catalyst particles 22 may be suspended within the input wax 10 in the low-temperature, low-pressure hydrogenation reactor 20. If comparing the same volume of hydrogenation catalyst, hydrogenation catalyst particles with a smaller size will provide a greater surface area, meaning one can use less hydrogenation catalyst to treat a particular volume of wax. Examples of the hydrogenation catalyst particles 22 that may be used in accordance with one or more embodiments of the present disclosure include edible oil hydrogenation catalysts, such as skeletal nickel catalysts or palladium-containing catalysts. The hydrogenation catalyst particles 22 may comprise a single type of catalyst particles or may comprise a catalyst mixture of two or more types of catalyst particles. At least one of the types of catalyst particles in the catalyst mixture would be suitable for hydrogenation. In such an embodiment, one or more other types of catalyst particles making up the catalyst mixture could have other (non-hydrogenation) functions, such as oligomerization, isomerization, or cracking. For example, in an embodiment with a catalyst mixture having a hydrogenation catalyst and an oligomerization catalyst, a process might include a first step of oligomerization performed under a nitrogen-containing atmosphere with typical conditions of a low temp (about

150° C.) and moderate pressure (about 150 psig), followed by a second step of hydrogenation as previously described. In an embodiment with a catalyst mixture having a hydrogenation catalyst and an isomerization catalyst, a process might include simultaneously isomerizing and hydrogenating the FT wax at conditions as previously described for hydrogenation. In an embodiment with a catalyst mixture having a hydrogenation catalyst and a hydrocracking catalyst, a process might include a first step of hydrocracking (which includes hydrogenation) at temperatures above 300° C. (for example, 350° C.) with hydrogen at a pressure of 150-350 psig, followed by a second step of finishing hydrogenation at previously described hydrogenation conditions.

[0047] Referring again to FIG. 1, the stirrer 24 mixes the hydrogen 15 and input wax 10 with the hydrogenation catalyst particles 22 within the low-temperature, low-pressure hydrogenation reactor 20 under operating conditions to form a slurry or mixture. The stirrer 24 may comprise for example a gas induction impeller, having a motor and gear box 17 and a sealing mechanism 18 or a liquid pump around with an eductor, to efficiently mix hydrogen 15 with the input wax 10 and hydrogenation catalyst particles 22. Other mixing or stirring mechanisms may also be used. For example, see US Patent No. 7,815,196, entitled "Magnetic Seal Assembly," and gas induction reactors available from Omega Kemix Pvt. Ltd:

<http://www.okpl.com/gas-induction-reactors.php>

[0048] Another example of a stirrer in accordance with one or more embodiments of the present disclosure includes a separate device to circulate hydrogen 15 to a sparger, although this option may be more expensive than previously mentioned alternatives.

[0049] In a hydrogenation reaction process, as the hydrogen 15 is mixed as part of the slurry with the hydrogenation catalyst particles 22 and the input wax 10, the hydrogen 15 saturates carbon double bonds of the olefins and the carbon-oxygen bonds of the oxygenates within the input wax 10 to form paraffins and water. The hydrogenation reaction process of the present disclosure may be performed in a batch mode, in a semi-batch mode (having staged additions of ingredients and removal of product) or, in one or more embodiments, may be performed in a continuous mode. A typical operating temperature for the low-temperature, low-pressure hydrogenation reactor 20 may range from about 100° to about 280° C., preferably, from about 150° to about 250° C., and more preferably from about 200° to about 230° C. Ideally, the temperature range selected would be high enough that the input wax 10 is in a liquid form, but low enough that any hydrocracking that might incidentally take place is limited to a desired, very low level or avoided.

[0050] A typical operating pressure for the low-temperature, low-pressure hydrogenation reactor 20 may range from about 0 psig to about 350 psig, preferably from about 50 psig to about 350 psig, and more preferably from about 250 psig to about 350 psig. Although the low operating pressure may provide a significant cost advantage, higher pressures could be also used, with equipment designed to handle the high pressures.

[0051] Continuing to refer to FIG. 1, a hydrogen gas vent 28 allows excess hydrogen to pass from the vapor space 26 in the low-temperature, low-pressure hydrogenation reactor 20 to a flowline to a desired destination. As examples, the hydrogen gas vented from the low-temperature, low-pressure hydrogenation reactor 20 may be sent to a burner for downstream process heating, recycled such as via a compressor or to a flare for disposal. When the hydrogenation reaction process reaches a desired level of completion, mixing stops to allow the hydrogenation catalyst particles 22 to separate from the now hydrogenated FT wax. Once a desired period for settling has passed, the hydrogenated wax 25, , passes through a reactor outlet 24 of the low-temperature, low-pressure hydrogenation reactor 20. The hydrogenated wax 25 passing through the reactor outlet 24 may contain some hydrogenation catalyst particles 22 that have not settled out, such as fine hydrogenation catalyst particles. From the reactor outlet 24, the hydrogenated wax 25 passes via a first hydrogenated wax flowline to a catalyst filter 30. As the hydrogenated wax 25 flows through the catalyst filter 30, the catalyst filter 30 removes hydrogenation catalyst particles 22 from the hydrogenated wax 25. A back-flush fluid 32 enters the catalyst filter 30. The backflush fluid and removed catalyst particles 36 is recycled via a backflush flowline to a third inlet in the low-temperature, low-pressure hydrogenation reactor 20. In one or more embodiments, the back-flush fluid 32 comprises the input wax 10 to the hydrogenation reactor, and the third inlet is the same as the first inlet. A filtered hydrogenated wax 35 may pass through a second hydrogenated wax flowline to a filtered hydrogenated wax storage tank 40 or other storage container.

[0052] The filtered, hydrogenated wax 35 may be considered a product. However, the filtered, hydrogenated wax 35 might have too wide a distribution of carbon numbers to be appropriate for typical applications. Accordingly, it may be desirable to split the filtered, hydrogenated wax 35 into two or more products with properties conforming to market requirements. In the embodiment illustrated in FIG. 1, the filtered hydrogenated wax 35 is split into two products, a first wax product 70, which may have a medium melting point, and a second wax product 80, which may have a high melting point. In one or more embodiments

of the present disclosure, the congeal point for the first wax product 70 may be about 60 ° C., while the congeal point for the second wax product 80 may be about 95 ° C.

[0053] Referring back to FIG. 1, from the filtered hydrogenated wax storage tank 40, the filtered hydrogenated wax 35 passes through a third hydrogenated wax flowline optionally to a heater 50, where the filtered hydrogenated wax 35 is pre-heated in preparation for a short path distillation step. In other embodiments, the temperature of the filtered hydrogenated wax 35 may be such that additional heating is not required. For example, if the temperature of the filtered wax is already at about 200-250° C., then the heating step may not be needed. In FIG. 1, the heated, filtered hydrogenated wax 55 may pass through a fourth hydrogenated wax flowline to a short path distillation system 60, where the heated, filtered hydrogenated wax 55 is separated into the first wax product 70, having a medium melting point, and the second wax product 80, having a high melting point. A vacuum system (not separately depicted) maintains a low absolute pressure within the short path distillation system 60. In other embodiments, other vacuum distillation methods or additional short path distillation stages may be used to separate the heated, filtered hydrogenated wax 55 into two or more wax products. In one or more embodiments of the present disclosure, three or more wax products are made. A non-condensable gas 62 passes through a port in the short path distillation system 60 and into a vacuum flowline 65 to the vacuum system. The use of the short path distillation system (at vacuum conditions) keeps required temperatures as low as possible and the residence time at elevated temperature as short as possible. This avoids secondary reactions (such as cracking) which may cause the quality of the FT wax products to deteriorate. Nevertheless, it is possible that the second wax product 80 (having the high melting point) may require a second pass hydrogenation, which could employ the same equipment as the first pass hydrogenation process described above. This is simple to implement as the process may be conducted as a batch operation and consequently the same equipment could process alternate batches of raw wax and batches of heavy wax in campaigns.

