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(54) Title: CONVERSION OF C₁-C₃ ALKANES AND FISCHER-TROPSCH PRODUCTS TO NORMAL ALPHA OLEFINS AND OTHER LIQUID HYDROCARBONS

(57) Abstract: Processes for converting C₁ to C₃ alkanes into high purity C₆ to C₂₄ normal alpha olefins and internal combustion engine grade fuels and/or lubricating oils comprising a sequence of fractionation and thermal cracking and/or hydrocracking operations. The C₆ to C₂₄ normal alpha olefin fractions generally have a purity of at least about 90 wt. %.

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**CONVERSION OF C₁-C₃ ALKANES AND FISCHER-TROPSCH
PRODUCTS TO NORMAL ALPHA OLEFINS
AND OTHER LIQUID HYDROCARBONS**

BACKGROUND OF THE INVENTION

The invention relates to a method for converting Fischer-Tropsch type reaction products rich in C₁₆-C₅₀ linear paraffins into high purity C₆-C₂₄ normal alpha olefins ("NAOs") having a purity of at least about 90 wt.%. This invention also relates to the conversion of C₁-C₃ alkane rich gases to more useful liquid hydrocarbons. In a further aspect it relates to the conversion of natural gas discharged in the recovery of crude oil, commonly referred to as flare gas, and excess C₁-C₃ alkanes produced as byproducts in various refinery operations, into more useful liquid hydrocarbon products such as normal alpha olefins, lubricating oil and liquid fuels. (The term liquid refers to hydrocarbons which are liquid at ambient conditions, including however, pentane.)

In the recovery of crude oil a large amount of natural gas (methane) is frequently encountered. In the past, depending on the location of the oil field, the value of the natural gas was frequently not considered to be worth the cost of recovery and transportation. Accordingly, in many cases, the natural gas which was generated was simply burned off. As well as being wasteful this practice is no longer considered acceptable from an environmental standpoint and in many cases prohibited by governmental regulations. A similar problem may also exist with respect to excess C₁-C₃ alkanes produced during petroleum refining operations or other chemical manufacturing operations to the extent it exceeds the fuel requirements of the facility. Thus, a need to convert natural gas or methane ethane and propane to more valuable products has been recognized for a number of years. Efforts have been undertaken since before World War II to convert methane to synthesis gas and synthesis gas (CO+H₂) into more desirable liquid products and are still continuing today. Typically these processes involve the use of the Fischer-Tropsch process, in which a less valuable material, e.g. coal or methane, is first converted to synthesis gas by incomplete

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1 oxidation and the synthesis gas converted to liquid or solid hydrocarbon products,
2 e.g., paraffins, olefins and oxygenates. The Fischer-Tropsch products may in turn be
3 upgraded to more useful products by a variety of operations. For example,
4 U.S. Patent Nos. 5,345,019 and 5,378,348 disclose a process for hydrocracking paraffins
5 produced by a Fischer-Tropsch to produce kerosene, gas oil, and base oil.
6 U.S. Patent No. 4,943,672 discloses a process for producing lubricating oil from
7 Fischer-Tropsch waxes by hydroisomerization. U.S. patent 4,579,986 is directed to a process
8 for making C₁₀-C₂₀ linear olefins which comprises thermal cracking, in the presence of steam,
9 C₂₀₊ paraffins obtained by a Fischer-Tropsch process using certain Fischer-Tropsch catalysts
10 containing cobalt and zirconium, titanium and/or chromium. The patent also teaches that in
11 addition to being useful as a feed for the preparation of linear C₁₀-C₂₀ olefins, the C₂₀₊ fraction
12 is useful for obtaining solid paraffins, lower olefins (primarily ethene), high VI lubricating
13 oil and middle distillates (Col. 4, lines 55-68) and that the C₁₉ - fraction may be used to
14 prepare lower olefins, high VI synthetic lubricants, solvents and specialty oils (Col. 5,
15 lines 1-23). U.S. Patent No. 4,594,172 discloses a process for preparing high VI synthetic
16 lubricants and U.S. Patent No. 5,371,308 discloses a process for preparing lower olefins from
17 a hydroprocessed synthetic oil fraction such as may be obtained from a Fischer-Tropsch
18 synthesis. The general thermal cracking of petroleum waxes to produce normal alpha olefins
19 is described in U.S. Patent No. 4,042,488 and in The Oil and Gas Journal, pages 102-104,
20 December 13, 1965.

21

22 Many improvements have also been made in the basic Fischer-Tropsch process since
23 its origins in the 1920s, such that even though the Fischer-Tropsch process still produces
24 a wide range of molecular weight products, the selectivity of the process may be
25 directed between lighter paraffin and heavier paraffins (e.g. C₂₀₊ waxes) by adjusting reaction
26 conditions and/or using different catalyst; see for example U.S. Patent Nos. 4,041,097;
27 4,522,939; 4,579,986; and 5,378,348 and S.T. Sie, et al. Conversion of Natural Gas to
28 Transportation Fuels via The Shell Middle Distillate Synthesis Process, Catalyst Today,
29 Vol. 8 (1991) pp. 371-394 B. Jager, Developments in Fischer-Tropsch Technology,
30 Studies in Surface Science and Catalysis, Vol. 107 (1997) pp. 219-224, and

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1 P. Chaumette, Gas to Liquid Conversion - Basic Features and Competitors,
2 Petrole et Techniques, No. 415 (July-August 1998) pp. 83-85.

3

4 One of the problems with thermal cracking, at least where high purity normal alpha olefins
5 are desired, is that the purity of the product is generally relatively poor because of the
6 presence of dienes and branched olefins. Thus in the past ethylene oligomerization has been
7 used where high purity normal alpha olefins are desired. Therefore, it would be desirable to
8 develop a process embodying thermal cracking which produces a high purity normal olefin
9 product. Further, although much work has been done with respect to Fischer-Tropsch
10 processes and upgrading the products therefrom, it would be desirable to develop improved
11 processes for converting Fischer-Tropsch reaction products into more valuable products
12 especially in locations where the transportation costs associated with methane or other
13 hydrocarbon gases are economically unattractive.

14

15

SUMMARY OF THE INVENTION

16

17 The present invention provides an efficient process for upgrading Fischer-Tropsch reaction
18 products and for converting natural gas and other gases containing large amounts of methane
19 ethane or propane or mixtures thereof into normal alpha olefins or other liquid hydrocarbon
20 products particularly normal alpha olefins. The invention further provides a process
21 embodying thermal cracking which produces a high purity C₆-C₂₄ normal alpha olefin
22 product at least equal or better than that produced using the more expensive ethylene
23 oligomerization processes. The C₆-C₂₄ normal alpha olefin products provided by the present
24 invention contain at least 90 wt.% and preferably at least 95 wt.% C₆-C₂₄ normal alpha
25 olefins. Further by using more rigorous separation processes purities of at least 98 wt.%
26 approaching 100% can be obtained.

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1 In one embodiment the present invention provides a process for upgrading Fischer-Tropsch
2 products or product fractions comprising at least about 90 wt.% C₁₆-C₅₀ linear paraffins into
3 high purity C₆-C₂₄ normal alpha olefin products which comprises the steps of:

4
5 a) thermal cracking the 90 wt.% C₁₆-C₅₀ linear paraffin mixture in the presence of steam at a
6 mole ratio of steam to said mixture of at least about 5:1, under thermal cracking
7 conditions adjusted to produce a cracking conversion of said mixture of about 30% or
8 less thereby yielding a reaction product mixture comprising a fraction boiling within the
9 C₆-C₂₄ normal alpha olefin boiling range, comprising at least 90 wt.% C₆-C₂₄ normal alpha
10 olefins.

11
12 b) fractionating the reaction product mixture of step a) into separate fractions comprising at
13 least one normal alpha olefin product fraction comprising normal alpha olefins selected
14 within the range of 6 to 24 carbon atoms in which said fraction has a normal alpha olefin
15 purity of at least about 90 wt.% and a higher boiling fraction boiling above about
16 740°F (393°C) comprising higher boiling olefins and paraffins;

17
18 In another embodiment of the above process, full boiling range Fischer-Tropsch products are
19 separated into a fuel fraction boiling below and about 540°F (282°C) a wax fraction boiling
20 between about 540°F to 1100°F (593°C) containing at least about 90 wt.% linear paraffins
21 and a high boiling fraction boiling from above about 1100°F (593°C). The wax fraction is
22 thermal cracked as described above and one or more of the other fractions are hydrocracked
23 to more valuable liquid hydrocarbon products. Similarly, the higher boiling fraction from
24 step b) above may also be upgraded by hydrocracking.

