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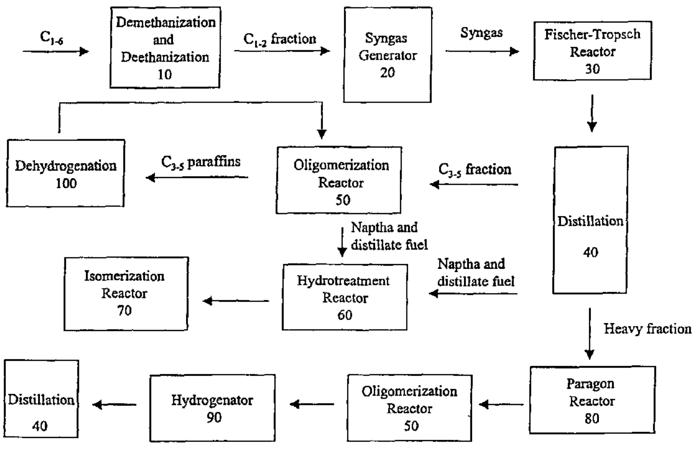
(54) Title: IMPROVED CONVERSION OF SYNGAS TO DISTILLATE FUELS



(57) Abstract: An integrated process for producing distillate fuel from syngas is disclosed. Syngas is reacted under Fischer-Tropsch conditions to form a product stream which includes a naptha fraction, a distillate fuel fraction and a fraction that includes mostly wax and heavy products. The wax fraction is subjected to the Paragon process, and the light olefins generated in this process are oligomerized to form additional iso-olefins, which are optionally reduced to form isoparaffins. Naptha and distillate fuels can be isolated from the oligomerization step, and wax and heavy fractions from the oligomerization step are optionally recycled to extinction. Preferably, at least a portion of the syngas used in the Fischer-Tropsch chemistry is derived from natural gas. The C_3+ products from the natural gas and the Fischer-Tropsch step are optionally subjected to molecular redistribution to produce additional ethane and a C_5+ fraction or dehydrogenated to form an additional feedstock for the oligomerization step. The distillate fuels formed in this process have relatively high octane and/or cetane values and also have low levels of sulfur and nitrogen impurities. The process is advantageous with respect to other processes because it requires significantly less hydrogen, and can be operated at considerably lower temperatures and pressures.

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IMPROVED CONVERSION OF SYNGAS TO DISTILLATE FUELS

BACKGROUND OF THE INVENTION

The majority of commercially available distillate fuels are derived from crude oil. Crude oil is in limited supply, and fuel derived from crude oil is often contaminated with sulfur and nitrogen compounds which contribute to acid rain. For these reasons, efforts have focused on methods for forming oil from feedstocks other than crude oil.

Several methods have been developed for converting natural gas to distillate fuels. One method involves converting methane to methanol, and then converting the methanol to higher molecular weight products. Another method involves converting methane to synthesis gas (Asyngas≅), a mixture of carbon monoxide and hydrogen gas, and subjecting the syngas to Fischer-Tropsch synthesis to form a mixture of products.

Fischer-Tropsch chemistry tends to produce either low molecular weight olefins or high molecular weight waxes, depending on the type of catalyst used and the process conditions (temperature, syngas ratio and other variables). The low molecular weight olefins can be oligomerized, and the waxes can be hydrocracked, with the products optionally isomerized, to provide hydrocarbons useful in gasoline compositions. The feedstock to the hydrocracker needs to be hydrotreated to remove oxygenates. Both the hydrotreating and hydrocracking steps require the use of hydrogen and are performed at relatively high temperatures and pressures. Accordingly, the steps needed to convert methane to distillate fuels using Fischer-Tropsch chemistry are relatively capital intensive.

It would be desirable to provide methods for forming distillate fuels from natural gas that are not as capital intensive. The present invention provides such methods.

SUMMARY OF THE INVENTION

In its broadest aspect, the present invention is directed to an integrated process for preparing distillate fuels from syngas (a mixture of carbon monoxide and hydrogen). Syngas is reacted under Fischer-Tropsch conditions to form a product stream which includes methane and a range of hydrocarbons from C_2 to about C_{50}.