[0054] In one or more embodiments, the short path distillation system may comprise a plurality of wiped film evaporators and/or short path distillation units or a combination of both. For example, the short path distillation system may include a wiped film evaporator, followed by two short path distillation units in series.

[0055] FIG. 2 presents a more detailed representation of a low-temperature, low-pressure hydrogenation reactor 200 and a catalyst filter 230 in accordance with one or more embodiments of the present disclosure. In the embodiment of FIG. 2, the FT wax enters the catalyst filter 230 from an FT wax flowline 202 and through first valve 203 as a back-flush fluid. The FT wax leaves the catalyst filter 230 carrying recovered hydrogenation catalyst particles, through a second valve 234 and a back-flush flowline 233 and enters the low-temperature, low-pressure hydrogenation reactor 200. The low-temperature, low-pressure hydrogenation reactor 200 includes at least one baffle 208 to enhance mixing. The low-temperature, low-pressure hydrogenation reactor 200 also includes a catalyst inlet 209, which can be used to load the catalyst or to add make-up catalyst, and a third valve 204. When the FT wax enters the low-temperature, low-pressure hydrogenation reactor 200, the low-temperature, low-pressure hydrogenation reactor 200 preferably already contains a plurality of hydrogenation catalyst particles 222. As the FT wax 210 is added to the low-temperature, low-pressure hydrogenation reactor 200, the FT wax 210 fills a voidage 227, which comprises space (or porosity) between the hydrogenation catalyst particles 222 within the low-temperature, low-pressure hydrogenation reactor 200 until a desired level 221 is reached, leaving a vapor space 226 inside the low-temperature, low-pressure hydrogenation reactor 220.

[0056] Continuing to refer to FIG. 2, after the catalyst and FT wax are in place in the low-temperature, low-pressure hydrogenation reactor 200 to a desired level 221, hydrogen gas can be added under pressure through a hydrogen inlet 216, and a fourth valve 205. The addition of the hydrogen gas pressurizes the interior of the low-temperature, low-pressure hydrogenation reactor 200 to a desired operating pressure. The vapor space 226 would contain hydrogen gas. A hollow-shaft gas induction impeller 224 having a hollow shaft 212, an impeller blade 213, a motor and gear box 217 and a sealing mechanism 218 stirs the FT wax, the hydrogen gas and the hydrogenation catalyst particles 222, creating a mixture and allowing a hydrogenation reaction to take place, under operating conditions of a temperature between about 80° C. and about 280° C. and a pressure selected between about atmospheric pressure and about 350 psi. Hydrogen from the vapor space 226 enters one or more ports 223 of the gas induction impeller 224, and passes through the hollow shaft 212 and out of one or more outlets 214 preferably in the impeller blade 213. As the gas induction impeller 224 turns and mixes the hydrogen gas with the FT wax and the hydrogenation catalyst particles, the mixing facilitates dissolving the hydrogen gas into a mixture 201. The surface area of the

hydrogenation catalyst particles 222 facilitates the transfer of hydrogen to molecules of the olefins and oxygenates of the FT wax 210 at the molecular level. The hydrogen gas forms bubbles, which rises through the mixture 201 to the vapor space 226, from which the hydrogen gas enters the hollow shaft 212. A vent (not depicted in FIG. 2), at or near the top of the low-temperature, low-pressure hydrogenation reactor 220 allows excess hydrogen to escape, at times, through a vent flowline. For example, excess hydrogen may escape through the vent flowline intermittently or at the end of a batch treatment.

[0057] Referring again to FIG. 2, once the hydrogenation reaction has occurred, the mixing stops and the hydrogenation catalyst particles are allowed to settle. After the settling step, nitrogen may be introduced to the low-temperature, low-pressure hydrogenation reactor 200 to remove the hydrogen gas and to move the hydrogenated wax to pass through a dip tube 227 to a hydrogenated wax flowline 228. The hydrogenated wax would likely contain some residual hydrogenation catalyst particles that did not settle out during the settling period. As the hydrogenated wax leaves the low-temperature low-pressure reactor 200, the level 221 drops and the vapor space 226 expands. In the embodiment depicted in FIG. 2, a heel 229 comprised of hydrogenated wax and catalyst particles is depicted as having been left in the low-temperature, low-pressure hydrogenation reactor 200, as the top of the heel 229 may be below the entry into the dip tube 227. In other embodiments, a heel may not be present. In a typical operation, the heel may be about 10% of the volume of the FT wax from a particular batch, but this may vary. In embodiments having a batch operation, the heel 229 may be mixed with and processed with the next batch of FT wax and hydrogen introduced into the low-temperature, low-pressure hydrogenation reactor 200.

[0058] From the hydrogenated wax flowline 228, the hydrogenated wax (with the hydrogenated catalyst particles the hydrogenated wax may be carrying) passes through a fifth valve 231 and into the catalyst filter 230. In the embodiment of FIG. 2, the catalyst filter 230 is a single candle style filter. In alternate embodiments, the catalyst filter may comprise more than a single candle-style filter. In alternate embodiments, other the catalyst filter may comprise other types of filters. Under nitrogen pressure, the hydrogenated wax (with the hydrogenated catalyst particles) passes through the candle filter 232, which recovers the hydrogenated catalyst particles. The filtered hydrogenated wax passes through a sixth valve 239 and a filtered hydrogenated wax flowline 237 to storage (not depicted in FIG. 2). As described above, fresh FT wax can be used as a back-flush fluid to return the recovered hydrogenated catalyst particles to the low-temperature, low-pressure hydrogenation reactor 200.

[0059] While FIG. 2 is one example of low-temperature, low-pressure hydrogenation reactor 200 that may be used with the present invention, many other types of low-temperature, low-pressure hydrogenation reactors, with different means for stirring or otherwise mixing the hydrogen gas, the inlet wax and the catalyst particles may also be used.

[0060] FIG. 3 is a block diagram of one or more embodiments in accordance with the present disclosure. An input FT wax is sent from tankers (not depicted) via a raw wax flowline 300 to a raw wax inlet 302 for a raw wax storage tank 301. Preferably, the input FT wax is an FT wax produced using a natural gas feedstock to create a syngas and a fixed bed FT reactor and a cobalt-based FT catalyst to turn the syngas to FT products, including the input FT wax. In other embodiments, other feedstocks could be used to create the syngas. The input FT wax may contain one or more olefins and/or oxygenates with double carbon bonds. The input FT wax is sent from a raw wax outlet 304 in the raw wax storage tank 301 through a first input flowline 305 to a first hydrogenator inlet 322 of a batch hydrogenator 320. The batch hydrogenator 320 contains catalyst particles (not depicted), which has been added through the first hydrogenator inlet 322, the second hydrogenator inlet 323 or a separate catalyst inlet (not depicted). The input FT wax is added into the batch hydrogenator 320 until a desired volume is reached, leaving a vapor space (not depicted) within the batch hydrogenator 320 above the top of the input FT wax and the catalyst particles. As an example, the batch hydrogenator 320 may treat 5000 gallons of input FT wax in a single batch. The batch hydrogenator 320 also includes a stirrer (not depicted) or other type of mixing mechanism in its interior to mix the input FT wax, the hydrogen and the catalyst particles. The FT wax may be at a desired operating temperature when it enters the batch hydrogenator (with or without heating prior to entering the batch hydrogenator) or the batch hydrogenator 320 may include a heating element, such as a jacket, to bring the FT wax to the desired operating temperature. Alternatively, a heat exchanger 370 may be used to heat the FT wax to the desired operating temperature. A fresh hydrogen gas feed is introduced under pressure from a hydrogen flowline 306 through a second hydrogenator inlet 323 in the batch hydrogenator 320, increasing the pressure of the batch hydrogenator 320 to a desired operating pressure.

