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(54) Title: IMPROVED CONVERSION OF SYNGAS FROM FISCHER-TROPSCH PRODUCTS VIA OLEFIN METATHESIS

(57) Abstract: A process for preparing distillate fuel compositions from a C_{2-6} olefinic fraction and a $C_{20}+$ fraction via molecular averaging is described. The fractions can be obtained, for example, from Fischer-Tropsch reactions, and/or obtained from the distillation or other processing of crude oil. Molecular averaging converts the fractions to a product that includes a significant fraction in the C_{5-20} range that can be used for preparing a distillate fuel composition. The product is preferably isomerized to increase the octane value and lower the pour, cloud and smoke point. The product can also be hydrotreated and/or blended with suitable additives for use as a distillate fuel composition.

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1   IMPROVED CONVERSION OF SYNGAS
2   FROM FISCHER-TROPSCH PRODUCTS
3   VIA OLEFIN METATHESIS
4
5   FIELD OF THE INVENTION
6
7   This invention relates to the olefination and subsequent molecular averaging
8   of the waxy fraction resulting from Fischer-Tropsch synthesis.
9
10   BACKGROUND OF THE INVENTION
11
12   The majority of distillate fuel used in the world today is derived from crude oil.
13   Crude oil is in limited supply, includes aromatic compounds believed to cause
14   cancer, and contains sulfur and nitrogen-containing compounds that can
15   adversely affect the environment. For these reasons, alternative methods for
16   generating distillate fuel have been developed.
17
18   One alternative method for generating distillate fuel involves converting
19   natural gas, which is mostly methane, to synthesis gas (syngas), which is a
20   mixture of carbon monoxide and hydrogen. The syngas is converted to a
21   range of hydrocarbon products, collectively referred to as syncrude, via
22   Fischer-Tropsch synthesis.
23
24   It is generally possible to isolate various fractions from a Fischer-Tropsch
25   reaction, for example, by distillation. The fractions include a gasoline fraction
26   (B.P. about 68-450°F/20-232°C), a middle distillate fraction (B.P. about
27   250-750°F/121-399°C), a wax fraction (B.P. about 650-1200°F/343-649°C)
28. primarily containing C_{20} to C_{50} normal paraffins with a small amount of
29   branched paraffins and a heavy fraction (B.P. above about 1200°F/649°C)
30   and tail gases.
31

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1   An advantage of using fuels prepared from syngas is that they do not contain

2   significant amounts of nitrogen or sulfur and generally do not contain aromatic

3   compounds. Accordingly, they have minimal health and environmental

4   impact.

5

6   However, a limitation associated with Fisher-Tropsch chemistry is that it tends

7   to produce a broad spectrum of products, ranging from methane to wax.

8   While the product stream includes a fraction useful as distillate fuel, it is not

9   the major product.

10

11 Fischer-Tropsch products tend to have appreciable amounts of olefins in the

12 light fractions (i.e., the naphtha and distillate fuel fractions), but less so in the

13 heavy fractions. Depending on the specifics of the Fischer-Tropsch process,

14 the naphtha can be expected to include more than 50% olefins, most of which

15 are alpha olefins. Distillate fuels will also contain some level of olefins

16 (typically between 10 and 30%) and the distillate waxy fractions can contain

17 smaller quantities.

18

19 One approach for preparing distillate fuels is to perform Fischer-Tropsch

20 synthesis at high alpha values that minimize the yield of light gases, and

21 maximize the yield of heavier products such as waxes. The wax from the

22 Fischer-Tropsch process typically causes the entire syncrude to be a solid

23 even at high temperatures, which is not preferred. The waxes are then

24 hydrotreated and hydrocracked to form distillate fuels. Since hydrocracking is

25 performed at relatively high temperatures and pressures, it is relatively

26 expensive.

27

28 It would be advantageous to provide a process which provides useful distillate

29 fuels from Fischer-Tropsch products but which does not require a

30 hydrocracking step. The present invention provides such a process.

31

1   <u>SUMMARY OF THE INVENTION</u>

2

3   In its broadest aspect, the present invention is directed to an integrated

4   process for producing distillate fuels, including jet fuel, gasoline and diesel.

5   The process involves the partial dehydrogenation of the wax fraction and/or

6   heavy fraction of a Fischer-Tropsch reaction to form olefins, which are reacted

7   with the olefins in the naphtha and/or light gas fraction of the Fischer-Tropsch

8   reaction in the presence of an olefin metathesis catalyst. The resulting

9   product has significantly less wax, and the product has an average molecular

10   weight between the molecular weight of the naphtha and/or light gas fractions

11   and the molecular weight of the wax and/or heavy fractions.

12

13   Fractions in the distillate fuel range can be isolated from the reaction mixture,

14   for example, via fractional distillation. The product of the molecular averaging

15   reaction tends to be highly linear, and is preferably subjected to catalytic

16   isomerization to improve the octane values and lower the pour, cloud and

17   freeze points. The resulting composition has relatively low sulfur values, and

18   relatively high octane values, and can be used in fuel compositions.

19

20   In one embodiment, one or both of the feeds to the molecular averaging

21   reaction is isomerized before the molecular averaging reaction. Incorporation

22   of isoparaffins into the molecular averaging reaction provides a product

23   stream that includes isoparaffins in the distillate fuel range which have

24   relatively high octane values.

25

26   In another embodiment, the alpha olefins in the light naphtha and gas are

27   converted into internal olefins (either normal internal or iso-internal olefins).

28   When these materials are averaged against the internal olefins derived from

29   dehydrogenation of the wax, the yield of intermediate fuels is increased.

30   Furthermore, the light naphtha and gas fractions may contain impurities such

31   as alcohols and acids. These oxygenates can be converted to additional

1   olefins by dehydration and decarboxylation. Traces of other impurities should

2   be reduced to acceptable levels by use of adsorbents and/or extractants.

3   ·

4   Preferably, after performing Fischer-Tropsch synthesis on syngas, and before

5   performing the molecular averaging reaction, hydrocarbons in the distillate

6   fuel range are separately isolated, for example, via fractional distillation. The

7   wax and/or heavy fraction are then dehydrogenated, the naphtha and/or light

8   gas fractions are added to the resulting olefinic mixture, and reaction mixture

9   is molecularly averaged by subjecting the olefins to olefin metathesis

10   conditions.

11

12   It is preferred that the wax and/or heavy fraction and the naphtha and/or light

13   gas fractions are derived from Fischer-Tropsch synthesis. However, at least a

14   portion of the low molecular weight olefins or the waxy fraction can be derived

15   from a source other than Fischer-Tropsch synthesis. Due to the nature of the

16   molecular averaging chemistry, the reactants cannot include appreciable

17   amounts (i.e., amounts that would adversely affect the catalyst used for

18   molecular averaging) of thiols, amines, or cycloparaffins.

19

20   It may be advantageous to take representative samples of each fraction and

21   subject them to molecular averaging reactions, adjusting the relative

22   proportions of the fractions until a product with desired properties is obtained.

23   Then, the reaction can be scaled up using the relative ratios of each of the

24   fractions that resulted in the desired product. Using this method, one can "dial

25   in" a molecular weight distribution which can be roughly standardized between

26   batches and result in a reasonably consistent product.

27

28   BRIEF DESCRIPTION OF THE DRAWINGS

29

30   The Figure is a schematic flow diagram representing one embodiment of the

31   invention.

32

1   <u>DETAILED DESCRIPTION OF THE INVENTION</u>

2

3   In its broadest aspect, the present invention is directed to an integrated

4   process for producing distillate fuels, such as jet fuel, gasoline and diesel fuel.

5   The process involves the partial dehydrogenation of the wax fraction and/or

6   heavy fraction of a Fischer-Tropsch reaction mixture to form olefins, which are

7   reacted with the olefins in the naphtha and light gas fraction of the

8   Fischer-Tropsch reaction in the presence of an olefin metathesis catalyst.

9   The resulting product has significantly less wax, and has an average

10   molecular weight between the molecular weight of the naphtha and/or light

11   gas fractions and the molecular weight of the wax and/or heavy fractions.

12   Hydrocarbons in the distillate fuel range can be isolated from the reaction

13   mixture via fractional distillation. The product of the molecular averaging

14   reaction tends to be highly linear, and is preferably subjected to catalytic

15   isomerization to improve the octane values and lower the pour, cloud and

16   freeze points. To maximize the yield of desired distillate fuels, the olefins in

17   the light naphtha can first be converted to internal olefins.

18

19   In one embodiment, at least a portion of one or both of the relatively low

20   molecular weight (for example, C_{2-6}) and/or relatively high molecular weight

21   (for example, $C_{20}+$) fractions is obtained from another source, for example, via

22   distillation of crude oil.

23

24   The process described herein is an integrated process. As used herein, the

25   term "integrated process" refers to a process which involves a sequence of

26   steps, some of which may be parallel to other steps in the process, but which

27   are interrelated or somehow dependent upon either earlier or later steps in the

28   total process.

29

30   An advantage of the present process is the effectiveness and relatively

31   inexpensive processing costs with which the present process may be used to

1   prepare high quality distillate fuels, and particularly with feedstocks which are

2   not conventionally recognized as suitable sources for such fuels. An

3   additional advantage is that the resulting fuel is highly paraffinic, and has

4   relatively low levels of sulfur, nitrogen and polynuclear aromatic impurities.

5

6   Distillate Fuel Composition

7

8   The distillate fuel prepared according to the process described herein typically

9   has an average molecular weight in the C_{5-20} range. The molecular weight

10   can be controlled by adjusting the molecular weight and proportions of the

11   high molecular weight (wax and/or heavy fraction) and the low molecular

12   weight (naphtha and/or light gas) fractions. Distillate fuel compositions with

13   boiling points in the range of between about 68-450°F, more preferably

14   between about 250-370°F, are preferred. The currently most preferred

15   average molecular weight is around C_{8-12}, which has a boiling point in the

16   range of roughly 345°F, depending on the degree of branching.

17   Specifications for the most commonly used diesel fuel (No. 2) are disclosed in

18   ASTM D 975 (See, for example, p. 34 of 1998 Chevron Products Company

19   Diesel Fuels Tech Review). The minimum flash point for diesel fuel is 52°C

20   (125°F). Specifications for jet fuel are disclosed in ASTM D 1655, standard

21   Specification for Aviation Turbine Fuels. The minimum flash point for jet fuel

22   is typically 38°C.

23

24   The process is adaptable to generate higher molecular weight fuels, for

25   example, those in the C_{15-20} range, or lower molecular weight fuels, for

26   example, those in the C_{5-8} range. Preferably, the majority of the composition

27   includes compounds within about 8, and more preferably, within about

28   5 carbons of the average.