Methane and ethane can be isolated from the product stream and recycled through a syngas generator. An olefin-rich C_{3-5} fraction can be isolated, and the olefins can be oligomerized to form distillate fuels. Naptha and distillate fuel fractions can also be isolated, and can optionally be subjected to further process steps, such as catalytic isomerization, to improve their octane and lower their pour point.

The remainder of the product stream includes mostly wax and heavy products. These products are subjected to the Paragon Process, and the light olefins generated in this process are oligomerized to form isoolefins in the distillate fuel range, as well as heavier products. The product stream from the oligomerization reactor is optionally hydrotreated. Naptha, distillate fuels and heavier products can be isolated from the product stream from the oligomerization reactor. The heavy products can be recycled to extinction. Any light (C_{3-4}) alkanes can be optionally subjected to molecular redistribution to form additional ethane and C_5+ alkanes.

The naphtha and distillate fuel produced by this process has high octane and cetane values, respectively, and also has low levels of sulfur and nitrogen impurities, which are known to contribute to acid rain. The process is advantageous with respect to other processes because it requires significantly less hydrogen, and can be operated at considerably lower temperatures and pressures.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic flow diagram representing one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to an integrated process for producing distillate fuels from syngas. As used herein, the term "integrated process" refers to a process comprising a sequence of steps, some of which may be parallel to other steps in the process, but which are interrelated or somehow dependent upon either earlier or later steps in the total process.

Methane and ethane, preferably derived from natural gas, can be sent through a syngas generator to form syngas. Fischer-Tropsch chemistry converts the syngas to a product stream which includes a variety of paraffins and olefins. The Fischer-Tropsch chemistry provides products which are highly linear and which include low levels of nitrogen and sulfur.

The product stream is separated into various fractions, including, for example, a C_2- fraction, an olefin-rich C_{3-5} fraction, a naptha fraction, a distillate fuel fraction, and a fraction including waxes and heavy products. The C_2- fraction can be recycled through the syngas generator. The olefins in the C_{3-5} fraction can be oligomerized to form distillate fuel. The naptha and distillate fuel fractions can be collected and optionally hydrotreated to reduce the olefin concentration and/or isomerized to increase the octane value and/or lower the pour point.

The fraction including the wax and heavy products is subjected to the Paragon Process to form a mixture of light olefins and a small amount of light paraffins. The light olefins including mainly propene, n-butene, isobutene, n-pentene and isopentene. The olefins are oligomerized to form naptha and distillate fuel. The products of the oligomerization step tend to be highly branched isoolefins, which can optionally be reduced with hydrogen to isoparaffins. In a preferred embodiment, the source of hydrogen for the reduction of the olefins is syngas, thus avoiding the need to set up a separate hydrogen plant.

Feedstocks for the Fischer-Tropsch Reaction

The preferred feedstock for use in generating syngas is methane and/or ethane, preferably derived from natural gas or recycled methane and/or ethane from various stages in the process described herein. Heavier hydrocarbons tend to coke up the syngas generator, and are not preferred. In addition to methane and ethane, natural gas includes some heavier hydrocarbons (C_{3-5} alkanes) and other impurities, e.g., carbon dioxide, nitrogen, helium, water and non-hydrocarbon acid gases. The methane and ethane can be isolated from the C_{3+} alkanes and other impurities to provide a feedstock rich in methane and ethane, for example, using demethanizer and deethanizer columns.

The presence of sulfur, nitrogen, halogen, selenium, phosphorus, mercury and arsenic contaminants in the feedstock is undesirable. For this reason, it is preferred to remove sulfur and other contaminants from the feed before performing the Fischer-Tropsch chemistry. Means for removing these contaminants are well known to those of skill in the art. For example, ZnO guardbeds are preferred for removing sulfur impurities. Means for removing other contaminants are well known to those of skill in the art.