[0061] Continuing to refer to FIG. 3, at operating conditions, a mixing system within the batch hydrogenator 320 mixes the hydrogen and input FT wax with the catalyst particles, creating a wax/catalyst/hydrogen mixture. The mixing system may comprise, for example, a hollow-shaft gas induction impeller. Over a period of, for example, four hours, a hydrotreating reaction, specifically, a hydrogenating reaction takes place, wherein the hydrogen reacts with the input FT wax to saturate the carbon double bonds of the olefins and

break the carbon-oxygen bond of the oxygenates to form paraffins and water. A typical operating temperature for the batch hydrogenator 320 ranges from about 150° to about 280° C. A typical operating pressure for the batch hydrogenator 320 ranges from about 50 psi to about 350 psi. The hydrogenating reaction is slightly exothermic (i.e., heat-creating). Circulating some of the wax/catalyst//hydrogen mixture through the (optional) external heat exchanger 370, as in FIG. 3, may be used heat (as previously mentioned) or, in some embodiments, to cool the wax/catalyst /hydrogen mixture and return the wax/catalyst /hydrogen mixture to the batch hydrogenator 320. If a cooling media is needed, the cooling media may be a closed loop thermal fluid that stays above the melting point of the wax and in turn is to be indirectly water cooled. Alternatively, a cooling jacket may be used on the batch hydrogenator 320. In the one or more embodiments of FIG. 3, a portion of the wax/catalyst /hydrogen mixture may be removed from the batch hydrogenator 320 through a first hydrogenator outlet 325 into a first mixture flowline 371, which carries the wax/catalyst /hydrogen mixture to a heat exchanger inlet 372. The portion of the wax/catalyst /hydrogen mixture passes through the heat exchanger inlet 372 into a heat exchanger 370, where the portion of the wax/catalyst /hydrogen mixture is heated (or, in alternate embodiments, is cooled). The heated (or, in alternate embodiments, cooled) portion of the wax/catalyst /hydrogen mixture is returned to the batch hydrogenator 320 by passing through a heat exchanger outlet 374, a second mixture flowline 375 and a third hydrogenator inlet 326.

[0062] Referring again to FIG. 3, a hydrogenator gas vent 324 of the batch hydrogenator 320 may allow excess hydrogen to pass from the vapor space through a first vent gas flowline 328 to a desired destination. As examples, the vented excess hydrogen may be sent to a burner for downstream process heating or to a flare for disposal. When the hydrogenating reaction process reaches a desired level of completion, a hydrogenated FT wax (which likely contains some catalyst particles) passes through a second hydrogenator outlet 327 of the batch hydrogenator 320 and through a first hydrogenated wax flowline 332 into a catalyst filter 330 via a filter inlet 333. As the hydrogenated FT wax flows through the catalyst filter 330, the catalyst filter 330 removes catalyst particles from the hydrogenated FT wax, creating a filtered hydrogenated FT wax. A first backflush fluid with removed catalyst particles is recycled out of the catalyst filter via a first backflush outlet 334. The first backflush fluid with removed catalyst particles is sent via a first backflush flowline 335 to a fourth hydrogenator inlet 329 in the batch hydrogenator 320, where the first backflush fluid with

removed catalyst particles can be mixed with the next batch of raw FT wax and hydrogen to be treated.

[0063] Looking again to FIG. 3, the filtered hydrogenated FT wax may pass from the catalyst filter 330 through a filter outlet 336 via a first filtered wax flowline 337 to a second tank inlet 342 of a hydrogenated wax storage tank 340 or other storage container. A second backflush that comprises filtered hydrogenated FT wax may be sent from the hydrogenated wax storage tank 340 to a second filter inlet 338 of the catalyst filter 330 via a second backflush outlet 344 and a second backflush flowline 345. From the hydrogenated wax storage tank 340, the filtered hydrogenated FT wax 335 passes through a hydrogenated wax storage tank outlet 346 and a second filtered wax flowline 348 to an optional heater 350 via a heater inlet 352. If needed, the heater 350 heats the filtered hydrogenated FT wax, creating a heated, filtered hydrogenated FT wax. In the one or more embodiments depicted in FIG. 3, the heated, filtered hydrogenated FT wax passes from the heater 350 via a heater outlet 354 and through a third filtered wax flowline 355 to a degasser 390, which removes a vent gas from the heated, filtered, hydrogenated FT wax, creating a de-gassed, heated, filtered, hydrogenated FT wax. The vent gas leaves the degasser 390 through a degasser vent 394 and passes through a vent flowline 395 to a vacuum system (not depicted in FIG. 3) or other desired location.

[0064] In the one or more embodiments of FIG. 3, additional processing is desired, so the de-gassed, heated, filtered, hydrogenated FT wax flows through a fifth filtered wax flowline 398 to a short path distillation system 360, where the de-gassed, heated, filtered, hydrogenated FT wax is separated into a first wax product and second wax product, each of which are sent via a first distillation system outlet 365 and a second distillation system outlet 367 to separate storage (not depicted in FIG. 3) via separate first and second product flowlines 372, 382. A distillation vent gas passes through a short-path distillation vent 363 and via a connection flowline 364 into the vent flowline 395 to the vacuum system or other desired location.

[0065] FIG. 4 is a flowchart for a process in accordance with one or more embodiments of the present disclosure. Unless already in place from a previous operation, hydrogenating catalyst particles are placed 405 within a low-temperature, low-pressure hydrogenation reactor having a mixing sub-system and a vent at the top for excess hydrogen. (Typically, 99 to almost 100% of the hydrogenating catalyst particles may be retained or recovered from a previous operation.) An input FT wax at a desired temperature is placed 410, up to a predetermined level, within the low-temperature, low-pressure hydrogenation reactor, leaving

a vapor space above the predetermined level. Hydrogen gas is added **415** under pressure, bringing the low-temperature, low-pressure hydrogenation reactor up to a desired operating pressure. Under operating conditions including a low temperature and a low pressure, the input FT wax, the hydrogen gas and the hydrogenating catalyst particles are mixed **420** together to create a mixture using the mixing subsystem. The mixing is intended to suspend the hydrogenating catalyst particles in the mixture and to disperse bubbles of hydrogen gas throughout the mixture. The mixing subsystem may comprise, for example, a hollow-shaft gas induction impeller. The mixing preferably continues until a hydrogenating reaction has taken place within the mixture. Typical operating conditions for the hydrogenation reactor include a temperature between about 80° C. and about 280° C. and a pressure selected between about atmospheric pressure and about 350 psi. The mixing is stopped **425** to allow the hydrogenating catalyst particles to settle from the mixture. A hydrogenated FT wax, which may include non-settled ("residual") hydrogenating catalyst particles, is removed **430** through an outlet from the low-temperature, low-pressure hydrogenation reactor. The hydrogenated FT wax and the residual hydrogenating catalyst particles are passed **435** through a catalyst filter to remove the residual hydrogenating catalyst particles and to create a filtered hydrogenated FT wax. The filtered hydrogenated wax may be stored **440** prior to further processing or transportation.