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- 1 The present invention also provides a process for converting C_1 - C_3 alkane gases, e.g. natural
2 gas, into more valuable products such as higher molecular weight liquid fuels and normal
3 alpha olefins (NAO) which comprises the steps of:
4
- 5 a) reforming said C_1 - C_3 alkanes into synthesis gas for example, by steam reforming, partial
6 oxidation or catalytic oxidation;
7
- 8 b) contacting the synthesis gas with a Fischer-Tropsch catalyst under reactive conditions to
9 yield two hydrocarbon product streams, one a wax containing product stream boiling
10 above about 540°F (282°C) comprising C_{16} - C_{50} linear paraffins, and a second product
11 boiling below about 540°F, comprising hydrocarbons boiling in the vacuum gas oil and
12 liquid fuel ranges (e.g., paraffins, oxygenates and middle distillate, gasoline) and tail
13 gases;
14
- 15 c) distilling the wax containing product of step b) into fractions comprising a linear
16 C_{16} - C_{50} paraffin fraction boiling in about the range of 540°F (282°C) to
17 1100°F (593°C) containing at least about 90 wt.% linear C_{16} - C_{50} paraffins, a liquid fuel
18 fraction boiling below about 540°F (282°C) and a heavy fraction boiling above about
19 1100°F (593°C);
20
- 21 d) thermal cracking the linear C_{16} - C_{50} paraffin fraction of step c) in the presence of steam at
22 a steam to said C_{16} - C_{50} paraffin fraction mole ratio of at least about 5:1 under thermal
23 cracking conditions adjusted to produce a conversion no greater than about 30 wt.% to
24 produce a reaction product mixture comprising a substantial amount of C_6 - C_{24} NAOs
25 without the formation of significant amounts of dienes;
26
- 27 e) fractionating the reaction product of step d) into NAO product fractions of varying chain
28 length within the range of C_6 - C_{24} having a NAO content of at least 90 wt.% and a higher
29 boiling fraction boiling above about 1100°F (593°C) containing branched olefin,
30 paraffins and NAO's having more than 24 carbon atoms;

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- 1 f) hydrocracking the liquid fuel portion of the second product of step b); the vacuum gas oil
2 fraction of step c) and the higher boiling fraction recovered in step e) with hydrogen in a
3 hydrocracker in the presence of a hydrocracking catalyst under hydrocracking conditions
4 to produce a mixture comprising gasoline and middle distillate; and
5
6 g) fractionating the reaction product of step f) and recovering at least one liquid fuel
7 fraction, and at least one higher boiling hydrocarbon fraction and recycling at least one of
8 said higher boiling hydrocarbon fractions back to said hydrocracker.

9
10 In another embodiment the invention provides a process for upgrading a substantially full
11 boiling range Fischer-Tropsch reaction product including tail gases through bright stock
12 boiling range hydrocarbons, which process comprises the steps of:

- 13
14 a) fractionating said Fischer-Tropsch reaction product into separate fractions comprising a
15 fraction boiling in the liquid fuel boiling range, a wax fraction boiling in about the range
16 of about 540°F to 1100°F comprising at least 90 wt.% C₁₆ to C₅₀ linear paraffins and a
17 high boiling fraction boiling above about 1100°F;
18
19 b) thermal cracking the wax fraction of step a) in the presence of steam at a mole ratio of
20 steam to said wax fraction of at least 5:1, under reactive conditions adjusted to produce a
21 conversion based on said wax fraction no greater than 30 wt.% to yield a reaction product
22 mixture containing a substantial amount of C₆-C₂₄ normal alpha olefins without the
23 formation of significant amounts of C₆ to C₂₄ dienes;
24
25 c) fractionating the reaction product of step b) into separate fractions comprising at least
26 one normal alpha olefin product fraction comprising a normal alpha olefin fraction
27 selected within the range of 6 to 24 carbon atoms having a C₆-C₂₄ normal alpha olefin
28 purity of at least 90 wt.% and a higher boiling fraction comprising higher boiling olefins
29 and paraffins;

30

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- 1 d) hydrocracking said higher boiling fraction of step c), and the liquid fuel fraction of
2 step a) with hydrogen in a hydrocracker in the presence of a catalyst comprising a
3 hydrogenation component and an acid catalyst cracking component, under hydrocracking
4 conditions to produce a liquid reaction product mixture comprising liquid fuel boiling
5 hydrocarbons; and
6
- 7 e) fractionating the liquid reaction product mixture of step d) into separate fractions
8 comprising a liquid fuel fraction, and at least one higher boiling hydrocarbon fraction and
9 recycling at least one of said higher boiling fraction back to said hydrocracker.

10

11 In another embodiment the invention provides a process comprising the steps of:

12

- 13 a) converting C_1 - C_3 alkanes into synthesis gas for example, by steam reforming, partial
14 oxidation or catalytic oxidation;
15
- 16 b) contacting the synthesis gas with a Fischer-Tropsch catalyst under reactive conditions to
17 yield a reaction product mixture of hydrocarbons comprising linear C_{16} - C_{50} paraffins,
18 vacuum gas oil, middle distillate, gasoline light oxygenates and light olefins;
19
- 20 c) fractionating the Fischer-Tropsch reaction product mixture of step b) into separate
21 fractions comprising a linear C_{16} - C_{50} paraffin fraction containing at least about 90 wt.%
22 linear C_{16} - C_{50} paraffin, at least one liquid fuel fraction and at least one higher boiling
23 fraction boiling above the temperature of the C_{16} - C_{50} rich fraction;
24
- 25 d) thermal cracking the linear C_{16} - C_{50} paraffin fraction of step c) in the presence of steam at
26 a mole ratio of steam under reactive conditions adjusted to produce a conversion based
27 on said linear C_{16} - C_{50} paraffin fraction of about 30 wt.% producing a mixture of NAO's of
28 varying chain length as a substantial product without the formation of significant
29 amounts C_6 - C_{24} dienes;

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- 1 e) fractionating the reaction product of step d) into NAO product fractions of varying chain
2 length within the range of six to twenty-four carbon atoms having an NAO purity of at
3 least 90 wt.% and a higher boiling fraction containing NAO's having more than
4 24 carbon atoms and branched olefins and paraffins;
5
6 f) hydrocracking at least one of the liquid fuel fraction and higher boiling fractions
7 recovered in step c) and the higher boiling fraction recovered in step e) with hydrogen in
8 the presence of a hydrocracking catalyst under hydrocracking conditions to produce a
9 reaction product comprising liquid fuel hydrocarbons; and
10
11 g) fractionating the reaction product of step f) and recovering at least one liquid fuel
12 fraction and at least one higher boiling hydrocarbon fraction and recycling at least
13 one higher boiling hydrocarbon fraction back to said hydrocracker.
14

15 Additional aspects of the invention will be apparent from the description which follows:
16

17 **BRIEF DESCRIPTION OF THE DRAWING**

18
19 The drawing is a schematic flow sheet of a preferred embodiment of the invention in which
20 two different boiling range products are recovered from the Fischer-Tropsch reaction and
21 upgraded.
22

23 **FURTHER DESCRIPTION OF THE INVENTION**

24
25 The present invention provides an efficient process for upgrading Fischer-Tropsch
26 reaction products and for converting natural gas and other gases containing large amounts
27 of methane, ethane or propane or mixtures thereof into normal alpha olefins or other
28 liquid hydrocarbon products. In general the major component of these gases is methane.
29 The invention is especially applicable to remote sites which produce a surplus of natural
30 gas or other C₁-C₃ alkanes gases, but which are too remote from markets for these gases

1 to justify the cost of transporting the C₁-C₃ alkanes. The invention also provides process
2 flexibility to adjust between waxes, normal α -olefins, liquid fuel products and lube oil
3 base stocks depending on the relative market demand for the products and provide a
4 thermal cracking process which produces a high purity C₆-C₂₄ normal alpha olefin
5 product without significant amounts of dienes and branched olefins; typically less than
6 about 10 wt.% and preferably less than about 5 wt.%. As used herein, liquid fuel refers to
7 hydrocarbon fractions boiling with the gasoline range and/or middle distillate range,
8 (e.g., diesel fuel and jet fuel). Thus, for example, the term liquid fuel fraction refers to a
9 gasoline fraction, a diesel fuel fraction, a jet fuel fraction or a fraction including both
10 gasoline and middle distillate.

11

12 Starting with the C₁-C₃ alkanes gases the alkanes are reformed to a mixture of hydrogen
13 and carbon monoxide. Reforming is well known in the art, and includes a variety of
14 technologies including steam reforming, partial oxidation, dry reforming, series
15 reforming, convective reforming, and autothermal reforming. All have in common the
16 production of syngas from methane and other light hydrocarbons, and an oxidant (steam,
17 oxygen, carbon dioxide, air, enriched air or combinations thereof). The effluent typically
18 contains some carbon dioxide and steam in addition to syngas and unreacted feed gases.
19 Series reforming, convective reforming and autothermal reforming incorporate
20 exothermic and endothermic syngas forming reactions in order to better utilize the heat
21 generated in the process. These processes for producing synthesis gas or syngas from
22 C₁-C₃ alkanes are well known to the art. Steam reforming is typically effected by
23 contacting C₁-C₃ alkanes with steam, preferably in the presence of a reforming catalyst, at
24 a temperature in the range of about 1300°F (705°C) to about 1675°F (913°C) and
25 pressures from about 10 psia (0.7 bars) to about 500 psia (34 bars). Suitable reforming
26 catalysts which can be used include, for example, nickel, palladium, nickel-palladium
27 alloys, and the like. Additional information regarding steam reforming C₁-C₃ alkanes,
28 e.g., methane, to syngas can be found in U.S. Patent No. 5,324,335 hereby incorporated
29 by reference in its entirety.