Demethanizers and other means for removing methane are well known to those of skill in the art, and are described, for example, in U.S. Patent No. 5,960,643 to Kuechler et al. and C.Collins, R. J. J. Chen and D. G. Elliot, "Trends in NGL Recovery for Natural and Associated Gases," GasTech, Ltd. of Rickmansworth, England, pages 287-303, GasTech LNG/LPG Conference 84, the contents of which are hereby incorporated by reference.

Demethanizer columns, which include one or more distillation towers, are typically used to separate methane and other more volatile components from ethane and less volatile components. High pressure demethanizers typically operate at pressures higher than 2.758 MPa (400 psi) and can produce overhead reflux by condensation against a pure component ethylene refrigeration. Demethanizer overhead temperatures of these systems are typically in the range of -85EC to -100EC. Ethylene refrigeration at approximately -101EC is typically used for chilling the overhead condenser. At pressures below 2.758 MPa, the overhead temperature is typically too low to use ethylene refrigeration unless a vacuum suction is used. However, that is not preferable due to potential air leakage into the system.

Deethanization

Methods for removing ethane from an alkane fraction are well known to those of skill in the art, and generally involve using a deethanizer. Ethane is preferably separated from propane and less volatile components. The ethane can be sent to directly to the syngas generator to form syngas.

Syngas Generation

Syngas generators and their use with methane and ethane as feedstocks are well known to those of skill in the art and are not described in detail here. Any nitrogen and/or helium present in the methane and ethane-containing feedstock can be tolerated in the syngas generator. Depending on the exact nature of the source, the feedstock can include heteroatom-containing impurities. These impurities should be removed before the feedstock is sent to the syngas generator. These impurities can be removed, for example, by hydrotreatment.

Fischer-Tropsch Chemistry

In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by contact with a Fischer-Tropsch catalyst under reactive conditions. Depending on the quality of the syngas, it may be desirable to purify the syngas prior to the Fischer-Tropsch reactor to remove carbon dioxide produced during the syngas reaction and any sulfur compounds, if they have not already been removed. This can be accomplished, for example, by contacting the syngas with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a packed column.

Examples of conditions for performing Fischer-Tropsch type reactions are well known to those of skill in the art. Suitable conditions are described, for example, in U.S. Patent Nos. 4,704,487, 4,507,517, 4,599,474, 4,704,493, 4,709,108, 4,734,537, 4,814,533, 4,814,534 and 4,814,538, the contents of each of which are hereby incorporated by reference in their entirety.

In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on a metal oxide support. The catalysts may also contain a noble metal promoter(s) and/or crystalline molecular sieves. Certain catalysts are known to provide chain growth probabilities that are relatively low to moderate, and the reaction products include a relatively high proportion of low molecular (C_{2-8}) weight olefins and a relatively low proportion of high molecular weight (C_{20}+) paraffins. Certain other catalysts are known to provide relatively high chain growth probabilities, and the reaction products include a relatively low proportion of low molecular (C_{2-8}) weight olefins and a relatively high proportion of high molecular weight (C_{20}+) paraffins. Such catalysts are well known to those of skill in the art and can be readily obtained and/or prepared. Catalysts with high chain growth probabilities (i.e., an alpha value greater than about 0.800) are preferred. The overall process including the Paragon Process and olefin oligomerization can efficiently convert the high molecular weight products to distillate fuel. Also, catalysts with high chain growth probabilities tend to produce less methane than catalysts with low chain growth probabilities, increasing the overall yield of distillate fuel.

Catalyst Selection

Catalysts with High Chain Growth Probabilities

Preferably, the Fischer-Tropsch reaction is run with a catalyst that provides relatively high chain growth probabilities to provide a product stream including a relatively large (C_{20}+) paraffin fraction. Preferably, the catalyst is a cobalt-containing catalyst. Ruthenium is also an effective Fischer-Tropsch catalyst, but is more expensive.

One suitable cobalt catalyst that can be used is described in U.S. Patent No. 4,579,986, as satisfying the relationship:

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

wherein:

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

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

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

Other suitable catalysts include those described in U.S. Patent Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320. U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture of CoO, Al_2O_3 and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth metal, with Mo-K on carbon being preferred.

U.S. Patent No. 4,088,671 discloses minimizing methane production by using a small amount of ruthenium on a cobalt catalyst. Supported ruthenium catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.