29

30   Another important property for the distillate fuel is that it has a relatively high

31   flash point for safety reasons. Preferably, the flash point is above 90°C, more

1   preferably above 110°C, still more preferably greater than 175°C, and most

2   preferably between 175°C and 300°C.

3

4   The distillate fuel can be used, for example, in diesel automobiles and trucks.

5   The high paraffinic nature of the fuel gives it high oxidation and thermal

6   stability. The fuel can also be used as a blending component with other fuels.

7   For example, the fuel can be used as a blending component with fuels derived

8   from crude oil or other sources.

9

10   Preferably, the reactants used in the molecular averaging reaction are

11   obtained from Fischer-Tropsch reactions, and therefore, contain virtually no

12   heteroatoms or aromatic compounds. Alternatively, the fuel can be obtained

13   by molecular averaging of other feedstocks, preferably in which at least the

14   heteroatoms, and more preferably the aromatics, have been removed.

15

16   Additives

17

18   The distillate fuel composition can include various additives, such as

19   lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives,

20   corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,

21   anti-wear agents, anti-foaming agents, detergents, rust inhibitors and the like.

22   Other hydrocarbons, such as those described in U.S. Patent No. 5,096,883

23   and/or U.S. Patent No. 5,189,012, may be blended with the fuel, provided that

24   the final blend has the necessary octane/cetane values, pour, cloud and

25   freeze points, kinematic viscosity, flash point, and toxicity properties. The

26   total amount of additives is preferably between 50-100 ppm by weight for

27   4-stroke engine fuel, and for 2-stroke engine fuel, additional lubricant oil may

28   be added.

29

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1   Diesel fuel additives are used for a wide variety of purposes; however, they

2   can be grouped into four major categories: engine performance, fuel stability,

3   fuel handling, and contaminant control additives.

4

5   Engine performance additives can be added to improve engine performance.

6   Cetane number improvers (diesel ignition improvers) can be added to reduce

7   combustion noise and smoke. 2-Ethylhexyl nitrate (EHN) is the most widely

8   used cetane number improver. It is sometimes also called octyl nitrate. EHN

9   typically is used in the concentration range of 0.05% mass to 0.4% mass and

10 may yield a 3 to 8 cetane number benefit. Other alkyl nitrates, ether nitrates

11 some nitroso compounds, and di-tertiary butyl peroxide can also be used.

12

13 Fuel and/or crankcase lubricant can form deposits in the nozzle area of

14 injectors — the area exposed to high cylinder temperatures. Injector

15 cleanliness additives can be added to minimize these problems. Ashless

16 polymeric detergent additives can be added to clean up fuel injector deposits

17 and/or keep injectors clean. These additives include a polar group that bonds

18 to deposits and deposit precursors and a non-polar group that dissolves in the

19 fuel. Detergent additives are typically used in the concentration range of

20 50 ppm to 300 ppm. Examples of detergents and metal rust inhibitors include

21 the metal salts of sulfonic acids, alkylphenols, sulfurized alkylphenols, alkyl

22 salicylates, naphthenates and other oil soluble mono and dicarboxylic acids

23 such as tetrapropyl succinic anhydride. Neutral or highly basic metal salts

24 such as highly basic alkaline earth metal sulfonates (especially calcium and

25 magnesium salts) are frequently used as such detergents. Also useful is

26 nonylphenol sulfide. Similar materials made by reacting an alkylphenol with

27 commercial sulfur dichlorides. Suitable alkylphenol sulfides can also be

28 prepared by reacting alkylphenols with elemental sulfur. Also suitable as

29 detergents are neutral and basic salts of phenols, generally known as

30 phenates, wherein the phenol is generally an alkyl substituted phenolic group,

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1   where the substituent is an aliphatic hydrocarbon group having about 4 to

2   400 carbon atoms.

3

4   Lubricity additives can also be added. Lubricity additives are typically fatty

5   acids and/or fatty esters. Examples of suitable lubricants include polyol esters

6   of C_{12}-C_{28} acids. The fatty acids are typically used in the concentration range

7   of 10 ppm to 50 ppm, and the esters are typically used in the range of 50 ppm

8   to 250 ppm.

9

10   Some organometallic compounds, for example, barium organometallics, act

11   as combustion catalysts, and can be used as smoke suppressants. Adding

12   these compounds to fuel can reduce the black smoke emissions that result

13   from incomplete combustion. Smoke suppressants based on other metals,

14   e.g., iron, cerium, or platinum, can also be used.

15

16   Anti-foaming additives such as organosilicone compounds can be used,

17   typically at concentrations of 10 ppm or less. Examples of anti-foaming

18   agents include polysiloxanes such as silicone oil and polydimethyl siloxane;

19   acrylate polymers are also suitable.

20

21   Low molecular weight alcohols or glycols can be added to diesel fuel to

22   prevent ice formation.

23

24   Additional additives are used to lower a diesel fuel's pour point (gel point) or

25   cloud point, or improve its cold flow properties. Most of these additives are

26   polymers that interact with the wax crystals that form in diesel fuel when it is

27   cooled below the cloud point.

28

29   Drag reducing additives can also be added to increase the volume of the

30   product that can be delivered. Drag reducing additives are typically used in

31   concentrations below 15 ppm.

32

1   Antioxidants can be added to the distillate fuel to neutralize or minimize

2   degradation chemistry. Suitable antioxidants include, for example, hindered

3   phenols and certain amines, such as phenylenediamine. They are typically

4   used in the concentration range of 10 ppm to 80 ppm. Examples of

5   antioxidants include those described in U.S. Patent No. 5,200,101, which

6   discloses certain amine/hindered phenol, acid anhydride and thiol ester-

7   derived products.

8

9   Acid-base reactions are another mode of fuel instability. Stabilizers such as

10   strongly basic amines can be added, typically in the concentration range of

11   50 ppm to 150 ppm, to counteract these effects.

12

13   Metal deactivators can be used to tie up (chelate) various metal impurities,

14   neutralizing their catalytic effects on fuel performance. They are typically

15   used in the concentration range of 1 ppm to 15 ppm.

16

17   Multi-component fuel stabilizer packages may contain a dispersant.

18   Dispersants are typically used in the concentration range of 15 ppm to

19   100 ppm.

20

21   Biocides can be used when contamination by microorganisms reaches

22   problem levels. Preferred biocides dissolve in both the fuel and water and

23   can attack the microbes in both phases. Biocides are typically used in the

24   concentration range of 200 ppm to 600 ppm.

25

26   Demulsifiers are surfactants that break up emulsions and allow fuel and water

27   phases to separate. Demulsifiers typically are used in the concentration

28   range of 5 ppm to 30 ppm.

29

30   Dispersants are well known in the lubricating oil field and include high

31   molecular weight alkyl succinimides being the reaction products of oil soluble

1   polyisobutylene succinic anhydride with ethylene amines such as

2   tetraethylene pentamine and borated salts thereof.

3

4   Corrosion inhibitors are compounds that attach to metal surfaces and form a

5   barrier that prevents attack by corrosive agents. They typically are used in

6   the concentration range of 5 ppm to 15 ppm. Examples of suitable corrosion

7   inhibitors include phosphosulfurized hydrocarbons and the products obtained

8   by reacting a phosphosulfurized hydrocarbon with an alkaline earth metal

9   oxide or hydroxide.

10

11   Examples of oxidation inhibitors include antioxidants such as alkaline earth

12   metal salts of alkylphenol thioesters having preferably C_5-C_{12} alkyl side chain

13   such as calcium nonylphenol sulfide, barium t-octylphenol sulfide,

14   dioctylphenylamine as well as sulfurized or phosphosulfurized hydrocarbons.

15   Additional examples include oil soluble antioxidant copper compounds such

16   as copper salts of C_{10-18} oil soluble fatty acids.

17

18   Examples of friction modifiers include fatty acid esters and amides, glycerol

19   esters of dimerized fatty acids and succinate esters or metal salts thereof.

20

21   Pour point depressants such as C_{8-18} dialkyl fumarate vinyl acetate

22   copolymers, polymethacrylates and wax naphthalene are well known to those

23   of skill in the art.

24   Examples of anti-wear agents include zinc dialkyldithiophosphate, zinc diaryl

25   diphosphate, and sulfurized isobutylene.

26

27   Additional additives are described in U.S. Patent No. 5,898,023 to Francisco

28   et al., the contents of which are hereby incorporated by reference.

29

1   <u>Feedstocks for the Molecular Averaging Reaction</u>

2

3   Examples of preferred feedstocks for the molecular averaging reaction include

4   feedstocks with an average molecular weight of C_{2-8} (low molecular weight

5   fraction) and $C_{20}+$ (high molecular weight fraction). Most preferably, the

6   feedstocks are obtained from Fischer-Tropsch synthesis. However,

7   numerous petroleum feedstocks, for example, those derived from crude oil,

8   are suitable for use. Examples include gas oils and vacuum gas oils,

9   residuum fractions from an atmospheric pressure distillation process,

10   solvent-deasphalted petroleum residues, shale oils, cycle oils, petroleum and

11   slack wax, waxy petroleum feedstocks, NAO wax, and waxes produced in

12   chemical plant processes. Straight chain n-paraffins either alone or with only

13   slightly branched chain paraffins having 20 or more carbon atoms are

14   sometimes referred to herein as waxes.

15

16   Depending on the olefin metathesis catalysts, the feedstocks may need to

17   exclude appreciable amounts of heteroatoms, diolefins, alkynes or saturated

18   C_6 cyclic compounds. If any heteroatoms or saturated C_6 cyclic compounds

19   are present in the feedstock, they may have to be removed before the

20   molecular averaging reaction. Heteroatoms, diolefins and alkynes can be

21   removed by hydrotreating. Saturated cyclic hydrocarbons can be separated

22   from the desired feedstock paraffins by adsorption with molecular sieves or by

23   deoiling or by complexing with urea.

24

25   Preferred petroleum distillates for use in the relatively low molecular weight

26   (C_{5-6} or less) fraction boil in the normal boiling point range of about 80°C or

27   less. Suitable feedstocks for use in the high molecular weight fraction include

28   any highly paraffinic stream, such as waxes and partially refined waxes (slack

29   waxes). The feedstock may have been subjected to a hydrotreating and/or

30   hydrocracking process before being supplied to the present process.

31   Alternatively, or in addition, the feedstock may be treated in a solvent

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1   extraction process to remove aromatics and sulfur- and nitrogen-containing

2   molecules before being dewaxed.

3   As used herein, the term "waxy petroleum feedstocks" includes petroleum

4   waxes. The feedstock employed in the process of the invention can be a

5   waxy feed which contains greater than about 50% wax, and in some

6   embodiments, even greater than about 90% wax. Such feeds can contain

7   greater than about 70% paraffinic carbon, and in some embodiments, even

8   greater than about 90% paraffinic carbon.