1 Partial oxidation of C_1 - C_3 alkanes to syngas is also conducted at high temperature and
2 while the partial oxidation may be conducted without a catalyst it is more effectively
3 conducted in the presence of a catalyst. In general Group VIII metals can be used as the
4 catalyst typically supported on a mineral oxide or synthetic support, e.g., alumina.
5 Typically, the partial oxidation is conducted at temperatures in about the range of
6 1500°F (815°C) to about 2000°F (1093°C) pressures in about the range from atmospheric
7 to 3000 psia (1 to 20.4 bars). Space velocities can vary over a very wide range and
8 typical range of 100 to 100,000 hr⁻¹ and even higher depending on the particular catalyst
9 used and the type of reactor. A discussion of nickel silica alumina and nickel/magnesium
10 oxide and cobalt/magnesium oxide and other oxidation catalysts may be found in A.
11 Santos et al., Oxidation of Methane to Synthesis Gas in Fluidized Bed Reactor using
12 MgO-Based Catalysts, Journal of Catalysis, Vol. 158 (1996) pp. 81-91 hereby
13 incorporated by reference in its entirety.

14

15 The partial oxidation may also be conducted using a perovskite catalyst partial oxidation
16 process such as described in U.S. Patent No. 5,149,516 hereby incorporated by reference
17 in its entirety. Perovskites are materials having essentially the same crystal structure as the
18 mineral perovskite ($CaTiO_3$) without limitation as to the elemental constituents thereof.
19 Such materials can be represented by the formula XYO_3 wherein X and Y can be variety
20 of elements. For example, X can be La, Ca, Sr, Ba, Na, K, Ag, Cd and mixtures thereof
21 and Y can be Ta, Co, Ti, Ga, Nb, Fe, Ni, Mn, Gr, V, Th, Pb, Sn, Mo, Zn and mixtures
22 thereof. Partial oxidation reactions using a perovskite catalyst are typically conducted at
23 temperatures in the range of about from 600 to 900°C, pressures of about from 0.1 to
24 100 bar and gas hourly space velocities of from 100 to 300,000 hr⁻¹. (These space
25 velocities are determined using a gas volume based on NTP conditions, i.e. room
26 temperature (about 25°C) and one atmosphere of pressure.) The mole ratio of lower
27 alkane can vary from 1:1 to 100:1 moles of alkane to oxygen. Regardless of the system
28 used to produce syngas it is desirable to remove any sulfur compounds, e.g., hydrogen
29 sulfide and mercaptans, contained in the C_1 - C_3 alkane feed. This can be effected by

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1 passing the C₁-C₃ alkanes gas through a packed bed sulfur scrubber containing zinc oxide
2 bed or another slightly basic packing material. If the amount of C₁-C₃ alkanes exceeds
3 the capacity of the synthesis gas unit the surplus C₁-C₃ alkanes can be used to provide
4 energy throughout the facility. For example, excess C₁-C₃ alkanes may be burned in a
5 steam boiler to provide the steam used in the thermal cracking step of the present process.

6
7 The syngas product is converted to liquid hydrocarbons by contact with a Fischer-Tropsch
8 catalyst under reactive conditions. Depending on the quality of the syngas it may be
9 desirable to purify the syngas prior to the Fischer-Tropsch reactor to remove carbon dioxide
10 produced during the syngas reaction and any sulfur compounds, if they have not already been
11 removed. This can be accomplished by contacting the syngas with a mildly alkaline solution
12 (e.g. aqueous potassium carbonate) in a packed column. In general Fischer-Tropsch catalysts
13 contain a Group VIII transition metal on a metal oxide support. The catalyst may also
14 contain a noble metal promoter(s) and/or crystalline molecular sieves. Pragmatically, the
15 two transition metals which are most commonly used in commercial Fischer-Tropsch
16 processes are cobalt or iron. Ruthenium is also an effective Fischer-Tropsch catalyst but is
17 more expensive than cobalt or iron. Where a noble metal is used, platinum and palladium
18 are generally preferred. Suitable metal oxide supports or matrices which can be used include
19 alumina, titania, silica, magnesium oxide, silica-alumina, and the like and mixtures thereof.

20
21 Although, Fischer-Tropsch processes produce a hydrocarbon product having a wide range of
22 molecular sizes the selectivity of the process toward a given molecular size range as the
23 primary product can be controlled to some extent by the particular catalyst used. In the
24 present process, it is preferred to produce linear C₁₆-C₅₀ paraffins as the primary product, and
25 therefore, it is preferred to use a cobalt catalyst, although iron catalysts may also be used.
26 Also, by hydrotreating the product other linear hydrocarbon products, e.g. oxygenates and
27 olefins, can be converted to the corresponding linear paraffins.

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1 One suitable Fischer-Tropsch catalyst which can be used is described in U.S. Patent
2 No. 4,579,986 as satisfying the relationship.

3

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

5

6 wherein

7

8 L = the total quantity of cobalt present on the catalyst, expressed as mg Co/ml catalyst,

9

10 S = the surface area of the catalyst, expressed as m²/ml catalyst, and

11

12 R = the weight ratio of the quantity of cobalt deposited on the catalyst by kneading to the
13 total quantity of cobalt present on the catalyst.

14

15 Preferably, the catalyst contains about 3-60 ppw cobalt, 0.1-100 ppw of at least one of
16 zirconium, titanium or chromium per 100 ppw of silica, alumina, or silica-alumina and
17 mixtures thereof. Typically, the synthesis gas will contain hydrogen, carbon monoxide and
18 carbon dioxide in a relative mole ratio of about from 0.25 to 2 moles of carbon monoxide
19 and 0.01 to 0.05 moles of carbon dioxide per mole of hydrogen. In the present process we
20 prefer to use a mole ratio of carbon monoxide to hydrogen of about 0.4 to 1, more preferably
21 0.5 to 0.7 moles of carbon monoxide per mole of hydrogen with only minimal amounts of
22 carbon dioxide; preferably less than 0.5 mole percent carbon dioxide.

23

24 In the present process the Fischer-Tropsch reaction is typically conducted at temperatures of
25 about from 300 to 700°F (149 to 371°C) preferably 400 to 500°F (204 to 228°C); pressures of
26 about from 10 to 500 psia (0.7 to 34 bar), preferably 30 to 300 psia (2 to 21 bar), and catalyst
27 space velocities of about from 100 to 10,000 cc/g/hr, preferably 300 to 3,000 cc/g/hr. The
28 reaction can be conducted in any suitable reactor, for example, fixed bed reactors containing
29 one or more catalyst beds, or slurry reactors, and/or fluidized bed reactor.

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1 The Fischer-Tropsch reaction product can be separated into the desired product fractions
2 e.g. a gasoline fraction (B.P. about 68-450°F) a middle distillate fraction (B.P. about
3 450-540°F) a wax fraction (B.P. about 540-1100°F) primarily containing C₁₆ to C₅₀ normal
4 paraffins with a small amount of branched paraffins and a heavy fraction (B.P. above about
5 1100°F). If higher normal alpha olefins product are desired or more middle distillate is
6 desired a higher wax fraction can be recovered C₂₀-C₅₀ normal paraffins (BP about
7 650-1100°F) and a middle distillate fraction BP about 450-650°F. Further, using a higher
8 linear paraffin cut, e.g. C₂₆-C₅₀ will facilitate the removal of uncracked linear paraffins from
9 the desired C₆-C₂₄ NAO product of the thermal cracking step, discussed below. With the
10 exception of the wax fraction, the other fractions are largely a matter of choice depending on
11 the products desired and the particular plant configuration; for example, a single liquid fuel
12 fraction may be taken off comprising both gasoline and middle distillate may be taken off
13 and multiple heavy cuts may be taken off. In some cases tail gases will be exhausted from
14 the reactor separate from the C₅ and higher hydrocarbons. The tail gas, primarily containing
15 hydrogen and C₁ to C₄ paraffins, can be used as fuel gas or can be treated to remove carbon
16 dioxide and used as a hydrogen or alkane recycle stream.

17

18 In a preferred embodiment, the Fischer-Tropsch reaction is conducted in a bubble column
19 slurry reactor. In this type of reactor synthesis gas is bubbled through a slurry comprising
20 catalyst particles in a suspending liquid. Typically the catalyst has a particle size of about
21 from 10-110 microns, preferably about from 20-80 microns, more preferably about from
22 25-65 micron and a density of about from 0.25 to 0.9 g/cc preferably about from
23 0.3-.75 g/cc. The catalyst typically comprises one of the aforementioned catalytic metals,
24 preferably cobalt on one of the aforementioned catalyst supports. Preferably the catalyst
25 comprises about 10 to 14 wt.% cobalt on a low density fluid support, for example alumina,
26 silica and the like having a density within the ranges set forth above for the catalyst. Since,
27 the catalyst metal may be present in the catalyst as oxides the catalyst is typically reduced
28 with hydrogen prior to contact with the slurry liquid. The starting slurry liquid is typically a
29 heavy hydrocarbon having a viscosity high enough to keep the catalyst particles suspended,
30 typically a viscosity between 4-100 centistokes at 100°C) and a low enough volatility to

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1 avoid vaporization during operation, typically an initial boiling point range of about from
2 350 to 550°C. The slurry liquid is preferably essentially free of contaminants such as sulfur,
3 phosphorous or chlorine compounds. Thus initially, it may be desirable to use a synthetic
4 hydrocarbon fluid such as a synthetic olefin oligomer as the slurry fluid. Ultimately, a
5 paraffin fraction of the product having the desired viscosity and volatility is typically
6 recycled as the slurry liquid. The slurry typically has a catalyst concentration of about
7 2-40 wt.% catalyst, preferably 5-20 wt.% and more preferably 7-15 wt.% catalyst based on
8 the total weight of the catalyst, i.e. metal plus support. The syngas feed typically has
9 hydrogen to carbon monoxide mole ratio of about from 0.5 to 4 moles of hydrogen per mole
10 of carbon monoxide preferably about from 1 to 2.5 and more preferably about 1.5 to 2.