In general, the amount of cobalt present in the catalyst is between about 1 and about 50 weight percent of the total catalyst composition, more preferably between about 10.0 and 25 weight percent.

Preferably, the catalyst contains between about 3 and 60 ppw cobalt, between 0.1 and 100 ppw of at least one of zirconium, titanium or chromium per 100 ppw of support (typically, silica, alumina, or silica-alumina and mixtures thereof).

Catalyst Supports

The type of support used can influence methane production. Suitable metal oxide supports or matrices which can be used to minimize methane production include alumina, titania, silica, magnesium oxide, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof.

Methane production can be decreased using supported ruthenium catalysts. Titania or titania-containing supports provide lower methane production than, for example, silica, alumina or manganese oxide supports. Accordingly, titania and titania-containing supports are preferred.

Typically, the catalysts have a particle size of between 10 and 110 microns, preferably between 20 and 80 microns, more preferably between 25 and 65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably between 0.3 and 0.75 g/cc. The catalysts typically include one or more of the above-mentioned catalytic metals, preferably including iron in the first stage and cobalt in the second stage, on one of the above-mentioned catalyst supports. Preferably, the cobalt-containing catalysts include about 10 to 14 percent cobalt on a low density fluid support, for example, alumina, silica and the like, having a density within the ranges set forth above for the catalyst.

Promoters and Noble Metals

Methane selectivity is also influenced by the choice of promoter. Alkali metal promoters are known for reducing the methane selectivities of iron catalysts. Noble metals, such as ruthenium, supported on inorganic refractory oxide supports, exhibit superior hydrocarbon synthesis characteristics with relatively low methane production. Where a noble metal is used, platinum and palladium are generally preferred. Accordingly, alkali metal promoters and/or noble metals can be included in the catalyst bed.

The disclosures of each of the patents and articles discussed above are incorporated herein by reference in their entirety.

Operating Conditions

Fischer-Tropsch reactions designed to produce a relatively high proportion of the C_{20}+ fraction are typically conducted in either a fixed bed reactor or a slurry reactor, where slurry reactors are preferred. The operating temperature of the fixed bed reactor is between about 200EC and 225EC, and the operating temperature of the slurry reactor is between about 225EC and 250EC, with a temperature around 240EC preferred. Typical synthesis gas linear velocity ranges in the reactor are from about 2 to 40 cm per sec., preferably from about 6 to 10 cm per sec. The pressure is preferably between about 1 and 30ATM, with pressures between 20 and 30 ATM being particularly preferred. Above about 30 ATM, carbonyls may be formed and, therefore, pressures significantly above 30 ATM are not preferred. Further,
the rate of reaction tends to increase with increased pressure, but tends to level off due to hydrodynamic problems at around 30 ATM.

The catalyst space velocities are typically between about 100 and 10,000 cc/g/h, preferably between about 300 and 3,000 cc/g/h, for both stages.

As discussed above, slurry reactors can be preferred for the Fischer-Tropsch reaction. Bubble column slurry reactors can be particularly preferred. Details regarding bubble column slurry reactors can be found, for example, in Y.T. Shah et al., "Design Parameters Estimations for Bubble Column Reactors," *AIChE Journal*, 28 No. 3 pp. 353-379 (May 1982); Ramachandran et al., Bubble Column Slurry Reactor, Three-Phase Catalytic Reactors, Chapter 10, pp. 308-332 Gordon and Broch Science Publishers (1983); Deckwer et al., "Modeling the Fischer-Tropsch Synthesis in the Slurry Phase," *Ind. Eng. Chem. Process Des. Dev.*, Vol. 21, No. 2, pp. 231-241 (1982); Kölbel et al., "The Fischer-Tropsch Synthesis in the Liquid Phase," *Catal. Rev.-Sci. Eng.*, Vol. 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982, the contents of each of which are hereby incorporated by reference in their entirety.