9

10   Examples of additional suitable feeds include waxy distillate stocks such as

11   gas oils, lubricating oil stocks, synthetic oils and waxes such as those

12   produced by Fischer-Tropsch synthesis, high pour point polyalphaolefins,

13   foots oils, synthetic waxes such as normal alpha-olefin waxes, slack waxes,

14   deoiled waxes and microcrystalline waxes. Foots oil is prepared by

15   separating oil from the wax, where the isolated oil is referred to as foots oil.

16

17   Fischer-Tropsch Chemistry

18

19   Preferably, the light gas/naphtha and the wax/heavy fractions are obtained via

20   Fischer-Tropsch chemistry. Fischer-Tropsch chemistry tends to provide a

21   wide range of products from methane and other light hydrocarbons to heavy

22   wax. Syngas is converted to liquid hydrocarbons by contact with a

23   Fischer-Tropsch catalyst under reactive conditions. Depending on the quality

24   of the syngas, it may be desirable to purify the syngas prior to the

25   Fischer-Tropsch reactor to remove carbon dioxide produced during the

26   syngas reaction and any sulfur compounds, if they have not already been

27   removed. This can be accomplished by contacting the syngas with a mildly

28   alkaline solution (e.g., aqueous potassium carbonate) in a packed column.

29

30   In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on

31   a metal oxide support. The catalyst may also contain a noble metal

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1   promoter(s) and/or crystalline molecular sieves. Pragmatically, the two

2   transition metals that are most commonly used in commercial

3   Fischer-Tropsch processes are cobalt or iron. Ruthenium is also an effective

4   Fischer-Tropsch catalyst but is more expensive than cobalt or iron. Where a

5   noble metal is used, platinum and palladium are generally preferred. Suitable

6   metal oxide supports or matrices which can be used include alumina, titania,

7   silica, magnesium oxide, silica-alumina, and the like, and mixtures thereof.

8

9   Although Fischer-Tropsch processes produce a hydrocarbon product having a

10   wide range of molecular sizes, the selectivity of the process toward a given

11   molecular size range as the primary product can be controlled to some extent

12   by the particular catalyst used. In the present process, it is preferred to

13   produce C_{20}-C_{50} paraffins as the primary product, and therefore, it is preferred

14   to use a cobalt catalyst, although iron catalysts may also be used. One

15   suitable catalyst that can be used is described in U.S. Patent No. 4,579,986

16   as satisfying the relationship:

17

18                      $(3 + 4R) > L/S > (0.3 + 0.4R)$,

19

20   wherein:

21

22   L =   the total quantity of cobalt present on the catalyst, expressed as mg

23   Co/ml catalyst,

24   S =   the surface area of the catalyst, expressed as m^2/ml catalyst, and

25   R =   the weight ratio of the quantity of cobalt deposited on the catalyst by

26   kneading to the total quantity of cobalt present on the catalyst.

27

28   Preferably, the catalyst contains about 3-60 ppw cobalt, 0.1-100 ppw of at

29   least one of zirconium, titanium or chromium per 100 ppw of silica, alumina, or

30   silica-alumina and mixtures thereof. Typically, the synthesis gas will contain

31   hydrogen, carbon monoxide and carbon dioxide in a relative mole ratio of

32   about from 0.25 to 2 moles of carbon monoxide and 0.01 to 0.05 moles of

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1   carbon dioxide per mole of hydrogen. It is preferred to use a mole ratio of

2   carbon monoxide to hydrogen of about 0.4 to 1, more preferably 0.5 to

3   0.7 moles of carbon monoxide per mole of hydrogen with only minimal

4   amounts of carbon dioxide; preferably less than 0.5 mole percent carbon

5   dioxide.

6

7   The Fischer-Tropsch reaction is typically conducted at temperatures between

8   about 300°F and 700°F (149°C to 371°C), preferably, between about 400°F

9   and 550°F (204°C to 228°C). The pressures are typically between about 10

10 and 500 psia (0.7 to 34 bars), preferably between about 30 and 300 psia (2 to

11 21 bars). The catalyst space velocities are typically between about from 100

12 and 10,000 cc/g/hr., preferably between about 300 and 3,000 cc/g/hr.

13

14 The reaction can be conducted in a variety of reactors for example, fixed bed

15 reactors containing one or more catalyst beds, slurry reactors, fluidized bed

16 reactors, or a combination of different type reactors.

17

18 In a preferred embodiment, the Fischer-Tropsch reaction is conducted in a

19 bubble column slurry reactor. In this type of reactor synthesis gas is bubbled

20 through a slurry that includes catalyst particles in a suspending liquid.

21 Typically, the catalyst has a particle size of between 10 and 110 microns,

22 preferably between 20 and 80 microns, more preferably between 25 and

23 65 microns, and a density of between 0.25 and 0.9 g/cc, preferably between

24 0.3 and 0.75 g/cc. The catalyst typically includes one of the aforementioned

25 catalytic metals, preferably cobalt on one of the aforementioned catalyst

26 supports when formation of $C_{20}+$ wax fractions is desired. Preferably, such a

27 catalyst comprises about 10 to 14 percent cobalt on a low density fluid

28 support, for example alumina, silica and the like having a density within the

29 ranges set forth above for the catalyst. Since the catalyst metal may be

30 present in the catalyst as oxides, the catalyst is typically reduced with

31 hydrogen prior to contact with the slurry liquid. The starting slurry liquid is

1   typically a heavy hydrocarbon with a viscosity (typically a viscosity between

2   4-100 centistokes at 100°C) sufficient to keep the catalyst particles

3   suspended. The slurry liquid also has a low enough volatility to avoid

4   vaporization during operation (typically an initial boiling point range of

5   between about 350°C and 550°C). The slurry liquid is preferably essentially

6   free of contaminants such as sulfur, phosphorous or chlorine compounds.

7   Initially, it may be desirable to use a synthetic hydrocarbon fluid such as a

8   synthetic olefin oligomer as the slurry fluid.

9

10   The slurry typically has a catalyst concentration of between about 2 and

11   40 percent catalyst, preferably between about 5 and 20 percent, and more

12   preferably between about 7 and 15 percent catalyst based on the total weight

13   of the catalyst, i.e., metal plus support. The syngas feed typically has a

14   hydrogen to carbon monoxide mole ratio of between about 0.5 and 4 moles of

15   hydrogen per mole of carbon monoxide, preferably between about 1 and

16   2.5 moles, and more preferably between about 1.5 and 2 moles.

17

18   The bubble slurry reactor is typically operated at temperatures within the

19   range of between about 150°C and 300°C, preferably between about 185°C

20   and 265°C, and more preferably between about 210°C and 230°C. The

21   pressures are within the range of between about 1 and 70 bar, preferably

22   between about 6 and 35 bar, and most preferably between about 10 and

23   30 bar (1 bar = 14.5 psia). Typical synthesis gas linear velocity ranges in the

24   reactor are from about 2 to 40 cm per sec., preferably from about 6 to 10 cm

25   per sec. Additional details regarding bubble column slurry reactors can be

26   found, for example, in Y. T. Shah et al., "Design Parameters Estimations for

27   Bubble Column Reactors", *AIChE Journal*, 28 No. 3, pp. 353-379 (May 1982);

28   Ramachandran et al., "Bubble Column Slurry Reactor, Three-Phase Catalytic

29   Reactors", Chapter 10, pp. 308-332, Gordon and Broch Science Publishers

30   (1983); Deckwer et al., "Modeling the Fischer-Tropsch Synthesis in the Slurry

31   Phase", *Ind. Eng. Chem. Process Des. Dev.*, v 21, No. 2, pp. 231-241 (1982);

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1   Kölbel et al., "The Fischer-Tropsch Synthesis in the Liquid Phase", *Catal.*

2   *Rev.-Sci. Eng.*, v. 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982,

3   the contents of each of which are hereby incorporated by reference in their

4   entirety.

5

6   The relatively high (for example, $C_{20}+$) and relatively low (for example, C_{2-6})

7   molecular weight fractions which are to be molecularly averaged are

8   described herein in terms of a Fischer-Tropsch reaction product. However,

9   these fractions can also be obtained through various modifications of the

10   literal Fischer-Tropsch process by which hydrogen (or water) and carbon

11   monoxide (or carbon dioxide) are converted to hydrocarbons (e.g., paraffins,

12   ethers, etc.) and to the products of such processes. Thus, the term

13   Fischer-Tropsch type product or process is intended to apply to

14   Fischer-Tropsch processes and products and the various modifications

15   thereof and the products thereof. For example, the term is intended to apply

16   to the Kolbel-Engelhardt process typically described by the reaction:

17                        $3CO + H_2O \rightarrow -CH_2- + 2CO_2$

18

19   The molecular averaging process described combines a low molecular weight

20   olefinic fraction (C_{2-6}, light gas/naphtha) and a high molecular weight fraction

21   ($C_{20}+$, wax/heavy fraction) which is dehydrogenated to form a high molecular

22   weight olefinic fraction prior to molecular averaging.

23

24   The two fractions can be obtained in separate Fischer-Tropsch reactions.

25   The low molecular weight fraction can be obtained using conditions in which

26   chain growth probabilities are relatively low to moderate, and the product of

27   the reaction includes a relatively high proportion of low molecular weight (C_{2-8})

28   olefins and a relatively low proportion of high molecular weight ($C_{30}+$) waxes.

29   The high molecular weight fraction can be obtained using conditions in which

30   chain growth probabilities are relatively high, and the product of the reaction

31   includes a relatively low proportion of low molecular weight (C_{2-8}) olefins and a

-18-

1   relatively high proportion of high molecular weight ($C_{30}+$) waxes. After the

2   wax product is dehydrogenated, it can be combined with the product of the

3   first Fischer-Tropsch reaction for molecular averaging.

4

5   Suitable catalysts, supports and promoters for separately forming the low and

6   high molecular weight fractions are described in detail below.

7

8   <u>Catalysts with low chain growth probabilities</u>

9

10   Suitable catalysts that provide relatively low (alpha values of between 0.600

11   and 0.700) to moderate (alpha values of between 0.700 and 0.800) chain

12   growth probabilities tend to provide high yields of light (C_{2-8}) alpha olefins.

13   Such catalysts are well known to those of skill in the art. Preferably, the

14   catalyst used in the first stage is an iron-containing catalyst. Iron itself can be

15   used and, when iron oxides are formed, can be reduced with hydrogen back

16   to iron. However, because the presence of iron fines in the product stream is

17   not preferred, and because iron oxides (rust) decrease the surface area of the

18   catalyst available for reaction, other iron-containing catalysts are preferred.