11

12 The bubble slurry reactor is typically operated at temperatures within the range of
13 150-300°C, preferably 185 to 265°C and more preferably 210-230°C and pressures within
14 the range of 1 to 70 bar, preferably 6-35 bar and most preferably 10 to 30 bar
15 (1 bar = 14.5 psia). Typical synthesis gas linear velocity ranges in the reactor from about 2 to
16 40 cm per sec. preferably 6 to 10 cm per sec. Additional details regarding bubble column
17 slurry reactors can, for example, be found in Y. T. Shah et al., Design Parameters
18 Estimations for Bubble Column Reactors, AIChE Journal, 28 No. 3 pp. 353-379 (May 1982);
19 Ramachandran et al., Bubble Column Slurry Reactor, Three-Phase Catalytic Reactors
20 Chapter 10, pp. 308-332 Gordon and Broch Science Publishers (1983); Deckwer et al.,
21 Modeling the Fischer-Tropsch Synthesis in the Slurry Phase, Ind. Eng. Chem. Process Des.
22 Dev. v 21, No. 2, pp. 231-241 (1982); Kölbel et al., The Fischer-Tropsch Synthesis in the
23 Liquid Phase, Catal. Rev.-Sci. Eng., v. 21(n), pp. 225-274 (1980) and U.S. Patent
24 No. 5,348,982, all of which are hereby incorporated by reference in their entirety.

25

26 The gaseous reaction product from the Fischer-Tropsch bubble slurry reactor comprises
27 hydrocarbons boiling below about 540°F (e.g., tail gases through middle distillates). The
28 liquid reaction product is recovered as or with the slurry and comprises hydrocarbons boiling
29 above about 540°F, e.g., vacuum gas oil through heavy paraffins. The minus 540°F product
30 can be separated into a tail gas fraction and a condensate fraction, i.e., about C₅ to C₁₆ normal

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1 paraffins and higher boiling hydrocarbons, using a high pressure and/or lower temperature
2 vapor-liquid separator or low pressure separators or a combination of separators. The tail gas
3 fraction may be used as described above. The condensate fraction can be fractionated into
4 the desired product fraction; e.g. gasoline, light middle distillate or more preferably can be
5 upgraded by hydrocracking. The F-T fraction boiling above about 540°F, is typically
6 separated into a wax fraction boiling in the range of about 540°F-1100°F primarily
7 containing C₁₆ to C₅₀ linear paraffins with relatively small amounts of higher boiling
8 branched paraffins, one or more liquid fuel fractions boiling below about 540°F and one or
9 more fractions boiling above about 1100°F. Typically, the separation is effected by
10 fractional distillation. Alternatively, if the Fischer-Tropsch reaction is designed to produce a
11 single process stream, then the entire product stream may be fractionated, generally after first
12 removing hydrogen and preferably other tail gases. This can be done by passing the product
13 stream through one or more vapor-liquid separators prior to fractionation.

14

15 Because the Fischer-Tropsch product typically contains linear oxygenates and olefins boiling
16 in the same range as the desired linear paraffins, either the F-T liquid reaction product or the
17 fraction boiling within the C₁₆ to C₅₀ linear paraffin range is preferably hydrotreated to
18 convert the oxygenates and olefins to paraffins. Thus, improving the yield of the desired
19 linear paraffins. Hydrotreating is well known to the art and can be effected using any suitable
20 hydrotreating procedure. Typically, hydrotreating is conducted at temperatures in about the
21 range of 650 to 800°F (427°C) and pressures in about the range of 800 to 3000 psi
22 (54 to 204 atms) in the presence of a catalyst comprising at least one Group VIII or Group VI
23 metal and more typically containing one metal from each group, e.g. cobalt-molybdenum;
24 nickel-tungsten, on a neutral mineral oxide support such as alumina and the like, at LHSV's
25 in the range of about from 0.25 to 2 hr⁻¹. Typically, the liquid hydrocarbon feed is contacted
26 with hydrogen at a ratio of at least 50 SCF of hydrogen per Bbl of feed and preferably
27 between about 1,000 to 5,000 SCF/Bbl.

28

29 The C₁₆ to C₅₀ paraffin fraction, or if desired a C₂₀ to C₅₀ or C₂₆ to C₅₀ fraction, is thermally
30 cracked into smaller chain length normal alpha olefins, e.g. C₆ to C₂₄. The thermal cracking

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1 can be conducted over a wide range of temperatures and pressures but is typically conducted
2 at temperatures in the range of about from 950°F (510°C) to 1900°F (1038°C) preferably
3 1000 to 1600°F (538 to 871°C) and pressures of about from 0.5 to 10 bars (7 to 147 psia)
4 preferably about from 1 to 5 bar (14.5 to 73.5 psia). Residence times or space velocity will
5 vary with the reactor temperatures and pressures. Typical residence times may vary from
6 about 0.1 to 2 seconds where high temperatures, e.g. above about 1300°F (704°C) are used,
7 to space velocities (LHSV) of about from 0.3 to 20 hr⁻¹ with lower temperatures. The
8 reaction may be conducted by passing the feed through a packed bed of inert material or by
9 using tube reactors or other types of reactors. Generally a catalyst is not used. The thermal
10 cracking is conducted in the presence of steam. The steam serves as a heat source for the
11 endothermic reactions and also as a diluent to isolate ethylene free radicals and suppress
12 undesired side reactions and coke formation. The severity of the thermal cracking conditions
13 will vary with the carbon chain length or molecular weight distribution of the feedstock and
14 the carbon chain length distribution desired in the reaction product and the desired cracking
15 conversion. Details of a typical steam thermal cracking process be found in U.S. Patent No.
16 4,042,488, hereby incorporated by reference its in entirety.

17
18 One of the problems with producing normal alpha olefins by paraffin thermal cracking is that
19 a significant amount of undesired dienes, which are not easily separated from the desired
20 normal alpha olefins, are also produced. However, in accordance with the present invention,
21 by using a high purity linear paraffin feed steam, at least 90 wt.% linear paraffins, and
22 keeping the conversion low and preferably using a high steam to feed mole ratio the amount
23 of dienes produced can be very substantially reduced thus permitting recovery of a high
24 purity C₆ to C₂₄ normal alpha olefin product fraction. The desired normal alpha olefin is
25 separated from the reaction product (e.g. fractional distillation) to remove unreacted starting
26 material as well as any higher boiling branched olefins and dienes. In practicing the present
27 invention the cracking conversion should be no greater than 30% based on weight of feed
28 and preferably no greater than 25 wt.%. In general best results in terms of yield of high
29 purity C₁₆-C₂₄ normal alpha olefins is obtained by controlling the conversion within the range
30 of 15 to 25 wt.%. This can be accomplished by adjusting the reaction temperatures,

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1 pressures and residence time (space velocity) within the ranges set forth above. Optimum
2 reaction conditions will also vary somewhat with the particular feedstock and can be
3 determined by routine process optimization. Typically mole ratios of steam to hydrocarbon
4 feed in about the range of from 2:1 to 7:1 preferably about from 3:1 to 5:1 and more
5 preferably about 5:1 moles of steam per mole of hydrocarbon feed can be used.

6
7 Because some higher dienes boiling in the C₁₆-C₅₀ normal paraffin boiling range will be
8 produced, even though small, it is preferred not to recycle the C₁₆-C₅₀ paraffin fraction of the
9 reaction product range back to the thermal cracking reactor. This is preferable to risking
10 ultimately increasing the diene content of the C₆-C₂₄ normal alpha olefin fraction product,
11 although a carefully monitored and controlled single recycle may be acceptable. Further
12 information regarding general thermal cracking can be had by reference to U.S. Patent
13 Nos. 5,146,022; 5,656,150; and 5,866,745 hereby incorporated by reference in their entirety.

14
15 The reaction product from the thermal reactor is typically fed to a fractional distillation
16 column, although other suitable separation procedures could also be used, to separate the
17 product into normal alpha olefins of the desired chain length range and to remove higher
18 boiling paraffins and branched olefins and any lower boiling material. The C₆-C₂₄ normal
19 alpha olefin fraction has a normal alpha olefin content of at least about 90 wt.% preferably at
20 least about 95% wt.%. Further by using more rigorous purification techniques such as
21 extractive distillation and/or adsorption, normal alpha olefin contents in excess of
22 95 wt.% up to about 99 wt.% and approaching 100% can be obtained. The normal alpha
23 olefin fractions either with or without further treatment are used as chemical intermediates
24 for a variety of products, including lubricants and surfactants.