[0066] FIG. 5 is a flowchart for a process in accordance with one or more embodiments of the present disclosure. Hydrogenation catalyst particles are placed **505** within a low-temperature, low-pressure hydrogenation reactor having a mixing sub-system and a vent at the top for excess hydrogen. Step **505** may be skipped if sufficient hydrogenation catalyst particles are already in place, for example in a heel left from a previous operation. An input FT wax at a desired temperature is placed **510**, up to a predetermined level, within the low-temperature, low-pressure hydrogenation reactor, leaving a vapor space above the predetermined level. If needed, the FT wax may be heated before placed within the low-temperature, low-pressure hydrogenation reactor. In one or more embodiments, the FT wax is heated to the desired temperature after being placed in the low-temperature, low-pressure hydrogenation reactor, such as through use of a heat exchanger system. Hydrogen gas under pressure is added **515** to the low-temperature, low-pressure hydrogenation reactor, bring the low-temperature, low-pressure hydrogenation reactor up to a desired operating pressure. Under operating conditions including a low temperature and a low pressure, the input FT wax, the hydrogen gas and the hydrogenating catalyst particles are mixed **520** together to

create a mixture using the mixing subsystem. The mixing preferably continues until the FT wax is hydrogenated to a desired extent. In a preferred embodiment, typical operating conditions for the hydrogenation reactor include a temperature between about 80° C. and about 280° C. and a pressure selected between about atmospheric pressure and about 350 psi. The pressure is preferably so limited to allow use of ANSI 300 flanges, but higher pressures could be used. The mixing stops and the low-temperature, low-pressure hydrogenation reactor is depressurized 525. An inert gas, such as nitrogen, is added 530 to the low-temperature, low-pressure hydrogenation reactor at a low pressure, preferably about 50 psig, to flush the hydrogen gas from the low-temperature, low-pressure hydrogenation reactor. The hydrogenation catalyst particles are allowed 535 to settle for a pre-determined time.

[0067] The hydrogenated FT wax, which may include residual hydrogenation catalyst particles, is removed 540 from the low-temperature, low-pressure hydrogenation reactor. A heel of settled catalyst particles and some hydrogenated FT wax may be left within the low-temperature, low-pressure hydrogenation reactor. The hydrogenated FT wax and residual hydrogenation catalyst particles are passed 545 through a catalyst filter to remove the residual hydrogenation catalyst particles and to create a filtered hydrogenated FT wax. The filtered hydrogenated FT wax may be stored 550 if further processing is not immediately desired. When further processing is desired, the stored, filtered hydrogenated FT wax is released 555 from storage. If needed, the filtered hydrogenated FT wax may be heated 560 in order to help the filtered hydrogenated FT wax to flow. The filtered hydrogenated FT wax next passes to a degasser, where the heated, filtered hydrogenated FT wax is de-gassed 570. The gas removed from the filtered hydrogenated FT wax passes through a degasser vent to a vacuum system or other desired location. In one or more embodiments, gas leaving the degasser is cooled in a condenser or cold trap, which recovers some light liquids with the non-condensable material passing to a first stage of the vacuum system. The discharge from the first stage vacuum pump goes to flare or other suitable location.

[0068] Referring again to refer to FIG. 5, the de-gassed, filtered hydrogenated FT wax is separated 580 into at least two FT wax products, including a lower melting point FT wax product and a higher melting point FT wax product. The separation may be accomplished using a short path distillation unit or by other separation systems. The lower melting point FT wax product is sent 582 to storage. The higher melting point FT wax product is sent 584 to the low-temperature, low-pressure hydrogenation reactor for additional hydrogenation. In alternate embodiments, the higher melting point FT wax product is sent to storage. In

alternate embodiments, the higher melting point FT wax product is sent to a second low temperature, low pressure hydrogenation reactor for additional hydrogenation. In alternate embodiments, the de-gassed, filtered, hydrogenated FT wax is separated into at least three FT wax products.

[0069] While some preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations. The use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, and the like.

[0070] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims that follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the preferred embodiments of the present invention. The inclusion or discussion of a reference is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent they provide background knowledge; or exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A method of hydrogenating a Fischer-Tropsch ("FT") wax, comprising:
 - a. placing an input FT wax up to a predetermined level within a low-temperature hydrogenation reactor, having a mixing sub-system and a vent at the top and containing hydrogenation catalyst particles, leaving a vapor space above the predetermined level;
 - b. adding hydrogen gas under pressure to the low-temperature hydrogenation reactor, bringing the low-temperature hydrogenation reactor up to a predetermined operating pressure;
 - c. mixing the input FT wax, the hydrogen gas and the hydrogenation catalyst particles together using the mixing subsystem under operating conditions including a low temperature and the pre-determined operating pressure to create a mixture, thus permitting the FT wax to become hydrogenated;
 - d. stopping the mixing and allowing the hydrogenation catalyst particles to settle for a period of time; and
 - e. removing the hydrogenated FT wax from the low-temperature hydrogenation reactor.
2. The method of Claim 1, wherein the removed hydrogenated FT wax includes a plurality of residual hydrogenation catalyst particles and further comprising:
 - f. sending the hydrogenated FT wax with the residual hydrogenation catalyst particles through a catalyst filter to remove at least a portion of the residual hydrogenation catalyst particles and to create a filtered hydrogenated FT wax.
3. The method of Claim 1, wherein the removed hydrogenated FT wax includes residual hydrogenation catalyst particles and further comprising passing the removed hydrogenated FT wax through a screen mesh in an outlet of the low-temperature, low-pressure hydrogenation reactor, the screen mesh designed to exclude the residual hydrogenation catalyst particles.
4. The method of Claim 1, further comprising:
 - g. storing the filtered hydrogenated FT wax.

5. The method of Claim 4, further comprising:
 - h. heating the filtered hydrogenated FT wax.
6. The method of Claim 1, further comprising:
 - i. pre-heating the FT wax prior to placing the FT wax as the input FT wax in the low temperature hydrogenation reactor.
7. The method of Claim 1, wherein the operating pressure is low and the low temperature hydrogenation reactor comprises a low-temperature, low-pressure hydrogenation reactor.
8. The method of Claim 1, further comprising:
 - j. removing the mixture from the low-temperature hydrogenation reactor;
 - k. sending the mixture through a heat exchanger to adjust the temperature of the mixture; and
 - l. returning the temperature-adjusted mixture to the low-temperature hydrogenation reactor.
9. The method of Claim 1, further comprising:
 - h. subjecting the filtered hydrogenated FT wax to a vacuum distillation process to produce at least a first FT wax product having a first range of carbon numbers and a second FT wax product having a second range of carbon numbers.
10. The method of Claim 9, wherein the first FT wax product has a congealing point between about 50° C and about 70° C.
11. The method of Claim 9, wherein the second FT wax product has a melting point between about 85° C and about 100° C.
12. The method of Claim 11, further comprising sending the second FT wax product to the low-temperature hydrogenation reactor, for supplemental hydrogenation.