19   Examples of suitable iron-containing catalysts include those described in U.S.

20   Patent No. 4,544,674 to Fiato et al.

21

22   In a preferred embodiment, the iron catalysts include at least about 10 to

23   about 60 weight percent iron. More preferably, they include between about 20

24   to about 60 weight percent iron, and most preferably about 30 to about

25   50 weight percent iron. These catalysts can be unsupported, but are

26   preferably promoted with a refractory metal oxide (SiO_2, Al_2O_3, etc.), alkali (K,

27   Na, Rb) and/or Group IB metals (Cu, Ag). These catalysts are usually

28   calcined, but usually not reduced, rather they are brought up to reaction

29   temperature directly in the CO/H_2 feed.

30

31   Co-precipitated iron-based catalysts, including those containing cobalt, can be

32   used. High levels of cobalt in an iron-cobalt alloy are known to produce

-19-

1   enhanced selectivity to olefinic products, as described in Stud. Surf. Sci.

2   Catal. 7, Pt/A, pg. 432 (1981).

3

4   Examples of co-precipitated iron-cobalt catalysts and/or alloys include those

5   described in U.S. Patent Nos. 2,850,515, 2,686,195, 2,662,090, and

6   2,735,862; AICHE 1981 Summer Nat'l Meeting Preprint No. 408, "The

7   Synthesis of Light Hydrocarbons from CO and H_2 Mixtures over Selected

8   Metal Catalysts" ACS 173rd Symposium, Fuel Division, New Orleans, March

9   1977; J. Catalysis 1981, No. 72(1), pp. 37-50; Adv. Chem. Ser. 1981, 194,

10   573-88; Physics Reports (Section C of Physics Letters) 12 No. 5 (1974)

11   pp. 335-374; UK patent application No. 2050859A; J. Catalysis 72, 95-110

12   (1981); Gmelins Handbuch der Anorganische Chemie 8, Auflage (1959),

13   pg. 59; Hydrocarbon Processing, May 1983, pp. 88-96; and Chem. Ing. Tech.

14   49 (1977) No. 6, pp. 463-468.

15

16   Methods for producing high surface area metal oxides are described, for

17   example, in the French article, "C. R. Acad. Sc. Paris", p. 268 (28 May 1969)

18   by P. Courte and B. Delmon. Metal oxides with a high surface area are

19   prepared by evaporating to dryness aqueous solutions of the corresponding

20   glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was

21   prepared was $CoFe_2O_4$.

22

23   Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic

24   ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction

25   and carbiding (see, for example, U.S. Patent No. 4,544,674 to Fiato et al.).

26   These catalysts tend to exhibit high activity and selectivity to C_2-C_6 olefins and

27   low methane production.

28

29   Catalysts with high chain growth probabilities

30

31   Catalysts that provide relatively high chain growth probabilities (alpha values

32   of between 0.800 and 0.900) can be used to form a product that mostly

-20-

1   includes C_{20}+ waxes. Any catalyst that provides relatively high chain growth

2   probabilities can be used. Preferably, the catalyst used in the second stage is

3   a cobalt-containing catalyst. Ruthenium is also an effective Fischer-Tropsch

4   catalyst but is more expensive.

5

6   One suitable cobalt catalyst that can be used is described in U.S. Patent

7   No. 4,579,986, as satisfying the relationship:

8

9   $$(3 + 4R) > L/S > (0.3 + 0.4R),$$

10

11 wherein:

12

13   L = the total quantity of cobalt present on the catalyst, expressed as

14   mg Co/ml catalyst;

15   S = the surface area of the catalyst, expressed as m^2/ml catalyst; and

16   R = the weight ratio of the quantity of cobalt deposited on the catalyst

17   by kneading to the total quantity of cobalt present on the catalyst.

18

19 Other suitable catalysts include those described in U.S. Patent

20 Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320.

21 U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture

22 of CoO, Al_2O_3 and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the

23 oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal

24 oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth

25 metal, with Mo-K on carbon being preferred.

26

27 U.S. Patent No. 4,088,671 discloses minimizing methane production by using

28 a small amount of Ru on a cobalt catalyst. Examples of supported ruthenium

29 catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are

30 disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.

31

1   In general, the amount of cobalt catalytic metal present is about 1 to about

2   50 weight percent of the total catalyst composition, more preferably from

3   about 10.0 to about 25 weight percent.

4

5   Preferably, the catalyst which provides high chain growth probabilities

6   contains about 3-60 ppw cobalt, 0.1-100 ppw of at least one of zirconium,

7   titanium or chromium per 100 ppw of silica, alumina, or silica-alumina and

8   mixtures thereof.

9

10   Catalyst Supports

11

12   The type of support used can influence methane production, which should be

13   minimized regardless of whether the catalyst used promotes high or low chain

14   growth probabilities. Suitable metal oxide supports or matrices which can be

15   used to minimize methane production include alumina, titania, silica,

16   magnesium oxide, silica-alumina, and the like, and mixtures thereof.

17   Examples include titania, zirconium titanate, mixtures of titania and alumina,

18   mixtures of titania and silica, alkaline earth titanates, alkali titanates, rare

19   earth titanates and mixtures of any one of the foregoing with supports

20   selected from the group consisting of vanadia, niobia, tantala, alumina, silica

21   and mixtures thereof.

22

23   In the case of supported ruthenium catalysts, the use of a titania or titania-

24   containing support will result in lower methane production than, for example, a

25   silica, alumina or manganese oxide support. Accordingly, titania and titania-

26   containing supports are preferred.

27

28   Typically, the catalysts have a particle size of between 10 and 110 microns,

29   preferably between 20 and 80 microns, more preferably between 25 and

30   65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably

31   between 0.3 and 0.75 g/cc. The catalysts typically include one of the above-

32   mentioned catalytic metals, preferably including iron for low molecular weight

1   olefin production and cobalt for C_{20}+ wax production, on one of the above-

2   mentioned catalyst supports. Preferably, the cobalt-containing catalysts

3   include about 10 to 14 percent cobalt on a low density fluid support, for

4   example, alumina, silica and the like, having a density within the ranges set

5   forth above for the catalyst.

6

7   Promoters and Noble Metals

8

9   Methane selectivity is also influenced by the choice of promoter. Alkali metal

10 promoters are known for reducing the methane selectivities of iron catalysts.

11 Noble metals, such as ruthenium, supported on inorganic refractory oxide

12 supports, exhibit superior hydrocarbon synthesis characteristics with relatively

13 low methane production. Where a noble metal is used, platinum and

14 palladium are generally preferred. Accordingly, alkali metal promoters and/or

15 noble metals can be included in the catalyst bed of the first stage provided

16 that they do not significantly alter the reaction kinetics from slow chain growth

17 probabilities to fast chain growth probabilities.

18

19 The disclosures of each of the patents discussed above are incorporated

20 herein by reference in their entirety.

21

22   The Separation of Product From the Fischer-Tropsch Reaction

23

24 The products from Fischer-Tropsch reactions generally include a gaseous

25 reaction product and a liquid reaction product. The gaseous reaction product

26 includes hydrocarbons boiling below about 650°F (e.g., tail gases through

27 middle distillates). The liquid reaction product (the condensate fraction)

28 includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil

29 through heavy paraffins).

30

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1   The minus 650°F product can be separated into a tail gas fraction and a

2   condensate fraction, i.e., about C_5 to C_{20} normal paraffins and higher boiling

3   hydrocarbons, using, for example, a high pressure and/or lower temperature

4   vapor-liquid separator or low pressure separators or a combination of

5   separators. The preferred fractions for preparing the distillate fuel

6   composition via molecular averaging generally include C_{2-5} and $C_{20}+$ paraffins

7   and olefins.

8

9   After removing the particulate catalyst, the fraction boiling above about 650°F

10   (the condensate fraction) can be separated into a wax fraction boiling in the

11   range of about 650°F-1200°F, primarily about containing C_{20} to C_{50} linear

12   paraffins with relatively small amounts of higher boiling branched paraffins,

13   and one or more fractions boiling above about 1200°F. However, both

14   fractions are preferably combined for molecular averaging.

15

16   Products in the desired range (for example, C_{5-20}, preferably around C_{8-12}) are

17   preferably isolated and used directly to prepare distillate fuel compositions.

18   Products in the relatively low molecular weight fraction (for example, C_{2-6}, light

19   gas/naphtha) and the relatively high molecular weight fraction (for example,

20   $C_{20}+$, wax/heavy fractions) can be isolated and combined for molecular

21   redistribution/averaging to arrive at a desired fraction. The product of the

22   molecular averaging reaction can be distilled to provide a desired C_{5-20}

23   fraction, and also relatively low and high molecular weight fractions, which can

24   be reprocessed in the molecular averaging stage.

25

26   More product in the desired range is produced when the reactants have

27   molecular weights closer to the target molecular weight. Of course, following

28   fractional distillation and isolation of the product of the molecular averaging

29   reaction, the other fractions can be isolated and re-subjected to molecular

30   averaging conditions.

31

-24-

1   Hydrotreating and/or Hydrocracking Chemistry

2

3   Fractions used in the molecular averaging chemistry may include heteroatoms

4   such as sulfur or nitrogen, diolefins and alkynes that may adversely affect the

5   catalysts used in the molecular averaging reaction. If sulfur impurities are

6   present in the starting materials, they can be removed using means well

7   known to those of skill in the art, for example, extractive Merox, hydrotreating,

8   adsorption, etc. Nitrogen-containing impurities can also be removed using

9   means well known to those of skill in the art. Hydrotreating and hydrocracking

10   are preferred means for removing these and other impurities from the heavy

11   wax feed component. Removal of these components from the light naphtha

12   and gas streams must use techniques that minimize the saturation of the

13   olefins in these streams. Extractive Merox is suitable for removing sulfur

14   compounds and acids from the light streams. The other compounds can be

15   removed, for example, by adsorption, dehydration of alcohols, and selective

16   hydrogenation. Selective hydrogenation of diolefins, for example, is well

17   known in the art. One example of a selective hydrogenation of diolefins in the

18   presence of olefins is UOP's DeFine process.

19

20   Accordingly, it is preferred that the heavy wax fractions be hydrotreated

21   and/or hydrocracked to remove the heteroatoms before performing the

22   molecular averaging process described herein. Hydrogenation catalysts can

23   be used to hydrotreat the products resulting from the Fischer-Tropsch,

24   molecular averaging and/or isomerization reactions, although it is preferred

25   not to hydrotreat the products from the Fischer-Tropsch reaction, since the

26   olefins necessary for the molecular averaging step would be hydrogenated.