25
26 The higher boiling paraffins and olefins fraction, e.g. above about C₂₄, from the thermal
27 reaction product fractionator, the condensate, the liquid fuel fractions and the
28 1100°F+ fractions are preferably upgraded by hydrocracking. This may be effected by
29 hydrocracking the respective products individually or by combining one or more of the
30 fractions. Preferably, fractions having similar boiling point ranges are combined to optimize

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1 hydrocracking conditions. For example, the condensate fraction from the minus
2 700°F Fischer-Tropsch product is preferably combined with the vacuum gas oil ("VGO")
3 boiling range fraction, and hydrocracked to higher quality liquid products. The
4 hydrocracking operation can be conducted as a block operation wherein the hydrocracker is
5 alternated between liquid fuel fractions and heavier fuel fractions or parallel hydrocrackers
6 can be used each processing a different distillation range feedstock. Hydrocracking can be
7 effected by contacting the particular fraction or combination of fractions, with hydrogen in
8 the presence of a suitable hydrocracking catalyst at temperatures in the range of about from
9 600 to 900°F (316 to 482°C) preferably 650 to 850°F (343 to 454°C) and pressures in the
10 range about from 200 to 4000 psia (13-272 atm) preferably 500 to
11 3000 psia (34-204 atm) using space velocities based on the hydrocarbon feedstock of about
12 0.1 to 10 hr⁻¹ preferably 0.25 to 5 hr⁻¹. Generally, more severe conditions within these
13 ranges will be used with higher boiling feedstocks and depending on whether gasoline,
14 middle distillate or lubricating oil is desired as the primary economic product. The
15 hydrocracking step reduces the size of the hydrocarbon molecules, hydrogenates olefin
16 bonds, hydrogenates aromatics, and removes traces of heteroatoms resulting in an
17 improvement in fuel or base oil product quality.

18

19 As is well known the hydrocracking catalysts contain a hydrogenation component and a
20 cracking component. The hydrogenation component is typically a metal or combination of
21 metals selected from Group VIII noble and non-noble metals and Group VIB metals. The
22 noble metals, particularly platinum or palladium, are generally more active but are
23 expensive. Non-noble metals which can be used include molybdenum, tungsten, nickel,
24 cobalt, etc. Where non-noble metals are used it is generally preferred to use a combination
25 of metals, typically at least one Group VIII metal and one Group VIB metal,
26 e.g., nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, and cobalt-tungsten. The
27 non-noble metal hydrogenation metal are usually present in the final catalyst composition as
28 oxides, or more preferably, as sulfides when such compounds are readily formed from the
29 particular metal involved. Preferred non-noble metal overall catalyst compositions contain
30 in excess of about 5 weight percent, preferably about 5 to about 40 weight percent

1 molybdenum and/or tungsten, and at least about 0.5, and generally about 1 to about
2 15 weight percent of nickel and/or cobalt determined as the corresponding oxides. The
3 sulfide form of these metals is most preferred due to higher activity, selectivity and activity
4 retention.

5
6 The hydrogenation components can be incorporated into the overall catalyst composition by
7 any one of numerous procedures. They can be added either to the cracking component or the
8 support or a combination of both. In the alternative, the Group VIII components can be
9 added to the cracking component or matrix component by co-mulling, impregnation, or ion
10 exchange and the Group VI components, i.e.; molybdenum and tungsten can be combined
11 with the refractory oxide by impregnation, co-mulling or co-precipitation. Although these
12 components can be combined with the catalyst support as the sulfides, that is generally not
13 the case. They are usually added as a metal salt which can be thermally converted to the
14 corresponding oxide in an oxidizing atmosphere or reduced to the metal with hydrogen or
15 other reducing agent. The non-nobel metal composition can then be sulfided by reaction
16 with a sulfur donor such as carbon bisulfide, hydrogen sulfide, hydrocarbon thiols, elemental
17 sulfur, and the like.

18
19 The cracking component is an acid catalyst material and may be a material such as
20 amorphous silica-alumina or may be a zeolitic or non-zeolitic crystalline molecular sieve.
21 Examples of suitable hydrocracking molecular sieves include zeolite Y, zeolite X and the so
22 called ultra stable zeolite Y and high structural silica:alumina ratio zeolite Y such as for
23 example described in U.S. Patent No. 4,401,556, 4,820,402 and 5,059,567. Small crystal
24 size zeolite Y, such as described in U.S. Patent No. 5,073,530 can also be used. The
25 disclosures of all of which patents are hereby incorporated by reference in their entirety.
26 Non-zeolitic molecular sieves which can be used include, for example
27 silicoaluminophosphates (SAPO), ferroaluminophosphate, titanium aluminophosphate and
28 the various ELAPO molecular sieves described in U.S. Patent No. 4,913,799 and the
29 references cited therein. Details regarding the preparation of various non-zeolite molecular
30 sieves can be found in U.S. Patent No. 5,114,563 (SAPO); 4,913,799 and the various

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1 references cited in U.S. Patent No. 4,913,799, hereby incorporated by reference in their
2 entirety. Mesoporous molecular sieves can also be included, for example the M41S family
3 of materials (J. Am. Chem. Soc. 1992, 114, 10834-10843), MCM-41 (U.S. Patent
4 Nos. 5,246, 689, 5,198,203, 5,334,368), and MCM-48 (Kresge et al., Nature 359 (1992) 710.)

5
6 In general amorphous silica-alumina is more selective for middle distillates, e.g., diesel fuel,
7 whereas crystalline molecular sieves are much more active and produce greater amounts of
8 lighter products, e.g., gasoline. The so-called high (structural) silica-alumina ratio
9 ($\text{Si}_2\text{O}_3:\text{Al}_2\text{O}_3$ =about 50) Y zeolites are less active than the conventional zeolite Y but, are
10 more selective for middle distillate and more active than amorphous silica-alumina. The
11 catalyst also typically contains a matrix or binder material resistant to the conditions used in
12 the hydrocracking reaction. Suitable matrix materials include synthetic or natural substances
13 as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be
14 either naturally occurring or in the form of gelatinous precipitates or gels including mixtures
15 of silica and metal oxides naturally occurring clays which can be composited with the
16 catalyst include those of the montmorillonite and kaolin families. These clays can be used in
17 the raw state as originally mined or initially subjected to calumination, acid treatment or
18 chemical modification.

19
20 The catalyst may be composited with a porous matrix material, such as alumina,
21 silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as
22 well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia,
23 silica-alumina-magnesia, and silica-magnesia zirconia. The relative proportions of
24 molecular sieve component and inorganic oxide matrix or binder may vary widely with the
25 molecular sieve content ranging from between 1 to 99, more usually 5 to 80, percent by
26 weight of the composite. The matrix may itself possess catalytic properties generally of an
27 acidic nature, such as for example where amorphous silica-alumina is used as a matrix or
28 binder for a molecular sieve. In general it is preferred to use a non-zeolite or low acidic
29 zeolite catalyst, e.g., high structural silica:alumina ratio Y zeolite, as the catalyst where
30 middle distillates is desired as the main commercial product and an acidic zeolite catalyst,

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1 e.g., conventional or ultra stabilized Y zeolite, where gasoline is desired as the main
2 commercial product.

3

4 Furthermore more than one catalyst type may be used in the reactor. The different catalyst
5 types can be separated into layers or mixed.

6

7 The hydrocrackate is then separated into various boiling range fractions. The separation is
8 typically conducted by fractional distillation preceded by one or more vapor-liquid separators
9 to remove hydrogen and/or other tail gases. The fractions separated will typically include a
10 gasoline fraction and a high boiling bottom fraction and one or more intermediate boiling
11 range fractions. The high boiling fraction is preferably recycled back to the hydrocracker.
12 The light tail gas fraction, i.e., methane, ethane, propene and any residual hydrogen is
13 withdrawn and can be for fuel gases or for hydrogen recovery which in turn can be recycled
14 back to the hydrocracker. Typical, liquid/vapor separator systems which can be used to
15 remove tail gases and hydrogen are, for example, described in U.S. Patent No. 3,402,122 and
16 4,159,937 hereby incorporated by reference in their entirety.

17

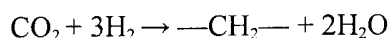
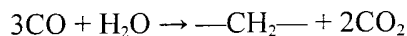
18 If desired the feed may be hydrotreated prior to hydrocracking to remove impurities and
19 heterorganics, e.g. oxygenates. Hydrotreating may be conducted in a separate reactor
20 preceding the hydrocracking or may be conducted in the same reactor, for example, as one or
21 more hydrotreating catalyst beds preceding one or more hydrocracking catalyst beds. The
22 hydrotreating bed may also serve as a screen to remove any particulate matter in the
23 feedstock or may itself be preceded with guard beds of crushed rock or other suitable
24 material. Hydrotreating can be effected by the same general procedure as described above
25 with respect to hydrotreating of the Fischer-Tropsch reaction product.

26

27 Although the invention is described herein in terms of a Fischer-Tropsch reaction or process
28 the invention also applies to the various modifications of the literal Fischer-Tropsch process
29 by which hydrogen (or water) and carbon monoxide (or carbon dioxide) are converted to
30 hydrocarbons (e.g. paraffins, ethers etc.) and to the products of such processes. Thus the

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term Fischer-Tropsch type process or product is intended to apply to Fischer-Tropsch processes and products and the various modifications thereof and the products thereof. For example, the term is intended to apply to the Kolbel-Engelhardt process typically described by the reactions



The present process can also be applied to upgrade Fischer-Tropsch products generally by applying the steps discussed above following the Fischer-Tropsch reaction to Fischer-Tropsch type products. Where such Fischer-Tropsch type products do not contain at least about 90 wt.% linear C₁₆ to C₅₀ paraffins the Fischer-Tropsch type product may be concentrated or purified by any suitable procedure, typically fractional distillation, to produce a fraction having the desired C₁₆ to C₅₀ linear paraffin concentration, preferably such Fischer-Tropsch type products, or at least the liquid portion thereof, should contain at least 20 wt.% linear C₂₀ to C₅₀ paraffins and more preferably should contain between 30-80 wt.% C₂₀ to C₅₀ paraffins for optimum benefit in the case of the fully integrated process. The Fischer-Tropsch type product preferably contains less than about 10 wt.% oxygenates, more preferably less than 5 wt.%.