13. The method of Claim 9, wherein the vacuum distillation comprises a short path distillation system.
14. The method of Claim 9, wherein the short path distillation system includes at least one wiped film evaporator and at least one short path distillation unit.
15. The method of Claim 2, wherein the removed, residual hydrogenation catalyst particles are recycled to the low-temperature hydrogenation reactor using a back-flush fluid.
16. The method of claim 15, wherein the back-flush fluid comprises FT wax to be used as the input FT wax.
17. The method of Claim 1, wherein the hydrogenation catalyst particles have an average size of less than about 250 microns.
18. The method of Claim 1, wherein the input FT wax was produced using a natural gas feedstock to create a syngas and using an FT reactor and a cobalt-based catalyst to change the syngas into FT products, including the input FT wax.
19. The method of Claim 1, wherein the hydrogenation catalyst particles comprise a palladium-based catalyst.
20. The method of Claim 1, wherein the hydrogenation catalyst particles comprise a skeletal nickel-based catalyst.
21. The method of Claim 2, wherein the catalyst filter comprises at least one catalyst candle filter suitable for use in filtering catalysts from hydrogenated edible oils.
22. The method of Claim 1, further comprising, after step b:

- (1) passing a fluid including the input FT wax from the low-temperature, low-pressure hydrogenation reactor to a heat exchanger to adjust the temperature of the FT wax; and
 - (2) returning the fluid at the adjusted temperature to the low-temperature, low-pressure hydrogenation reactor.
23. The method of Claim 1, wherein the step of removing the hydrogenated FT wax from the low-temperature hydrogenation reactor is accomplished while leaving a heel inside the low-temperature reactor.
24. The method of Claim 7, wherein the low pressure for the operating conditions is below about 350 psig.
25. The method of Claim 24, wherein the low pressure for the operating conditions is below about 100 psig.
26. The method of Claim 1, wherein the low temperature for the operating conditions is below about 280° C.
27. The method of Claim 26, wherein the low temperature for the operating conditions is below about 200° C.
28. The method of Claim 1, wherein the hydrogenation catalyst particles comprise a catalyst mixture of at least two catalysts.
29. The method of Claim 28, wherein at least one of the types of catalysts in the catalyst mixture has a function other than hydrogenation.
30. A method of hydrogenating a Fischer-Tropsch ("FT") wax, comprising:
- a. placing an input FT wax, at a low temperature of below about 200° C, up to a predetermined level within a low-temperature, low-pressure hydrogenation reactor leaving a vapor space above the predetermined level, the low-temperature, low-pressure hydrogenation reactor having a vent at the top,

- containing hydrogenation catalyst particles, and including a mixing subsystem comprising a motor and gear box, a seal, a hollow shaft gas impeller system;
- b. adding hydrogen gas under pressure to the low-temperature low-pressure hydrogenation reactor, bringing the low-temperature low-pressure hydrogenation reactor up to a pre-determined low operating pressure of below about 100 psig;
 - c. mixing the input FT wax, the hydrogen gas and the hydrogenation catalyst particles together using the mixing subsystem under operating conditions including a low temperature and the pre-determined operating pressure to create a mixture, thus permitting the FT wax to become hydrogenated;
 - d. depressurizing the low-temperature low-pressure hydrogenation reactor;
 - e. flushing the hydrogen gas from the vapor space of the low-temperature low-pressure hydrogenation reactor using nitrogen at a low pressure;
 - f. stopping the mixing and allowing the hydrogenation catalyst particles to settle for a period of time, leaving at least one residual hydrogenation catalyst particle suspended in the hydrogenated FT wax;
 - g. removing at least a portion of the hydrogenated FT wax and the at least one residual hydrogenation catalyst particle from the low-temperature, low-pressure hydrogenation reactor through a dip tube by adding nitrogen under a low pressure to the low-temperature, low-pressure hydrogenation reactor;
 - h. sending the removed hydrogenated FT wax and the at least one residual hydrogenation catalyst particle through a catalyst filter to remove at least one residual hydrogenation catalyst particle and to create a filtered hydrogenated FT wax;
 - i. degassing the filtered hydrogenated FT wax;
 - i. subjecting the degassed, filtered hydrogenated FT wax to a vacuum distillation process in a short path distillation system to produce at least a first FT wax product having a a congealing point between about 50° C and about 70° C and a second FT wax product having a congealing point between about 85° C and about 100° C; and
 - j. sending the second FT wax product to the low-temperature, low-pressure hydrogenation reactor, for supplemental hydrogenation.

31. The method of Claim 30, further comprising:

- k. removing the mixture from the low-temperature, low-pressure hydrogenation reactor;
- l. sending the mixture through a heat exchanger to adjust the temperature of the mixture; and
- m. returning the temperature-adjusted mixture to the low-temperature, low-pressure hydrogenation reactor.

32. A system for hydrogenating a Fischer-Tropsch ("FT") wax, the system comprising:

- a. a hydrogenation reactor for FT wax designed for operating conditions of a low temperature and a pre-determined pressure, the hydrogenation reactor for FT wax comprising:
 - i. a mixing sub-system, wherein the mixing subsystem is suitable to mix the FT wax with a plurality of hydrogenation catalyst particles and the hydrogen gas at the operating conditions to produce a mixture and allow the FT wax to become hydrogenated;
 - ii. a vent at the top for excess hydrogen;
 - iii. a first inlet to allow input of the hydrogen gas under pressure, which brings the hydrogenation reactor up to the pre-determined pressure;
 - iv. a second inlet for the FT wax; and
 - v. an outlet to allow egress of a fluid comprising the hydrogenated FT wax after the mixing has stopped and the hydrogenation catalyst particles have been permitted to settle for a period of time.

33. The system of Claim 32, wherein the low-temperature hydrogenation reactor for FT wax comprises a low-temperature, low-pressure hydrogenation reactor.

34. The system of Claim 32, further comprising:

- b. a catalyst filter to remove residual hydrogenation catalyst particles from the hydrogenated FT wax to create a filtered, hydrogenated FT wax, the catalyst filter having a filter inlet fluidly connected to the outlet of the hydrogenation reactor, a first outlet for egress of the filtered, hydrogenated FT wax, an inlet

for backflush fluid and a back-flush outlet for egress of the back-flush fluid and removed residual hydrogenation catalyst particles, the back-flush outlet being fluidly connected with an inlet of the hydrogenation reactor.

35. The system of Claim 34, further comprising:

- c. a storage tank for storing the filtered, hydrogenated FT wax, having a tank inlet fluidly connected to the filter outlet of the catalyst filter and having a tank outlet.

36. The system of Claim 32, wherein the mixing sub-system comprises a gas induction system having a motor and gear box, a seal, a hollow shaft with a port positioned to be within the vapor space to allow hydrogen into the hollow shaft, an impeller blade connected to the lower end of the hollow shaft and having one or more outlets to allow hydrogen gas to pass from the hollow shaft into the mixture.

37. The system of Claim 32, further comprising:

- d. a heater for pre-heating the FT wax to a low temperature upstream of the hydrogenation reactor.

38. The system of Claim 32, further comprising:

- e. a vacuum distillation sub-system to produce from the heated, filtered FT hydrogenated wax a first FT wax product having a congealing point within a first range of congealing points and a second FT wax product having congealing point within a second range of congealing points, the vacuum distillation sub-system having a subsystem inlet and a sub-system outlet; and
- f. a degasser, placed upstream of the vacuum distillation sub-system inlet to remove excess gas from the heated, filtered FT hydrogenated wax, wherein the degasser includes a degasser input and includes a degasser output that is fluidly connected to the subsystem inlet of the vacuum distillation sub-system.

39. The system of Claim 38, wherein the vacuum distillation sub-system comprises at least one wiped film evaporator and at least two short path distillation units.