27

28   As used herein, the terms "hydrotreating" and "hydrocracking" are given their

29   conventional meaning and describe processes that are well known to those

30   skilled in the art. Hydrotreating refers to a catalytic process, usually carried

31   out in the presence of free hydrogen, in which the primary purpose is the

32   desulfurization and/or denitrification of the feedstock. Generally, in

1   hydrotreating operations, cracking of the hydrocarbon molecules, i.e.,

2   breaking the larger hydrocarbon molecules into smaller hydrocarbon

3   molecules, is minimized and the unsaturated hydrocarbons are either fully or

4   partially hydrogenated.

5

6   Hydrocracking refers to a catalytic process, usually carried out in the

7   presence of free hydrogen, in which the cracking of the larger hydrocarbon

8   molecules is a primary purpose of the operation. Desulfurization and/or

9   denitrification of the feed stock usually will also occur.

10

11   Catalysts used in carrying out hydrotreating and hydrocracking operations are

12   well known in the art. See, for example, U.S. Patent Nos. 4,347,121 and

13   4,810,357 for general descriptions of hydrotreating, hydrocracking, and typical

14   catalysts used in each process.

15

16   Suitable catalysts include noble metals from Group VIIIA, such as platinum or

17   palladium on an alumina or siliceous matrix, and unsulfided Group VIIIA and

18   Group VIB, such as nickel-molybdenum or nickel-tin on an alumina or

19   siliceous matrix. U.S. Pat. No. 3,852,207 describes suitable noble metal

20   catalysts and mild hydrotreating conditions. Other suitable catalysts are

21   described, for example, in U.S. Patent Nos. 4,157,294 and 3,904,513. The

22   non-noble metal (such as nickel-molybdenum) hydrogenation metal are

23   usually present in the final catalyst composition as oxides, or more preferably

24   or possibly, as sulfides when such compounds are readily formed from the

25   particular metal involved. Preferred non-noble metal catalyst compositions

26   contain in excess of about 5 weight percent, preferably about 5 to about

27   40 weight percent molybdenum and/or tungsten, and at least about 0.5, and

28   generally about 1 to about 15 weight percent of nickel and/or cobalt

29   determined as the corresponding oxides. The noble metal (such as platinum)

30   catalyst contains in excess of 0.01 percent metal, preferably between 0.1 and

31   1.0 percent metal. Combinations of noble metals may also be used, such as

32   mixtures of platinum and palladium.

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1   The hydrogenation components can be incorporated into the overall catalyst

2   composition by any one of numerous procedures. The hydrogenation

3   components can be added to matrix component by co-mulling, impregnation,

4   or ion exchange and the Group VI components, i.e., molybdenum and

5   tungsten can be combined with the refractory oxide by impregnation,

6   co-mulling or co-precipitation. Although these components can be combined

7   with the catalyst matrix as the sulfides, that may not be preferred, as the sulfur

8   compounds may interfere with some molecular averaging or Fischer-Tropsch

9   catalysts.

10

11 The matrix component can be of many types including some that have acidic

12 catalytic activity. Ones that have activity include amorphous silica-alumina or

13 may be a zeolitic or non-zeolitic crystalline molecular sieve. Examples of

14 suitable matrix molecular sieves include zeolite Y, zeolite X and the so-called

15 ultra stable zeolite Y and high structural silica:alumina ratio zeolite Y such as

16 that described in U.S. Patent Nos. 4,401,556, 4,820,402 and 5,059,567.

17 Small crystal size zeolite Y, such as that described in U.S. Patent

18 No. 5,073,530, can also be used. Non-zeolitic molecular sieves which can be

19 used include, for example, silicoaluminophosphates (SAPO),

20 ferroaluminophosphate, titanium aluminophosphate, and the various ELAPO

21 molecular sieves described in U.S. Patent No. 4,913,799 and the references

22 cited therein. Details regarding the preparation of various non-zeolite

23 molecular sieves can be found in U.S. Patent Nos. 5,114,563 (SAPO);

24 4,913,799 and the various references cited in U.S. Patent No. 4,913,799.

25 Mesoporous molecular sieves can also be used, for example, the M41S family

26 of materials (*J. Am. Chem. Soc.* 1992, 114, 10834-10843), MCM-41 (U.S.

27 Patent Nos. 5,246, 689, 5,198,203 and 5,334,368), and MCM-48 (Kresge

28 et al., *Nature* 359 (1992) 710).

29

30 Suitable matrix materials may also include synthetic or natural substances as

31 well as inorganic materials such as clay, silica and/or metal oxides such as

32 silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-berylia,

1   silica-titania as well as ternary compositions, such as silica-alumina-thoria,

2   silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia zirconia.

3   The latter may be either naturally occurring or in the form of gelatinous

4   precipitates or gels including mixtures of silica and metal oxides. Naturally

5   occurring clays which can be composited with the catalyst include those of the

6   montmorillonite and kaolin families. These clays can be used in the raw state

7   as originally mined or initially subjected to calumniation, acid treatment or

8   chemical modification.

9

10   Furthermore, more than one catalyst type may be used in the reactor. The

11   different catalyst types can be separated into layers or mixed. Typical

12   hydrotreating conditions vary over a wide range. In general, the overall LHSV

13   is about 0.25 to 2.0, preferably about 0.5 to 1.0. The hydrogen partial

14   pressure is greater than 200 psia, preferably ranging from about 500 psia to

15   about 2000 psia. Hydrogen recirculation rates are typically greater than

16   50 SCF/Bbl, and are preferably between 1000 and 5000 SCF/Bbl.

17   Temperatures range from about 300°F to about 750°F, preferably ranging

18   from 450°F to 600°F.

19

20   The contents of each of the patents and publications referred to above are

21   hereby incorporated by reference in its entirety.

22

23   Molecular Redistribution/Averaging

24

25   As used herein, "molecular redistribution" is a process in which a mixture of

26   olefins with a relatively wide size distribution is converted into an olefin stream

27   with a relatively narrow size distribution. The terms "molecular averaging" and

28   "disproportionation" are also used herein to describe molecular averaging.

29

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1   In the process described herein, a high molecular weight wax fraction is

2   partially dehydrogenated and combined with low molecular weight olefins.

3   The combined olefins are then subjected to olefin metathesis conditions.

4

5   A typical dehydrogenation/hydrogenation catalyst includes a platinum

6   component and a typical metathesis catalyst includes a tungsten component.

7   Examples of suitable catalysts are described in U.S. Patent No. 3,856,876,

8   the entire disclosure of which is herein incorporated by reference. The

9   individual steps in the overall molecular averaging reaction are discussed in

10   detail below.

11

12   Dehydrogenation

13

14   The catalyst used to dehydrogenate the relatively high molecular weight

15   paraffin fraction must have dehydrogenation activity. It is necessary to

16   convert at least a portion of the paraffins in the relatively high molecular

17   weight feed to olefins, which are believed to be the actual species that

18   undergo olefin metathesis.

19

20   Platinum and palladium or the compounds thereof are preferred for inclusion

21   in the dehydrogenation/hydrogenation component, with platinum or a

22   compound thereof being especially preferred. As noted previously, when

23   referring to a particular metal in this disclosure as being useful in the present

24   invention, the metal may be present as elemental metal or as a compound of

25   the metal. As discussed above, reference to a particular metal in this

26   disclosure is not intended to limit the invention to any particular form of the

27   metal unless the specific name of the compound is given, as in the examples

28   in which specific compounds are named as being used in the preparations.

29

30   The dehydrogenation step can be conducted by passing the linear paraffin

31   feed over a dehydrogenation catalyst under dehydrogenating reaction

32   conditions. The dehydrogenation is typically conducted in the presence of

1   hydrogen and correspondingly a certain percentage of oxygenates, e.g., linear

2   alcohols, will be hydrogenated to the corresponding paraffins and then

3   dehydrogenated to the corresponding internal olefins. Thus, the linear

4   hydrocarbon feed may contain a substantial amount of linear oxygenates. On

5   a mole percent basis, this may be up to about 50 mol.% linear oxygenates

6   although it is preferably less than 30 mol.%. On a weight percent basis of

7   oxygen, this will generally be much less, because the linear hydrocarbons are

8   typically made up of only one or two oxygen atoms per molecule.

9

10   In order to reduce or eliminate the amount of diolefins produced or other

11   undesired by-products, the reaction conversion to internal olefins should

12   preferably not exceed 50% and more preferably should not exceed 30%

13   based on the linear hydrocarbon content of the feed. Preferably, the minimum

14   conversion should be at least 15 wt. % and more preferably at least 20 wt. %.

15

16   Because of the low dehydrogenation conversions, feedstocks with a higher

17   proportion of linear hydrocarbons having carbon atom numbers in the upper

18   range of the desired normal alpha olefin (NAO) products are preferred to

19   facilitate separation of the desired NAO's based on boiling point differences

20   between the NAO and unreacted paraffins. Preferably, the final carbon

21   numbers in the NAO product are within 50 carbon atoms of the initial carbon

22   numbers in the linear paraffinic hydrocarbon feed. More preferably, the final

23   carbon numbers are within 25 carbon atoms, and most preferably within

24   10 carbon atoms.

25

26   The dehydrogenation is typically conducted at temperatures between about

27   500°F and 1000°F (260°C and 538°C), preferably between about 600°F and

28   800°F (316°C and 427°C). The pressures are preferably between about 0.1

29   and 10 atms, more preferably between about 0.5 and 4 atms absolute

30   pressure (about 0.5 to 4 bars). The LHSV (liquid hourly space velocity) is

1   preferably between about 1 and 50 hr^{-1}, preferably between about 20 and

2   40 hr^{-1}. The products generally and preferably include internal olefins.

3

4   Since longer chained paraffins are more easy to dehydrogenate than shorter

5   chained paraffins, more rigorous conditions, e.g., higher temperatures and/or

6   lower space velocities, within these ranges are typically used where shorter

7   chain paraffins are dehydrogenated. Conversely, lower temperatures and/or

8   higher space velocities, within these ranges, are typically used where longer

9   chained paraffins are dehydrogenated. The dehydrogenation is also typically

10 conducted in the presence of a gaseous diluent, typically and preferably

11 hydrogen. Although hydrogen is the preferred diluent, other art-recognized

12 diluents may also be used, either individually or in admixture with hydrogen or

13 each other, such as steam, methane, ethane, carbon dioxide, and the like.

14 Hydrogen is preferred because it serves the dual-function of not only lowering

15 the partial pressure of the dehydrogenatable hydrocarbon, but also of

16 suppressing the formation of hydrogen-deficient, carbonaceous deposits on

17 the catalytic composite. Hydrogen is typically used in amounts sufficient to

18 insure a hydrogen to hydrocarbon feed mole ratio of about from 2:1 to 40:1,

19 preferably in the range of about from 5:1 to 20:1.