For the purposes of further understanding of the invention an embodiment of the invention will now be described with reference to the drawing.

Example 1

Referring to the Figure, an embodiment of the invention will be described using a bubble slurry Fischer-Tropsch reactor. Natural gas 1, is fed by line 2 to scrubber 3 containing a packed bed of zinc oxide to remove any hydrogen sulfide or mercaptan gases contained in the natural gas. A portion of the natural gas is split off via line 2a to provide fuel for boiler 2b. The sulfur free natural gas, is fed via line 4 to syngas reactor 6 where it is reacted

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1 with oxygen provided by oxygen line 5 to effect partial oxidation of the methane. Fixed bed
2 reactor 6 contains a packed bed of perovskite LaCoO_3 catalyst and is operated at a
3 temperature of about 720°C and a pressure of about 1 bar (atmospheric pressure) and a
4 space velocity of about $27,400\text{ hr}^{-1}$ to produce a syngas containing about 2 mol of
5 hydrogen per mole of carbon monoxide. If needed the mol ratio of hydrogen to
6 carbon monoxide may be adjusted by passing the syngas through a membrane separator
7 (not shown). The syngas reaction product having a mole ratio of hydrogen to
8 carbon monoxide of about 2 is fed via line 7 to Fischer-Tropsch bubble column slurry
9 reactor 8 containing a 12 wt.% cobalt on low density alumina catalyst having a particle
10 size of about 25 to 65 microns and a density of about 0.4 to 7 g/cc in a 8 cs, at
11 100°C , synfluid slurry liquid. Prior to mixing with the slurry liquid the catalyst is
12 reduced by contact with a 5 vol.% hydrogen, 95 vol.% nitrogen gas at about
13 $200\text{--}250^\circ\text{C}$ for about 12 hours and then increasing the temperature to about
14 $350\text{--}400^\circ\text{C}$ and maintaining this temperature for about 24 hours while slowly increasing
15 the hydrogen content of the gas until the reducing gas is essentially 100% hydrogen.
16 Reactor 8 is operated at a temperature of about from 210 to 230°C , a pressure of
17 25-30 bar and a synthesis gas linear velocity of about 6 to 10 cm/sec to produce a liquid
18 hydrocarbon product containing a high proportion of C_{20} to C_{50} paraffins (the wax
19 product) discharged via line 8a and a light product boiling below about
20 650°F (343°C) containing middle distillate and tail gases discharged via line 8b. Tail
21 gases are removed from the light fraction, for example by using one or more liquid/gas
22 separators, not shown, operating at lower temperatures and/or pressures and the remaining
23 light product stream (condensate) comprising C_5 and higher hydrocarbons boiling below
24 650°F (343°C) is fed to hydrocracker 26. The F-T wax product is fed via line 8a to
25 hydrotreater 9 operated at about 700°F (371°C) to 750°F (399°C) and a pressure of about
26 60-65 atms and a LHSV of about 1 hr^{-1} over a nickel-tungsten on alumina catalyst. The
27 hydrotreated product is fed via line 9a to fractional distillation column 10 where it is
28 fractionated into a wax fraction boiling above about 700°F (371°C) primarily containing at
29 least 90 wt.% $\text{C}_{20}\text{--}\text{C}_{50}$ linear paraffins, a high boiling bright stock fraction boiling above about

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1 1100°F and a liquid fuel fraction boiling below about 700°F. The wax fraction is fed via
2 line 14 to thermal cracking reactor 16. Prior to entering the reactor the high boiling fraction
3 feed is combined with steam furnished by line 15 from boiler 2b at a mole ratio of about
4 5 mol of steam per mole of the wax fraction feed. The thermal cracking reaction is initially
5 conducted in reactor 16 at a temperature of about 1050°F (566°C) to 1150°F (621°C), a
6 pressure of about 15 psia and a space velocity of about 2 hr⁻¹ and then adjusted to produce a
7 conversion of about 25%. The reaction product from thermal cracker 16 is fed via line 17 to
8 fractional distillation column 18 where it is fractionated into four normal alpha olefin
9 fractions of varying carbon chain length and correspondingly boiling points. Thus, the lower
10 boiling C₆-C₉ normal alpha olefins are taken off as product fractions via line 19a, C₉-C₁₁
11 normal alpha olefins via line 20, C₁₁-C₁₄ normal alpha olefins via line 21, C₁₅ to C₁₉ normal
12 alpha olefins via line 22 and finally the higher boiling C₂₀-C₂₄ normal alpha olefins via
13 line 23. In accordance with the invention, the C₆-C₂₄ normal alpha olefin streams will have a
14 purity of at least about 90 wt.%. Hydrocarbon gases having five carbon atoms or less are
15 discharged via line 19 and may be used as a fuel to supply energy to other plant operations.
16 The bottoms fraction comprising uncracked material and larger chain length olefins, and
17 higher boiling branched olefins and paraffins is fed to hydrocracker 26 via line 24 instead of
18 being recycled back to thermal cracker 16. This avoids build up of dienes and branched
19 olefins in the reactor and correspondingly produces a purier normal alpha-olefin product
20 because the higher boiling dienes and branched olefins are not cracked into lower boiling
21 dienes and branched olefins which would be taken off with the C₆-C₂₄ normal alpha olefin
22 product fractions. Instead the high boiling fraction containing higher boiling dienes,
23 branched olefins and paraffins and uncracked paraffins are hydrocracked into more valuable
24 products such as gasoline and middle distillates.
25

26 Referring to distillation column 10, the liquid fraction is taken off and fed
27 hydrocracker 26 via line 10a. The bright stock fraction boiling above about
28 1100°F (593°C), is fed via line 10b to hydrocracker 26 or more preferably at least a portion
29 of the bright stock fraction is taken off via line 13 for processing as a heavy lube stock.
30 Similarly a portion of the of the C₂₀-C₅₀ paraffin fraction from column 10 may be taken off

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1 via line 42 for neutral lube oil processing. (Lube oil processing involves separate
2 hydrocracking not shown and optional hydrofinishing not shown). Hydrogen is fed to the
3 hydrocracker 26 via line 25.

4
5 Hydrocracker 26 is a fixed bed reactor containing a nickel-tungsten silica-alumina catalyst
6 and is operated at a temperature of from 650 to 850°F, a pressure of 500 to 3500 psia and a
7 catalyst space velocity of 0.1 hr^{-1} to 10 hr^{-1} . The reaction product from the hydrocracker is
8 fed via line 27 to a series of vapor-liquid separators, shown in the drawing as a single
9 box 28, to remove hydrogen from the reaction product. The hydrogen recovered from
10 separator 28 is combined with fresh make up hydrogen 25 and recycled back to the
11 hydrocracker via lines 29 or alternatively fed directly to hydrocracker 26. The liquid
12 hydrocrackate from the vapor liquid separators 28 is fed via line 30 to fractional distillation
13 column 31 where it is fractionated into a fuel fraction and a lube oil fraction and taken off via
14 lines 33 and 34 respectively. Lower boiling hydrocarbons and any residual hydrogen is taken
15 off via line 32 tail gases and used as an energy source for other plant operations. The bottom
16 fraction containing uncracked feed and other higher hydrocarbons is recycled back to the
17 hydrocracker via line 35.

18
19 Obviously many modifications and variations of the invention described herein can be made
20 without departing from the essence and scope thereof.

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1 WHAT IS CLAIMED IS:

2

3 1. A process for converting a Fischer-Tropsch type reaction product fraction comprising at
4 least about 90 wt.% C₁₆-C₅₀ linear paraffins into high purity C₆-C₂₄ normal alpha olefins
5 which comprises the steps of:

6

7 a) thermal cracking said reaction product in the presence of at least 5 moles of steam
8 per mole of said reaction product at a conversion based on said reaction product no
9 greater than 30 wt.% thereby producing a product mixture comprising a fraction
10 boiling in the C₆-C₂₄ normal alpha olefin range containing at least about
11 90 wt.% C₆-C₂₄ normal alpha olefins; and

12

13 b) separating the product mixture of step a) to recover one or more fractions boiling
14 within the boiling range of C₆-C₂₄ normal alpha olefins having a normal alpha olefin
15 purity of at least about 90 wt.%.

16

17 2. The process according to Claim 1 wherein said separation in step b) is conducted by
18 fractional distillation.

19

20 3. The process according to Claim 1 wherein said product mixture is fractionated in said
21 step b) by extractive fractional distillation to produce one or more normal alpha olefin
22 fractions within the range of C₆-C₂₄ and wherein said fractions have a normal alpha olefin
23 purity of at least about 95 wt.%.

24

25 4. The process of according to Claim 1 wherein said reaction product is thermal cracked to
26 a conversion between about from 15 to 25 wt.%.