40. The system of Claim 33, wherein the operating conditions for the low-temperature, low-pressure hydrogenation reactor include a pressure below about 350 psig and a temperature below about 280° C.
41. The system of Claim 32, further comprising:
- g. a heat exchanger fluidly connected to the hydrogenation reactor to permit removal of a portion of a fluid including the FT wax from the hydrogenator, adjusting the temperature of the fluid, and returning the fluid to the hydrogenation reactor.
42. An apparatus for hydrogenating a Fischer-Tropsch ("FT") wax, the apparatus comprising:
- a. a hydrogenation reactor shell designed for low temperature and low pressure operating conditions and having a vent at the top for excess hydrogen;
 - b. a first inlet in the hydrogenation reactor shell to allow hydrogen gas to enter the hydrogenation reactor shell under a low pressure;
 - c. a second inlet suitable for an FT wax;
 - d. a mixing mechanism inside the hydrogenation reactor shell, suitable for mixing a mixture comprised of hydrogenation catalyst particles, the FT wax at a low temperature and a hydrogen gas to facilitate hydrogenating the FT wax.
43. The apparatus of Claim 42, further comprising:
- d. a third inlet in the hydrogenation reactor shell to allow input of catalyst particles; and
 - e. an outlet to allow egress of a fluid comprising a hydrogenated FT wax.
44. The apparatus of Claim 42, wherein low temperature and low pressure operating conditions include a pressure below about 350 psig and a temperature below about 280° C.
45. The apparatus of Claim 42, wherein low temperature and low pressure operating conditions include a pressure below about 120 psig and a temperature below about 100° C.

46. The apparatus of Claim 43, further comprising:

- f. a heat exchanger system fluidly connected to the hydrogenation reactor shell to permit removal of a portion of the mixture from the hydrogenator, adjusting the temperature of the mixture, and returning the temperature-adjusted mixture to the hydrogenator.