20

21 Suitable dehydrogenation catalysts which can be used include Group VIII

22 noble metals, e.g., iron, cobalt, nickel, palladium, platinum, rhodium,

23 ruthenium, osmium, and iridium, preferably on an oxide support.

24

25 Less desirably, combinations of Group VIII non-noble and Group VIB metals

26 or their oxides, e.g., chromium oxide, may also be used. Suitable catalyst

27 supports include, for example, silica, silicalite, zeolites, molecular sieves,

28 activated carbon alumina, silica-alumina, silica-magnesia, silica-thoria, silica-

29 berylia, silica-titania, silica-aluminum-thora, silica-alumina-zirconia kaolin

30 clays, montmorillonite clays and the like. In general, platinum on alumina or

31 silicalite afford very good results in this reaction. Typically, the catalyst

32 contains about from 0.01 to 5 wt. %, preferably 0.1 to 1 wt. % of the

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1   dehydrogenation metal (e.g., platinum). Combination metal catalysts such as

2   those described in U.S. Patent Nos. 4,013,733; 4,101,593 and 4,148,833, the

3   contents of which are hereby incorporated by reference in their entirety, can

4   also be used.

5

6   Preferably, hydrogen and any light gases, such as water vapor formed by the

7   hydrogenation of oxygenates, or hydrogen sulfide formed by the

8   hydrogenation of organic sulfur are removed from the reaction product prior to

9   olefin metathesis, for example, by using one or more vapor/liquid separators.

10 In general, where the feedstock is hydrotreated prior to the dehydrogenation,

11 these gases will be removed by gas/liquid phase separation following the

12 hydrotreatment. Since dehydrogenation produces a net gain in hydrogen, the

13 hydrogen may be taken off for other plant uses or as is typically the case,

14 where the dehydrogenation is conducted in the presence of hydrogen, a

15 portion of the recovered hydrogen can be recycled back to the

16 dehydrogenation reactor. Further information regarding dehydrogenation and

17 dehydrogenation catalysts can, for example, be found in U.S. Patents

18 Nos. 4,046,715; 4,101,593; and 4,124,649, the contents of which are hereby

19 incorporated by reference in their entirety. A variety of commercial processes

20 also incorporate dehydrogenation processes, in their overall process scheme,

21 which dehydrogenation processes may also be used in the present process to

22 dehydrogen the paraffinic hydrocarbons. Examples of such processes

23 include the dehydrogenation process portion of the Pacol process for

24 manufacturing linear alkylbenzenes, described in Vora et al., Chemistry and

25 Industry, 187-191 (1990); Schulz R. C. et al., Second World Conference on

26 Detergents, Montreaux, Switzerland (October 1986); and Vora et al., Second

27 World Surfactants Congress, Paris France (May 1988), hereby incorporated

28 by reference in their entirety.

29

30 If desired, diolefins produced during the dehydrogenation step may be

31 removed by known adsorption processes or selective hydrogenation

32 processes which selectively hydrogenate diolefins to monoolefins without

-32-

1   significantly hydrogenating monoolefins. One such selective hydrogenation

2   process known as the DeFine process is described in the Vora et al.

3   Chemistry and Industry publication cited above. If desired, branched

4   hydrocarbons may be removed before or after the dehydrogenation process

5   or after the olefin metathesis process described below by any suitable

6   process, typically by adsorption. One commercial adsorption process for

7   removing branched hydrocarbons and aromatics from linear paraffins is

8   known as the Molex or Sorbex process described in McPhee, Petroleum

9   Technology Quarterly, pages 127-131, (Winter 1999/2000) which description

10   is hereby incorporated by reference.

11

12   Olefin Metathesis

13

14   The relatively low molecular weight fractions (i.e., C_{2-6}) and relatively high

15   molecular weight fraction (i.e., at or above C_{20}) are metathesized to form a

16   desired fraction (i.e., around C_{5-20}). This involves using an appropriate olefin

17   metathesis catalyst under conditions selected to convert a significant portion

18   of the relatively high molecular weight and relatively low molecular weight

19   fractions to a desired fraction.

20

21   The low molecular weight olefin fraction can be used directly in the olefin

22   metathesis reaction. As discussed above, at least a portion of the relatively

23   high molecular weight waxy fraction must be converted into olefins in a

24   process known as dehydrogenation or unsaturation before it can participate in

25   the reaction. The resulting olefins are combined with the low molecular

26   weight olefins and the reaction mixture is subjected to olefin metathesis

27   conditions. The metathesized olefins are then optionally converted into

28   paraffins in a process known as hydrogenation or saturation, although they

29   can be used in distillate fuel compositions without first having been

30   hydrogenated.

31

1   Various catalysts are known to catalyze the olefin metathesis reaction. The

2   catalyst mass used in the olefin metathesis reaction must have olefin

3   metathesis activity. Olefin metathesis typically uses conventional catalysts,

4   such as W/SiO_2 (or inexpensive variations). Usually, the olefin metathesis

5   catalyst will include one or more of a metal or the compound of a metal from

6   Group VIB or Group VIIB of the Periodic Table of the Elements, which include

7   chromium, manganese, molybdenum, rhenium and tungsten. Preferred for

8   inclusion in the olefin metathesis component are molybdenum, rhenium,

9   tungsten, and the compounds thereof. Particularly preferred for use in the

10   olefin metathesis component is tungsten or a compound thereof. As

11   discussed, the metals described above may be present as elemental metals

12   or as compounds of the metals, such as, for example, as an oxide of the

13   metal. It is also understood that the metals may be present on the catalyst

14   component either alone or in combination with other metals.

15

16   The chemistry does not require using hydrogen gas, and therefore does not

17   require relatively expensive recycle gas compressors. The chemistry is

18   typically performed at mild pressures (100-5000 psig). The chemistry is

19   typically thermoneutral and, therefore, there is no need for additional

20   equipment to control the temperature.

21

22   Depending on the nature of the catalysts, olefin metathesis (and

23   dehydrogenation) may be sensitive to impurities in the feedstock, such as

24   sulfur- and nitrogen-containing compounds and moisture, and these must be

25   removed prior to the reaction. Typically, if the paraffins being metathesized

26   result from a Fischer-Tropsch reaction, they do not include an appreciable

27   amount of sulfur. However, if the paraffins resulted from another process, for

28   example, distillation of crude oil, they may contain sufficient sulfur impurities

29   to adversely effect the olefin metathesis chemistry.

30

31   The presence of excess hydrogen in the olefin metathesis zone can effect the

32   equilibrium of the olefin metathesis reaction and to deactivate the catalyst.

1   Since the composition of the fractions may vary, some routine

2   experimentation will be necessary to identify the contaminants that are

3   present and identify the optimal processing scheme and catalyst to use in

4   carrying out the invention.

5

6   The process conditions selected for carrying out the olefin metathesis step will

7   depend upon the olefin metathesis catalyst used. In general, the temperature

8   in the reaction zone will be within the range of from about 400°F (200°C) to

9   about 1000°F (540°C), with temperatures in the range of from about 500°F

10   (260°C) to about 850°F (455°C) usually being preferred. In general, the

11   conversion of the olefins by olefin metathesis increases with an increase in

12   pressure. Therefore, the selection of the optimal pressure for carrying out the

13   process will usually be at the highest practical pressure under the

14   circumstances. Accordingly, the pressure in the reaction zone should be

15   maintained above 100 psig, and preferably the pressure should be maintained

16   above 500 psig. The maximum practical pressure for the practice of the

17   invention is about 5000 psig. More typically, the practical operating pressure

18   will below about 3000 psig. The feedstock to the olefin metathesis reactor

19   should contain a minimum of olefins, and preferably should contain no added

20   hydrogen.

21

22   Saturated and partially saturated cyclic hydrocarbons (cycloparaffins,

23   aromatic-cycloparaffins, and alkyl derivatives of these species) can form

24   hydrogen during the molecular averaging reaction. This hydrogen can inhibit

25   the reaction, thus these species should be substantially excluded from the

26   feed. The desired paraffins can be separated from the saturated and partially

27   saturated cyclic hydrocarbons by deoiling or by use of molecular sieve

28   adsorbents, or by deoiling or by extraction with urea. These techniques are

29   well known in the industry. Separation with urea is described by Hepp, Box

30   and Ray in Ind. Eng. Chem., 45: 112 (1953). Fully aromatic cyclic

31   hydrocarbons do not form hydrogen and can be tolerated. Polycyclic

1   aromatics can form carbon deposits, and these species should also be

2   substantially excluded from the feed. This can be done by use of

3   hydrotreating and hydrocracking.

4

5   Tungsten catalysts are particularly preferred for carrying out the molecular

6   averaging step, because the molecular averaging reaction will proceed under

7   relatively mild conditions. When using the tungsten catalysts, the temperature

8   should be maintained within the range of from about 400°F (200°C) to about

9   1000°F (540°C), with temperatures above about 500°F (260°C) and below

10   about 800°F being particularly desirable.

11

12   The olefin metathesis reaction described above is reversible, which means

13   that the reaction proceeds toward a roughly thermodynamic equilibrium limit.

14   Therefore, since the feed to the olefin metathesis zone has two streams of

15   paraffins at different molecular weights, equilibrium will drive the reaction to

16   produce a product stream having a molecular weight between that of the two

17   streams. The zone in which the olefin metathesis occurs is referred to herein

18   as an olefin metathesis zone. It is desirable to reduce the concentration of the

19   desired products in the olefin metathesis zone to as low a concentration as

20   possible to favor the reactions in the desired direction. As such, some routine

21   experimentation may be necessary to find the optimal conditions for

22   conducting the process.

23

24   In the event the catalyst deactivates with the time-on-stream, specific

25   processes that are well known to those skilled in art are available for the

26   regeneration of the catalysts.

27

28   Any number of reactors can be used, such as fixed bed, fluidized bed,

29   ebulated bed, and the like. An example of a suitable reactor is a catalytic
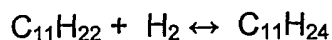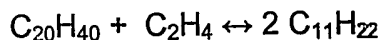
30   distillation reactor.

31

1 When the relatively high molecular weight and relatively low molecular weight

2 fractions are combined, it may be advantageous to take representative

3 samples of each fraction and subject them to olefin metathesis, while

4 adjusting the relative amounts of the fractions until a product with desired

5 properties is obtained. Then, the reaction can be scaled up using the relative

6 ratios of each of the fractions that resulted in the desired product. Using this

7 method, one can "dial in" a molecular weight distribution which can be roughly

8 standardized between batches and result in a reasonably consistent product.

9

10 Following olefin metathesis, the olefins are optionally converted back into

11 paraffins using a hydrogenation catalyst and hydrogen. While it is not

12 intended that the present invention be limited to any particular mechanism, it

13 may be helpful in explaining the choice of catalysts to further discuss the

14 sequence of chemical reactions which are believed to be responsible for

15 molecular averaging of the paraffins.