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- 1 5. The process according to Claim 1 wherein said product mixture is fractionated in step b)
2 by adsorption to produce one or more normal alpha olefin fractions within the range of
3 C₆-C₂₄ and wherein said fractions have a normal alpha olefin purity of at least 95 wt.%.
4
- 5 6. The process according to Claim 1 wherein said Fischer-Tropsch type reaction product is
6 a Fischer-Tropsch reaction product.
7
- 8 7. A process for upgrading Fischer-Tropsch type reaction products comprising a first
9 hydrocarbon reaction product boiling above about 540°F (282°C) comprising
10 C₁₆-C₅₀ paraffins liquid fuel hydrocarbons and oxygenates and a second reaction product
11 boiling below about 540°F (282°C) comprising tail gases, paraffins, olefins and
12 oxygenates which process comprises the steps of:
13
- 14 a) fractionating said first hydrocarbon reaction product into separate fractions
15 comprising a fraction boiling in the liquid fuel boiling range, a wax fraction boiling
16 in about the range of about 540°F-1100°F comprising at least about
17 90 wt.% C₁₆-C₅₀ linear paraffins, and a fraction boiling above about 1100°F;
18
- 19 b) thermal cracking the wax fraction of step a) in the presence of steam at a mole ratio
20 of steam to said wax fraction of about from 3:1 to 5:1, under reactive conditions
21 adjusted to provide a conversion no greater than about 30 wt.% of said wax fraction
22 thereby yielding a reaction product mixture containing substantial amounts of normal
23 alpha olefins of varying chain length within the range of C₆-C₂₄, without the
24 production of significant amounts of C₆-C₂₄ dienes and wherein the fraction of said
25 reaction product mixture boiling within the C₆ to C₂₄ normal alpha olefin boiling
26 range contains at least 90 wt.% C₆ to C₂₄ normal alpha olefins;

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- 1 c) fractionating the reaction product of step b) into separate fractions comprising at least
2 one normal alpha olefin product fraction comprising normal alpha olefins selected
3 within the range of 6 to 24 carbon atoms and a higher boiling fraction boiling above
4 about 730°F (388°C) comprising higher boiling olefins and paraffins;
5
- 6 d) separating said second Fischer-Tropsch reaction product into a tail gas fraction and a
7 condensate fraction boiling below about 540°F comprising C₅ and higher carbon atom
8 hydrocarbons,
9
- 10 e) hydrocracking said condensate fraction of step d), the higher boiling fraction of
11 step c) and the liquid fuel fraction of step a) with hydrogen under hydrocracking
12 conditions in the presence of a catalyst comprising a hydrogenation component and
13 an acid catalyst cracking component in a hydrocracker under hydrocracking
14 conditions to produce a liquid reaction product mixture comprising a liquid fuel
15 boiling fraction and a higher boiling fraction; and
16
- 17 f) fractionating the liquid reaction product mixture of step e) into separate fractions
18 comprising at least one liquid fuel boiling range fraction and at least one higher
19 boiling fraction and recycling at least one higher boiling fraction back to said
20 hydrocracker.
21
- 22 8. The process of Claim 7 wherein said step b) is conducted at a temperature of about from
23 1000°F (538°C) to 1600°F (871°C) in the presence of about from 0.2 to 1 part by wt. of
24 steam per part by wt. of said wax fraction.
25
- 26 9. The process of Claim 7 wherein said catalyst of step e) contains at least one non-noble
27 Group VIII metal and at least one Group VIB metal and an acid catalyst component.

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- 1 10. The process according to Claim 7 wherein said first hydrocarbon reaction product is
2 contacted with hydrogen under hydrotreating reactive conditions in the presence of a
3 hydrotreating catalyst thereby converting oxygenates and olefins into paraffins.
4
- 5 11. The process according to Claim 7 wherein said wax fraction is contacted with hydrogen
6 under hydrotreating reactive conditions in the presence of a hydrotreating catalyst thereby
7 converting oxygenates and olefins into paraffins.
8
- 9 12. A process for converting C₁-C₃ alkanes into liquid hydrocarbon products comprising
10 C₆-C₂₄ normal alpha olefins and fuels which comprises the steps of:
11
- 12 a) reforming said C₁-C₃ alkanes into a syngas having a mole ratio of hydrogen to carbon
13 monoxide of about from 1 to 3 moles of hydrogen per mole of carbon monoxide;
14
- 15 b) contacting the syngas product of step a) with a Fischer-Tropsch catalyst under
16 Fischer-Tropsch reaction conditions to yield a first hydrocarbon reaction product
17 boiling above about 540°F comprising a major amount of C₁₆-C₅₀ linear paraffins and
18 lesser amounts of oxygenates and higher boiling hydrocarbons and a second reaction
19 product boiling below about 540°F comprising tail gases, oxygenates and liquid fuel
20 paraffins and oxygenates;
21
- 22 c) fractionating said first reaction product of step b) into separate fractions comprising a
23 fraction boiling in the liquid fuel boiling range, a wax fraction boiling in the range of
24 about 540°F-1100°F comprising at least about 90 wt.% C₁₆-C₅₀ linear paraffins and a
25 high boiling fraction boiling above about 1100°F;
26
- 27 d) thermal cracking the wax fraction of step e) in the presence of steam at a mole ratio
28 of steam to said wax fraction of about from 3:1 to 5:1, under reactive conditions
29 adjusted to provide a conversion no greater than about 30 wt.% of said wax fraction
30 thereby yielding a reaction product mixture containing substantial amounts of C₆-C₂₄,

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1 alpha olefins of varying chain length without the production of significant amounts of
2 C₆-C₂₄ dienes and wherein the fraction of said reaction product boiling within the
3 C₆ to C₂₄ normal alpha olefin boiling range contains at least 90 wt.% C₆ to C₂₄ normal
4 alpha olefins;

5

6 e) fractionating the reaction product of step d) into separate fractions comprising at least
7 one normal alpha olefin product fraction comprising a normal alpha olefin fraction
8 selected within the range of 6 to 24 carbon atoms and having a normal alpha olefin
9 purity of at least 90 wt.% and a higher boiling fraction comprising higher boiling
10 olefins and paraffins;

11

12 f) hydrocracking said higher boiling fraction of step e) the liquid fuel fraction and the
13 high boiling fraction of step c) and with hydrogen in the presence of a catalyst
14 comprising a hydrogenation component and an acid catalyst cracking component
15 under hydrocracking conditions to produce a liquid reaction product mixture
16 comprising a liquid fuel boiling fraction and a higher boiling fraction; and

17

18 g) fractionating the liquid reaction product mixture of step f) into separate fractions
19 comprising at least one liquid fuel fraction and at least one higher boiling fraction
20 and recycling at least one said higher boiling fraction back to said hydrocracker.

21

22 13. The process of Claim 12 wherein said second reaction product of step b) is separated into
23 a tail gas fraction and a C₅ and higher carbon atom hydrocarbon fraction boiling below
24 about 540°F and hydrocracking said C₅ and higher carbon atom hydrocarbon fraction
25 with hydrogen in the presence of a hydrocracking catalyst comprising a hydrogenation
26 component and an acid cracking component under hydrocracking conditions.

27

28 14. The process of Claim 12 wherein said step b) is conducted in a bubble slurry reactor.

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- 1 15. The process of Claim 12 wherein said step d) is conducted at a temperature of about from
2 650 to 1900°F in the presence of about 0.2 to 1 part per weight of steam per part by
3 weight of said wax fraction.
4
- 5 16. The process of Claim 12 wherein said catalyst of step f) contains at least one non-noble
6 Group VIII metal and at least one Group VIB metal and an acid catalyst component.
7
- 8 17. The process according to Claim 12 wherein said first hydrocarbon reaction product is
9 contacted with hydrogen under hydrotreating reactive conditions in the presence of a
10 hydrotreating catalyst thereby converting oxygenates and olefins into paraffins.
11
- 12 18. The process according to Claim 12 wherein said wax fraction is contacted with hydrogen
13 under hydrotreating reactive conditions in the presence of a hydrotreating catalyst
14 thereby converting oxygenates and olefins into paraffins.
15
- 16 19. A process for upgrading a Fischer-Tropsch reaction product boiling above about
17 540°F containing C₁₆ to C₅₀ linear paraffins, oxygenates, hydrocarbons boiling in the
18 liquid fuel ranges and linear boiling hydrocarbons and wherein said reaction product
19 contains at least 20 wt.% of C₁₆ to C₅₀ linear paraffins and less than 5 wt.% of said
20 oxygenates, which process comprises the steps of:
21
- 22 a) fractionating said Fischer-Tropsch reaction product into separate fractions
23 comprising a fraction boiling in the liquid fuel boiling range, a wax fraction boiling
24 in about the range of 540°F to 1100°F comprising at least about
25 90 wt.% C₁₆ to C₅₀ linear paraffins and a high boiling fraction boiling above about
26 1100°F.
27
- 28 b) thermal cracking the wax fraction of step a) in the presence of steam at a mole ratio
29 of steam to said wax fraction of at least 5:1, under reactive conditions adjusted to
30 provide a conversion no greater than about 30 wt.% of said wax fraction thereby

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- 1 yielding a reaction product mixture containing normal alpha olefins of varying chain
2 length within the range of C₆ to C₂₄, without the production of significant amounts of
3 C₆ to C₂₄ dienes and wherein the fraction of said reaction product boiling within the
4 C₆ to C₂₄ normal alpha olefin boiling range contains at least 90 wt.% C₆ to C₂₄ normal
5 alpha olefins;
6
- 7 c) fractionating the reaction product of step b) into separate fractions comprising at least
8 one normal alpha olefin product fraction comprising normal alpha olefins selected
9 within the range of 6 to 24 carbon atoms having purity of said normal alpha olefins of
10 at least 90 wt.% and a higher boiling fraction comprising higher boiling olefins and
11 paraffins;
12
- 13 d) hydrocracking said higher boiling fraction of step c), and the liquid fuel fraction of
14 step a) with hydrogen in a hydrocracker in the presence of a catalyst comprising a
15 hydrogenation component and an acid catalyst cracking component, under
16 hydrocracking conditions to produce a liquid reaction product mixture comprising a
17 liquid fuel boiling fraction; and
18
- 19 e) fractionating the liquid reaction product mixture of step d) into separate fractions
20 comprising a liquid fuel fraction, and at least one higher boiling hydrocarbon fraction
21 and recycling at least one of said higher boiling fraction back to said hydrocracker.
22
- 23 20. The process of Claim 19 wherein said step b) is conducted at a temperature of about from
24 1000°F (538°C) to 1600°F (871°C) in the presence of about from 0.2 to 1 part by wt. of
25 steam per part by wt. of said wax fraction.
26
- 27 21. The process of Claim 19 wherein said catalyst of step d) contains at least one non-noble
28 Group VIII metal and at least one Group VIB metal and an acid catalyst component.