FIG. 1

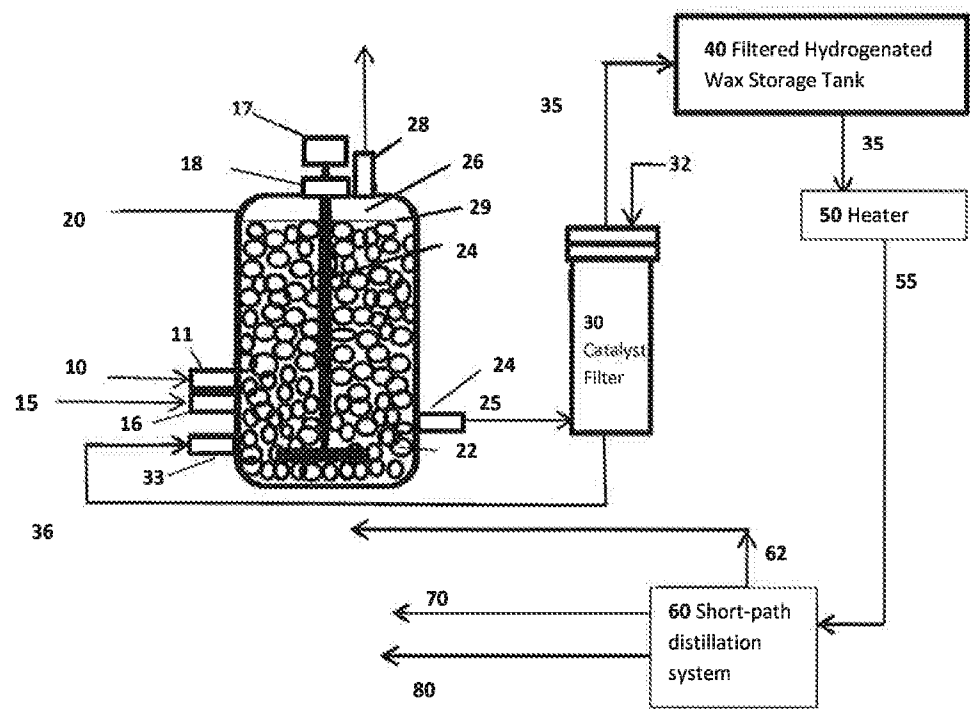


FIG. 2

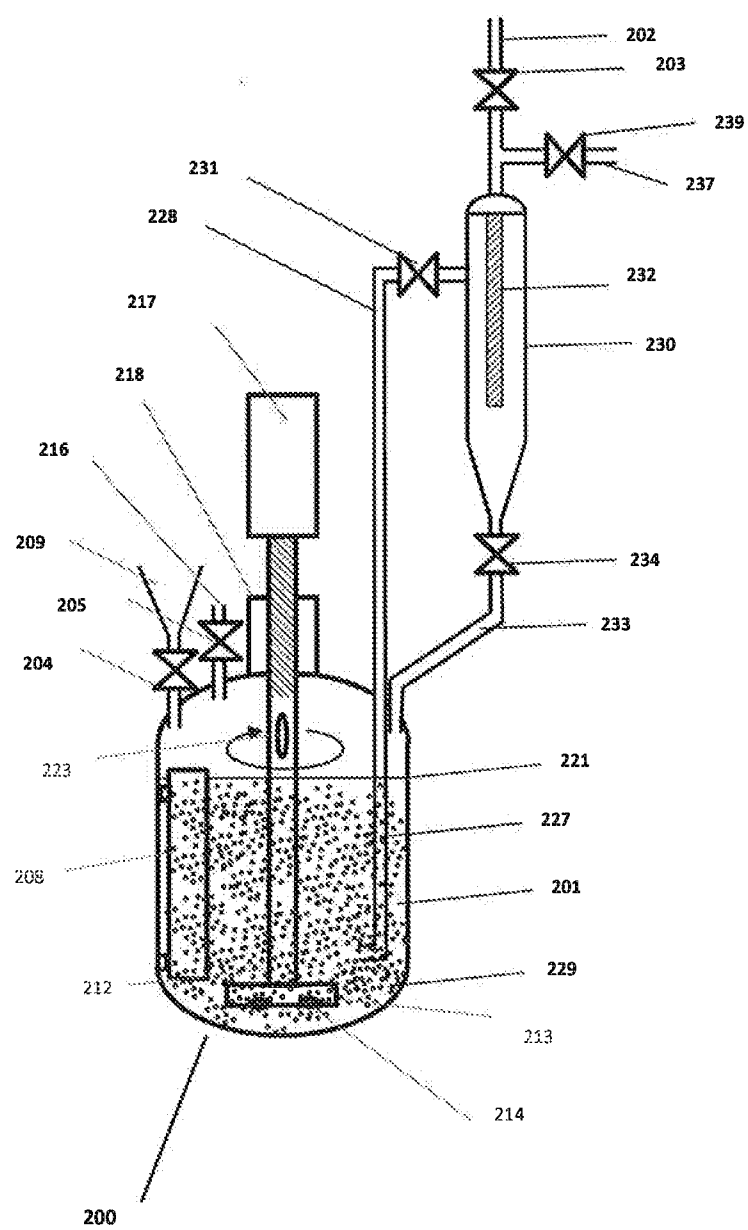


FIG. 3

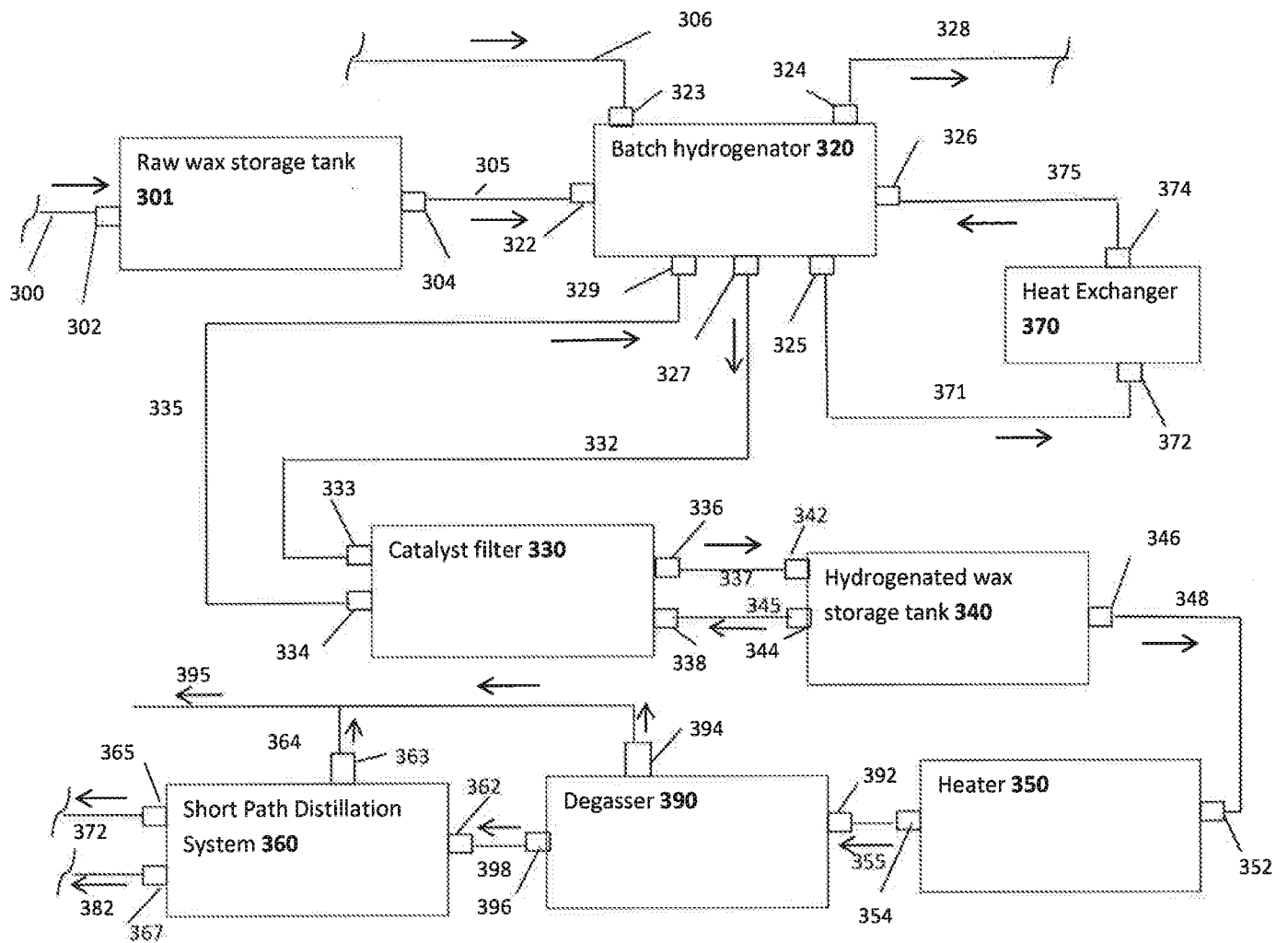


FIG. 4

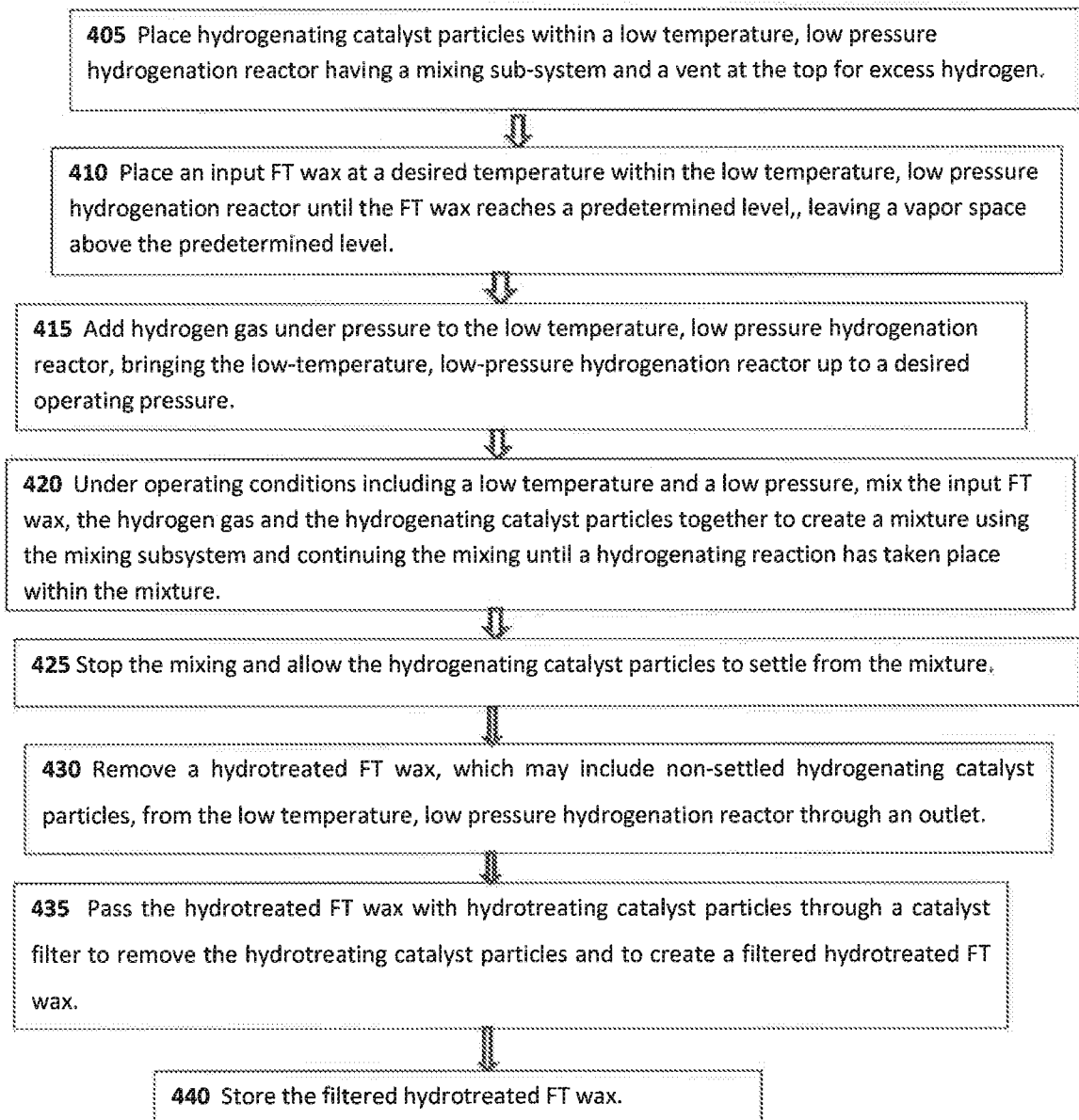
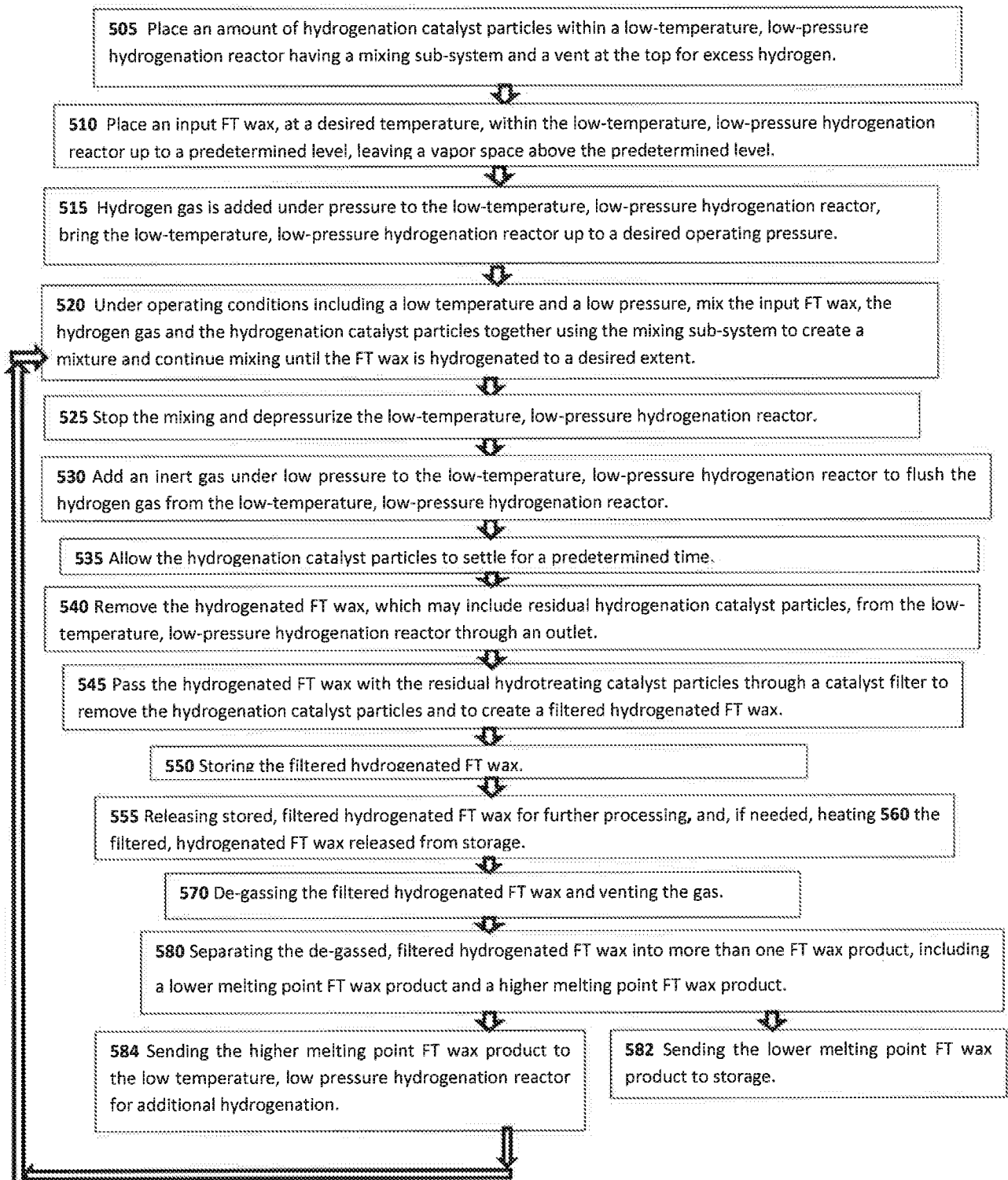