16

17 As an example, the following is the general sequence of reactions for ethylene

18 and a C_{20} paraffin, where the C_{20} paraffin is first dehydrogenated to form an

19 olefin and combined with ethylene, the two olefins are molecularly averaged,

20 and, in this example, the resulting metathesized olefins are hydrogenated to

21 form paraffins:

22

23 $$C_{20}H_{42} \leftrightarrow C_{20}H_{40} + H_2$$

24

25 $$C_{20}H_{40} + C_2H_4 \leftrightarrow 2\ C_{11}H_{22}$$

26

27 $$C_{11}H_{22} + H_2 \leftrightarrow C_{11}H_{24}$$

28

29 <u>Refractory Materials</u>

30

31 In most cases, the metals in the catalyst mass (dehydrogenation and olefin

32 metathesis) will be supported on a refractory material. Refractory materials

1   suitable for use as a support for the metals include conventional refractory

2   materials used in the manufacture of catalysts for use in the refining industry.

3   Such materials include, but are not necessarily limited to, alumina, zirconia,

4   silica, boria, magnesia, titania and other refractory oxide material or mixtures

5   of two or more of any of the materials. The support may be a naturally

6   occurring material, such as clay, or synthetic materials, such as silica-alumina

7   and borosilicates. Molecular sieves, such as zeolites, also have been used as

8   supports for the metals used in carrying out the dual functions of the catalyst

9   mass. See, for example, U.S. Patent No. 3,668,268. Mesoporous materials

10 such as MCM-41 and MCM-48, such as described in Kresge, C.T., et al.,

11 *Nature* (Vol. 359) pp. 710-712, 1992, may also be used as a refractory

12 support. Other known refractory supports, such as carbon, may also serve as

13 a support for the active form of the metals in certain embodiments. The

14 support is preferably non-acidic, i.e., having few or no free acid sites on the

15 molecule. Free acid sites on the support may be neutralized by means of

16 alkali metal salts, such as those of lithium. Alumina, particularly alumina on

17 which the acid sites have been neutralized by an alkali salt, such as lithium

18 nitrate, is usually preferred as a support for the

19 dehydrogenation/hydrogenation component, and silica is usually preferred as

20 the support for the metathesis component. The preferred catalyst/support for

21 the dehydrogenation step is Pt/silicalite, as this combination is believed to

22 show the best resistance to fouling.

23

24 The amount of active metal present on the support may vary, but it must be at

25 least a catalytically active amount, i.e., a sufficient amount to catalyze the

26 desired reaction. In the case of the dehydrogenation/hydrogenation

27 component, the active metal content will usually fall within the range from

28 about 0.01 weight percent to about 50 weight percent on an elemental basis,

29 with the range of from about 0.1 weight percent to about 20 weight percent

30 being preferred. For the olefin metathesis component, the active metals

31 content will usually fall within the range of from about 0.01 weight percent to

1   about 50 weight percent on an elemental basis, with the range of from about

2   0.1 weight percent to about 25 weight percent being preferred.

3

4   Since only the C_{20}+ wax fraction is subjected to dehydrogenation conditions,

5   the dehydrogenation catalyst and the olefin metathesis catalyst are typically

6   present in separate reactors. However, for olefin metathesis catalysts which

7   can tolerate the presence of the hydrogen generated in the dehydrogenation

8   step, it may be possible to perform both steps in a single reactor. In a reactor

9   having a layered fixed catalyst bed, the two components may, in such an

10   embodiment, be separated in different layers within the bed.

11

12   If it is desirable to hydrogenate the olefins from the molecular averaging

13   chemistry, it may be necessary to include an additional hydrogenation step in

14   the process, since the hydrogenation of the olefins must take place after the

15   molecular averaging step.

16

17   Isomerization Chemistry

18

19   Optionally, the fractions being molecularly averaged or the products of the

20   molecular averaging chemistry are isomerized, so that the products have

21   more branched paraffins, thus improving their pour, cloud and freeze points.

22   Isomerization processes are generally carried out at a temperature between

23   200°F and 700°F, preferably 300°F to 550°F, with a liquid hourly space

24   velocity between 0.1 and 2, preferably between 0.25 and 0.50. The hydrogen

25   content is adjusted such that the hydrogen to hydrocarbon mole ratio is

26   between 1:1 and 5:1. Catalysts useful for isomerization are generally

27   bifunctional catalysts comprising a hydrogenation component (preferably

28   selected from the Group VIII metals of the Periodic Table of the Elements,

29   and more preferably selected from the group consisting of nickel, platinum,

30   palladium and mixtures thereof) and an acid component. Examples of an acid

31   component useful in the preferred isomerization catalyst include a crystalline

-39-

1   zeolite, a halogenated alumina component, or a silica-alumina component.

2   Such paraffin isomerization catalysts are well known in the art.

3

4   Optionally, but preferably, the resulting product is hydrogenated. The

5   hydrogen can come from a separate hydrogen plant, can be derived from

6   syngas, or made directly from methane and other light hydrocarbons.

7

8   After hydrogenation, which typically is a mild hydrofinishing step, the resulting

9   distillate fuel product is highly paraffinic. Hydrofinishing is done after

10 isomerization. Hydrofinishing is well known in the art and can be conducted

11 at temperatures between about 190°C to about 340°C, pressures between

12 about 400 psig to about 3000 psig, space velocities (LHSV) between about

13 0.1 to about 20, and hydrogen recycle rates between about 400 and

14 1500 SCF/bbl.

15

16 The hydrofinishing step is beneficial in preparing an acceptably stable

17 distillate fuels. Distillate fuels that do not receive the hydrofinishing step may

18 be unstable in air and light due to olefin polymerization. To counter this, they

19 may require higher than typical levels of stability additives and antioxidants.

20

21 The process will be readily understood by referring to the flow diagram in the

22 figure. In the flow scheme contained in the figure, the process of the present

23 invention is practiced in batch operation. However, it is possible to practice

24 the present invention in continuous operation.

25

26 Box 10 is a reactor that reacts syngas in the presence of an appropriate

27 Fischer-Tropsch catalyst to form Fischer-Tropsch products. These products

28 are fractionally distilled (Box 20), and a light gas/naphtha fraction is sent to a

29 reactor (Box 70) for molecular averaging. A C_{5-20} fraction is isolated in

30 Box 30, and a relatively high molecular weight ($C_{20}+$) fraction is sent to a

31 reactor for dehydrogenation (Box 40), then a reactor (Box 70) for molecular

-40-

1   averaging. Following molecular averaging, the reaction mixture is fractionally

2   distilled (Box 20) and the desired product isolated in Box 30. Following

3   product isolation, the product can optionally be isomerized (Box 50) and

4   blended (Box 60) to form a desired distillate fuel composition.

5

6   The following examples will help to further illustrate the invention but are not

7   intended to be a limitation on of the scope of the process.

8

9   Example 1

10

11   A petroleum derived C_{30}-C_{200} linear hydrocarbon feedstock that includes at

12   least 70 wt.% linear paraffins with up to 50 mole% of oxygenates (e.g. linear

13   alcohols) wax is dehydrogenated as follows. The linear hydrocarbon feed is

14   fed to a hydrotreater containing a packed bed of platinum on alumina catalyst.

15   Hydrogen is fed to the hydrotreater at a ratio of about 3,000 SCF per Bbl of

16   linear hydrocarbon feed. The hydrotreater is operated at a temperature of

17   about 600°F to 650°F (316°C to 343°C), a pressure of about 10 atm to

18   120 atm, and a liquid space velocity (LHSV) of about 0.5 hr^{-1} to 1 hr^{-1}. The

19   hydrotreater hydrogenates olefins and oxygenates (e.g., alcohols) in the feed

20   to the corresponding paraffins and converts organics sulfur and nitrogen

21   compounds to hydrogen sulfide and ammonia which are preferably removed

22   from the liquid reaction products as gases along with hydrogen and scrubbed

23   out of the hydrogen gas.

24

25   The entire hydrogenated product is fed to a vapor/liquid separator where the

26   gas phase (hydrogen, ammonia, hydrogen sulfide, and any light

27   hydrocarbons, e.g., C_1-C_2 alkanes) is separated and discharged. The

28   hydrogenated C_{30}-C_{200} hydrocarbon liquid phase is fed to a dehydrogenation

29   reactor along with recycled hydrogen and, if needed, any made-up hydrogen.

30   Hydrogen is supplied to the reactor at a ratio of about 1,000 SCF of hydrogen

31   per barrel of hydrocarbon feed, including any recycle. The dehydrogenation

1   reactor is a fixed bed reactor containing 0.5 wt. % platinum on alumina

2   catalyst bed. The reactor is initially operated at a LHSV of about 40 hr^{-1}, a

3   temperature of about from 700°F to 750°F (371°C to 399°C), and a pressure

4   of about 2 atm. The conditions can be adjusted as needed to give about a

5   30% conversion of paraffin to internal olefins. For example, higher LHSVs

6   and lower temperatures give lower conversions and vice versa. The entire

7   reaction product is fed to a vapor/liquid separator where the hydrogen is taken

8   off. A portion of the hydrogen is recycled back to the dehydrogenation reactor

9   and the remainder can be used for other plant purposes.

10

11   The liquid reaction product is fed to a fixed bed olefin metathesis reactor

12   containing a catalyst bed that includes a metathesis catalyst, such as

13   tungsten on silica. Low molecular weight olefins, such as those from a

14   Fischer-Tropsch reaction, are also fed to the reactor at a suitable mole ratio of

15   low molecular weight olefins to wax olefins such that the average molecular

16   weight of the reactants is in a desired range. As in the case of the

17   dehydrogenation reaction, the reaction conditions may be adjusted as needed

18   to provide the desired conversion.

19

20   The reaction product is fed to a fractional distillation column and a desired

21   fraction is isolated. The product can be hydrotreated if desired, preferably

22   using syngas or recycled hydrogen as the hydrogen source. Unreacted low

23   molecular weight hydrocarbons and wax hydrocarbons can be recycled back

24   to the dehydrogenation reactor and/or to the olefin metathesis reactor.

25

26   Example 2

27

28   An integrated syngas, Fischer-Tropsch and molecular averaging process

29   starting from natural gas is described. Impurities in natural gas are removed

30   by passing the gas through an amine scrubber and a sulfur scrubber. The

31   amine scrubber removes acid gases such as hydrogen sulfide, mercaptans

1   and carbon dioxide. The sulfur scrubber contains a packed bed of zinc oxide

2   and removes any traces of sulfur gases, e.g., hydrogen sulfide or mercaptan

3   gases remaining in the natural gas.