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- 1 22. The process according to Claim 19 wherein said Fischer-Tropsch reaction product is
2 contacted with hydrogen under hydrotreating reactive conditions in the presence of a
3 hydrotreating catalyst thereby converting oxygenates and olefins into paraffins.
4
- 5 23. The process according to Claim 19 wherein after fractionation said wax fraction is
6 contacted with hydrogen under hydrotreating reactive conditions in the presence of a
7 hydrotreating catalyst thereby converting oxygenates and olefins into paraffins.
8
- 9 24. A process for converting C₁-C₃ alkanes into liquid hydrocarbon products comprising
10 normal alpha olefins and fuels which comprises the steps of:
11
- 12 a) reforming said C₁-C₃ alkanes into a syngas having a mole ratio of hydrogen to carbon
13 monoxide of about from 1 to 3 moles of hydrogen per mole of carbon monoxide;
14
- 15 b) contacting the syngas product of step a) with a Fischer-Tropsch catalyst under
16 Fischer-Tropsch reaction conditions to yield a liquid hydrocarbon reaction product
17 boiling in about the range of 68°F to 1300°F comprising at least about
18 20 wt.% C₁₆ to C₅₀ linear paraffins, and lesser amounts of oxygenates;
19
- 20 c) fractionating the reaction product of step b) into separate fractions comprising a
21 fraction boiling in the liquid hydrocarbon fuel range; a wax fraction boiling in about
22 the range of 540°F to 1100°F comprising at least 90 wt.% C₁₆ to C₅₀ linear paraffins;
23 and a high boiling hydrocarbon fraction boiling above 1100°F; and
24
- 25 d) thermal cracking the wax fraction of step c) in the presence of at least five moles of
26 steam per mole of said wax fraction under reactive conditions adjusted to provide a
27 conversion, based on said wax fraction no greater than 30 wt.% thereby yielding a
28 reaction product mixture containing normal alpha olefins of varying chain length
29 within the range of C₆ to C₂₄, uncracked linear paraffins without the production of
30 significant amounts of C₆ to C₂₄ dienes and wherein the fraction boiling within the

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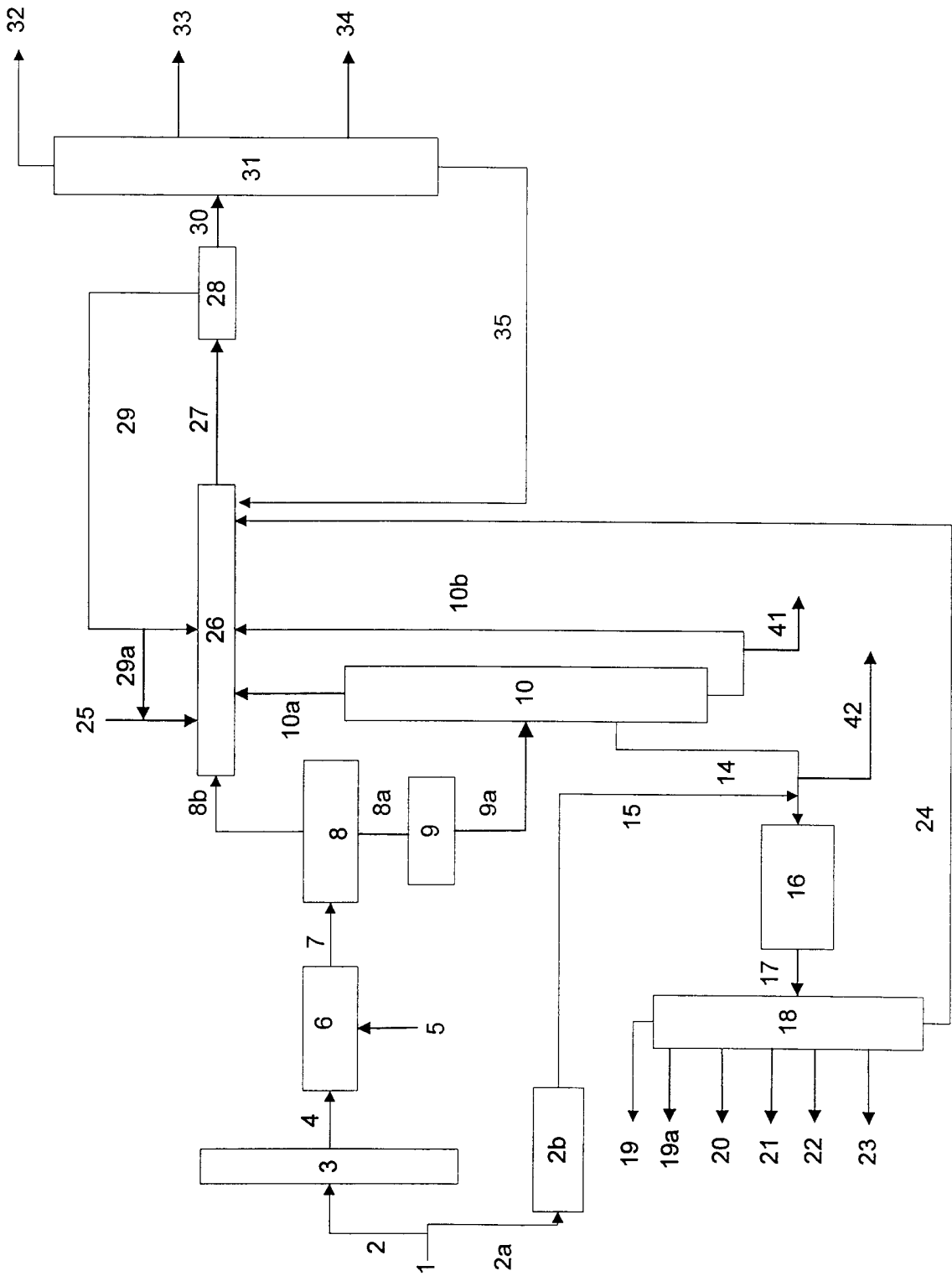
- 1 boiling range of C₆ to C₂₄ normal alpha olefins contains at least
2 90 wt.% C₆ to C₂₄ normal alpha olefins;
3
- 4 e) fractionating the reaction product of step d) into separate fractions comprising at least
5 one normal alpha olefin product fraction comprising normal alpha olefins selected
6 within the range of 6 to 24 carbon atoms and a higher boiling fraction comprising
7 higher boiling olefins and paraffins and wherein said normal alpha olefin fractions
8 have a purity of at least about 90 wt.%;
9
- 10 f) hydrocracking the fuel fraction and higher boiling fraction of step c) and the higher
11 boiling fraction of step e) by contacting said fraction with hydrogen in the presence
12 of a catalyst comprising a hydrogenation component and an acid catalyst cracking
13 component, under hydrocracking conditions to produce a liquid reaction product
14 mixture comprising a fuel boiling fraction;
15
- 16 g) fractionating the liquid reaction product mixture of step f) into separate fractions
17 comprising a liquid fuel boiling range fraction, and at least one higher boiling
18 hydrocarbon fraction and recycling at least one of said higher boiling fraction back to
19 said hydrocracker.
20
- 21 25. The process of Claim 24 wherein said step b) is conducted in a bubble slurry reactor.
22
- 23 26. The process of Claim 24 wherein said step d) is conducted at a temperature of about from
24 650 to 1900°F in the presence of about 0.2 to 1 part per weight of steam per part by
25 weight of said wax fraction.
26
- 27 27. The process of Claim 24 wherein said catalyst of step f) contains at least one non-noble
28 Group VIII metal and at least one Group VIB metal and an acid catalyst component.
29

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1 28. The process according to Claim 24 wherein said liquid hydrocarbon reaction product of
2 step (b) is contacted with hydrogen under hydrotreating reactive conditions in the
3 presence of a hydrotreating catalyst thereby converting oxygenates and olefins into
4 paraffins.

5

6 29. The process according to Claim 24 wherein said wax fraction is contacted with hydrogen
7 under hydrotreating reactive conditions in the presence of a hydrotreating catalyst
8 thereby converting oxygenates and olefins into paraffins.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/34539

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G9/00 C10G69/06 C10G55/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 37737 A (SCHUEMANN SASOL GMBH & CO KG ;MARLAND CHRISTOPHER (ZA); MERWE JOSI) 29 July 1999 (1999-07-29) the whole document ---	1-29
A	US 4 133 841 A (COSYNS JEAN ET AL) 9 January 1979 (1979-01-09) the whole document ---	1-29
A	US 5 371 308 A (GOSSELINK JOHN W ET AL) 6 December 1994 (1994-12-06) the whole document ---	1-29
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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E earlier document but published on or after the international filing date

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

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

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

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

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* & * document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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