FIG. 5



INTERNATIONAL SEARCH REPORT

international application No.

PCT/US2014/052052

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 1/04 (2014.01)

CPC - C07C 1/04 (2014.11)

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)

IPC(8) - C07C 1/00, 1/04, 2/00; C10G 1/04, 2/00 (2014.01)

CPC - C07C 1/00, 1/04, 2/00; C10G 1/04, 2/00, 2/30 (2014.11) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 208/20, 24, 27, 46, 106, 107; 518/700 (keyword delimited)

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

Orbit, Google Patents, Google Scholar.

Search terms used: hydrogenation Fischer Tropsch wax reactor filter catalyst particles hydrogen h2 temperature

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/0199545 A1 (HASSAN et al) 12 August 2010 (12.08.2010) entire document	1-7, 15-20, 23-29
Y	US 2011/0313063 A1 (SORAKER et al) 22 December 2011 (22.12.2011) entire document	1-7, 15-20, 23-29
Y	US 2006/0069296 A1 (DIECKMANN et al) 30 March 2006 (30.03.2006) entire document	5
Y	US 6,068,760 A (BENHAM et al) 30 May 2000 (30.05.2000) entire document	18
Y	US 2004/0249214 A1 (AMEY et al) 09 December 2004 (09.12.2004) entire document	19, 20
Y	US 6,429,338 B1 (BURDENIUC et al) 06 August 2002 (06.08.2002) entire document	23
Y	US 2009/0065393 A1 (PETRI) 12 March 2009 (12.03.2009) entire document	28, 29
A	US 2007/0193923 (DIERICKX et al) 23 August 2007 (23.08.2007) entire document	1-31

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

23 December 2014

Date of mailing of the international search report

15 JAN 2015

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

international application no.

PCT/US2014/052052

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-31

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: Claims 1-31 are drawn to a method for hydrogenating a Fischer-Tropsch ("FT") wax.

Group II: Claims 32-46 are drawn to a system and apparatus for hydrogenating a Fischer-Tropsch ("FT") wax.

The inventions listed in Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, a method for hydrogenating a Fischer-Tropsch ("FT") wax, are not present in Group II; and the special technical features of Group II, a system and apparatus for hydrogenating a Fischer-Tropsch ("FT") wax, are not present in Group I.

Groups I and II share the technical features of a system for hydrogenating a Fischer-Tropsch ("FT") wax, the system comprising:
a. a hydrogenation reactor for FT wax designed for operating conditions of a low temperature and a pre-determined low pressure, the hydrogenation reactor for FT wax comprising: i. a mixing sub-system, wherein the mixing subsystem is suitable to mix the FT wax with a plurality of hydrogenation catalyst particles and the hydrogen gas at the operating conditions to produce a mixture and allow the FT wax to become hydrogenated; ii. a vent at the top; iii. a first inlet to allow input of the hydrogen gas under pressure, which brings the hydrogenation reactor up to the pre-determined low pressure; and iv. an outlet to allow egress of the hydrogenated FT wax after the mixing has stopped and the hydrogenation catalyst particles have been permitted to settle for a period of time. However, these features do not represent a contribution over the prior art.

Specifically, US 2010/0199545 A1 to Hassan et al. teaches a system for hydrogenating a wax (Abstract), the system comprising: a. a hydrogenation reactor for wax designed for operating conditions of a low temperature and a pre-determined low pressure (Para. [0008]; Para. [0013]; see PCT/US14/52052 Applicant's Specification, Paras. [0033] and [0034], ...the term "low-pressure" with respect to a hydrogenation reactor means below about 350 psig...the term "low-temperature" with respect to a hydrogenation reactor means under about 280° C), the hydrogenation reactor for wax comprising: i. a mixing sub-system, wherein the mixing subsystem is suitable to mix the wax with a plurality of hydrogenation catalyst particles and the hydrogen gas at the operating conditions to produce a mixture and allow the wax to become hydrogenated (Para. [0008]; Para. [0011]; Para. [0051], the feed stream may further comprise a particulate solid catalyst component); ii. a vent at the top (Para. [0083], excess unreacted hydrogen gas may exit reactor 10 via gas line 17; Para. [0055], reactor 10 may comprise an exit line 17 for vent gas); iii. a first inlet to allow input of the hydrogen gas under pressure, which brings the hydrogenation reactor up to the pre-determined low pressure (Para. [0070]); and iv. an outlet to allow egress of the hydrogenated wax after the mixing has stopped (Para. [0033], hydrogenated products are extracted via line 16).

Further, US 6,068,760 A to Benham et al. teach a Fischer-Tropsch ("FT") wax (Abstract), and catalyst particles that have been permitted to settle for a period of time (Abstract; Col. 2, Lns. 38-54).

The inventions listed in Groups I and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.