4

5   The treated natural gas is fed, together with steam, to a syngas reactor where

6   it is reacted with air or oxygen to effect partial oxidation of the methane. The

7   fixed bed reactor contains a methane reforming, nickel-based catalyst and is

8   operated at a temperature between 400°C and 600°C, at a pressure of

9   between 15 and 30 bar, and at a space velocity of about 8,000 hr^{-1}. The

10   resulting syngas contains between 1.8 and 3.5 moles of hydrogen per mole of

11   carbon monoxide. If needed, the mole ratio of hydrogen to carbon monoxide

12   may be adjusted by using more steam, adding a carbon dioxide rich stream or

13   passing the syngas through a membrane separator.

14

15   The syngas is fed to a Fischer-Tropsch bubble column slurry reactor

16   containing a 12 wt. % cobalt on low density alumina catalyst with a particle

17   size of about 25 to 65 microns and a density of about 0.4 to 7 g/cc in a 8 cs.

18   (100°C) synfluid slurry liquid. Before mixing with the slurry liquid, the catalyst

19   is reduced by contact with a 5 vol.% hydrogen, 95 vol.% nitrogen gas at about

20   200-250°C for about 12 hours. After contact with the hydrogen, the

21   temperature is increased to about 350-400°C, and this temperature is

22   maintained for about 24 hours while the hydrogen content of the gas is slowly

23   increased until the reducing gas is essentially 100% hydrogen. The reactor is

24   operated at a temperature between about 210°C and 230°C, a pressure of

25   25-30 bar, and a synthesis gas linear velocity of about 6 to 10 cm/sec. The

26   resulting liquid hydrocarbon product contains a high proportion of C_{26} to C_{50}

27   paraffins (the wax product) and a light product boiling below about 650°F

28   (282°C) containing middle distillate and tail gases. Tail gases are removed

29   from the light fraction, for example, by using one or more liquid/gas separators

30   operating at lower temperatures and/or pressures and the remaining light

31   product stream (condensate) comprising C_5 and higher hydrocarbons boiling

1   below 650°F (343°C), which are predominantly olefins, are isolated and sent

2   to the olefin metathesis reactor.

3

4   The Fischer-Tropsch wax product is fractionated into a wax fraction boiling

5   above about 650°F (343°C), primarily containing C_{26}-C_{50} linear paraffins, a

6   high boiling bright stock fraction boiling above about 1100°F, and a liquid fuel

7   fraction boiling below about 650°F. The C_{26}-C_{50} linear paraffin fraction is fed

8   to a hydrotreater. Hydrogen is furnished to the hydrotreater at a ratio of about

9   500 SCF per Bbl of hydrocarbon feed. The hydrotreater is a fixed bed reactor

10   containing a 0.5 wt. % palladium on alumina catalyst. The hydrotreater is

11   operated at a LHSV of about from 0.5 to 1 hr^{-1}, a temperature in the range of

12   about 500°F to 550°F (260°C to 288°C), and a pressure of about

13   100-120 atms. The hydrotreater hydrogenates the oxygenates, e.g., linear

14   alcohols, and olefins in the feed to paraffins and converts any traces of

15   organic sulfur into hydrogen sulfide. The hydrogenated reaction product is fed

16   to liquid/vapor separator where the excess hydrogen and any hydrogen

17   sulfide is removed as the gaseous phase. Depending on the purity of the

18   hydrogen phase, it may be recycled back to the hydrotreater with makeup

19   hydrogen or may be first passed through one or more scrubbers, not shown,

20   before being recycled or used for other plant uses. The hydrogenated liquid

21   phase is discharged and fed to the dehydrogenation reactor along with any

22   recycle. Hydrogen is furnished to reactor at a ratio of about 1,000 SCF of

23   hydrogen per 1 Bbl of hydrocarbon feed including any recycle.

24

25   The dehydrogenation reactor includes a catalyst bed containing a 0.5 wt. %

26   platinum on silicalite catalyst. The dehydrogenation reactor is initially

27   operated at a reaction temperature of about 700°F to 790°F and a pressure of

28   about 2 atm and at a LHSV of about 35 hr^{-1}. The conditions then adjusted as

29   needed give a conversion of C_{20}-C_{50} linear paraffin to internal olefin of about

30   30%. The dehydrogenation reaction product can be passed to a vapor/liquid

31   phase separator where hydrogen and any light gases, e.g., water vapor

1   generated by any trace oxygenates not hydrogenated in the hydrotreater, are

2   discharged. The liquid product includes both internal olefins and unreacted

3   paraffins and is sent to a molecular averaging reactor containing a 5 wt. %

4   tungsten on silica catalyst. It is combined with low molecular weight olefins

5   from the Fischer-Tropsch reaction.

6

7   The reaction mixture is then passed to a distillation column. Low molecular

8   weight olefins and unreacted C_{30}-C_{50} hydrocarbons are taken off and recycled

9   back to either dehydrogenation reactor or, depending on the olefin content, to

10   the molecular averaging reactor. Product in the desired range is also isolated.

11

12   While the present invention has been described with reference to specific

13   embodiments, this application is intended to cover those various changes and

14   substitutions that may be made by those skilled in the art without departing

15   from the spirit and scope of the appended claims.

1   WHAT IS CLAIMED IS:

2

3   1.   A process for preparing a distillate fuel composition, the process

4   comprising:

5

6   (a)   combining a fraction with an average molecular weight below about

7   C_6 and which includes at least 20% olefins with a fraction with

8   average molecular weight above about C_{20} which includes at least

9   10% olefins in a suitable proportion such that, when the molecular

10   weights of the fractions are averaged, the average molecular

11   weight is the desired molecular weight for a distillate fuel

12   composition;

13

14   (b)   subjecting the olefins in the fractions to olefin metathesis to provide

15   a product with a desired molecular weight; and

16

17   (c)   isolating the product.

18

19   2.   The process of claim 1, wherein the fraction with an average molecular

20   weight below about C_6 is greater than 35 percent olefins.

21

22   3.   The process of claim 1, wherein the fraction with an average molecular

23   weight below about C_6 is greater than 50 percent olefins.

24

25   4.   The process of claim 1, wherein the fraction with an average molecular

26   weight above about C_{20} is between about 25 and 50 percent olefins.

27

28   5.   The process of claim 1, wherein the fraction with an average molecular

29   weight above about C_{20} is greater than 35 percent olefins.

30

1   6.   The process of claim 1, wherein at least a portion of the fraction with

2   average molecular weight above about C_{20} is obtained via a

3   Fischer-Tropsch process.

4   7.   The process of claim 6, wherein at least a portion of the fraction with

5   average molecular weight above about C_{20} is dehydrogenated prior to

6   the olefin metathesis step.

7

8   8.   The process of claim 1, wherein at least a portion of one or both of the

9   fractions are derived from crude oil.

10

11   9.   The process of claim 1, wherein the product is isolated via fractional

12   distillation.

13

14   10.   The process of claim 1, wherein at least a portion of the product is

15   combined with an additive selected from the group consisting of

16   lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives,

17   corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,

18   anti-wear agents, dispersants, anti-foaming agents, pour point

19   depressants, detergents, and rust inhibitors.

20

21   11.   The process of claim 1, wherein one or more of the fractions are

22   obtained via a process other than Fischer-Tropsch chemistry, and the

23   fractions include heteroatoms, further comprising hydrotreating the

24   fraction(s) including heteroatoms to remove the heteroatoms prior to the

25   olefin metathesis reaction.

26

27   12.   The process of claim 1, further comprising isomerizing at least a portion

28   of the product.

29

30   13.   The process of claim 1, further comprising hydrogenating at least a

31   portion of the olefins in the product.

1   14. The process of claim 1, wherein the product has an average molecular
2   weight between C_5 and C_{20}.

3

4   15. The process of claim 1, wherein the product has a boiling point in the
5   range of between 68°F and 450°F.

6

7   16. The process of claim 1, wherein the product has a boiling point in the
8   range of between about 250°F and 370°F.

9

10   17. A process for preparing a distillate fuel composition, the process
11   comprising:

12

13   (a) performing Fischer-Tropsch synthesis on syngas to provide a
14   product stream;

15

16   (b) fractionally distilling the product stream and isolating a C_{2-6} fraction
17   and a $C_{20}+$ fraction;

18

19   (c) dehydrogenating or partially dehydrogenating the $C_{20}+$ fraction;

20

21   (d) combining the dehydrogenated or partially dehydrogenated $C_{20}+$
22   fraction with the C_{2-6} fraction in a suitable proportion such that,
23   when the molecular weights of the fractions are averaged, the
24   average molecular weight is between approximately C_5 and C_{20};

25

26   (e) subjecting the olefins in the fractions in step (e) to olefin
27   metathesis; and

28

29   (f) isolating a product in the C_{5-20} range.

30

1   18. The process of claim 17, further comprising isomerizing at least a portion
2   of the product.
3
4   19. The process of claim 17, further comprising hydrotreating at least a
5   portion of the olefins in the product.
6
7   20. The process of claim 17, further comprising blending at least a portion of
8   the product with one or more additional distillate fuel compositions.
9
10 21. The process of claim 17, further comprising blending at least a portion of
11   the product with one or more additives selected from the group
12   consisting of lubricants, emulsifiers, wetting agents, densifiers, fluid-loss
13   additives, corrosion inhibitors, oxidation inhibitors, friction modifiers,
14   demulsifiers, anti-wear agents, dispersants, anti-foaming agents, pour
15   point depressants, detergents, and rust inhibitors.
16
17 22. A process for preparing a distillate fuel composition, the process
18   comprising:
19
20   (a) performing Fischer-Tropsch synthesis on syngas using a catalyst
21   which provides low to moderate chain growth probabilities to
22   provide a product stream including at least 5% C_{2-8} olefins;
23
24   (b) performing Fischer-Tropsch synthesis on syngas using a catalyst
25   which provides high chain growth probabilities to provide a product
26   stream including predominantly $C_{20}+$ paraffins;
27
28   (c) dehydrogenating or partially dehydrogenating the $C_{20}+$ paraffinic
29   product stream;
30
31   (d) combining the dehydrogenated or partially dehydrogenated $C_{20}+$
             product stream with the C_{2-8} product stream in a suitable proportion

1   such that, when the molecular weights of the fractions are

2   averaged, the average molecular weight is between approximately

3   C_5 and C_{20};

4

5   (e)   subjecting the olefins in the fractions in step (d) to olefin

6   metathesis; and

7

8   (f)   isolating a product in the C_{5-20} range.

9

10   23. The process of claim 22, wherein the C_{2-8} product stream from the

11   Fischer-Tropsch synthesis step includes at least 10% olefins.

12

13   24. The process of claim 22, wherein the C_{2-8} product stream from the

14   Fischer-Tropsch synthesis step includes at least 20% olefins.