Since the catalyst metal may be present in the catalyst in the form of an oxide, the catalyst may be reduced with hydrogen prior to contact with the slurry liquid. The starting slurry liquid is typically a heavy hydrocarbon with a viscosity sufficient to keep the catalyst particles suspended (typically between 4 and 100 centistokes at 100EC). The slurry liquid also has a low enough volatility to avoid vaporization during operation (typically an initial boiling point range of between about 350EC and 550EC). The slurry liquid is preferably essentially free of contaminants such as sulfur, phosphorous or chlorine compounds. Initially, it may be desirable to use a synthetic hydrocarbon fluid such as a synthetic olefin oligomer as the slurry fluid.

Often, a paraffin fraction of the product having the desired viscosity and volatility is recycled as the slurry liquid. The slurry typically has a catalyst concentration of between about 2 and 40 percent catalyst, preferably between about 5 and 20 percent, and more preferably between about 7 and 15 percent catalyst based on the total weight of the catalyst, i.e., metal plus support.

Although the reactions described herein are described in terms of Fischer-Tropsch reactions, they can optionally be performed using various modifications of the literal Fischer-Tropsch process where hydrogen (or water) and carbon monoxide (or carbon dioxide) are converted to hydrocarbons (e.g., paraffins, ethers, etc.). Thus, the term Fischer-Tropsch type product or process 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 reaction:

$$3CO + H_2O \ 6 \ \ XCH_2X + 2CO_2$$

The carbon dioxide can be returned to the syngas generator and combined with methane and air to form more syngas.

The Separation of Products From the Fischer-Tropsch Reaction

As discussed above, the Fischer-Tropsch reaction yields a mixture of water, methane, ethane, unreacted syngas, carbon dioxide and heavier hydrocarbons. Water, carbon dioxide, and unreacted syngas are preferably removed from the product stream. Carbon dioxide can be selectively removed from unreacted syngas, for example, using membrane separation technology. Methane and ethane are preferably bled off to a syngas generator and recycled.

A number of hydrocarbon fractions can be isolated from the product stream, using, for example, a high pressure and/or lower temperature vapor-liquid separator or low pressure separators or a combination of separators.

A C_2- fraction can be isolated via conventional distillation techniques and recycled through the syngas generator. An olefin-rich C_{3-5} fraction can be isolated and the olefins oligomerized to form distillate fuel, preferably in combination with the olefins derived from the Paragon Process.

Naptha and distillate fuel fractions can be isolated and either used directly in fuel compositions or subjected to additional process steps such as hydrotreatment and/or isomerization. Catalysts and methods for hydrotreating and isomerizing hydrocarbons are well known to those of skill in the art.

The remaining products tend to have boiling points above about 650EF and include a wax fraction boiling in the range of about 650EF-1200EF after removing particulate catalyst fines and one or more fractions boiling above about 1200EF. These fractions can be isolated from the lighter fractions using techniques known to those of skill in the art.

The wax and heavy fractions primarily contain C_{20} to C_{50} linear paraffins with relatively small amounts of higher boiling branched paraffins. The fractions can be separated by fractional distillation or, preferably, are kept together and converted to an olefin-rich product stream using the Paragon Process. These fractions can optionally be hydrotreated at this stage to remove any oxygenated products before the fractions are subjected to the Paragon Process and oligomerization step as discussed in detail below.

Hydrotreatment

Catalysts useful for hydrotreating the various fractions are well known in the art. See, for example, U.S. Patent Nos. 4,347,121 and 4,810,357 for general descriptions of hydrotreating catalysts and conditions. Suitable catalysts include noble metals from Group VIIIA, such as platinum or palladium on an alumina or siliceous matrix, and Group VIIIA and Group VIB, such as nickel-molybdenum or nickel-tin on an alumina or siliceous matrix. U.S. Pat. No. 3,852,207 describes suitable noble metal catalysts and mild hydrotreating conditions. Other suitable catalysts are described, for example, in U.S. Patent Nos. 4,157,294 and 3,904,513.

The non-noble metal (such as nickel-molybdenum) hydrogenation metal are usually present in the final catalyst composition as oxides, or more preferably or possibly, as sulfides when such compounds are readily formed from the particular metal involved. Preferred non-noble metal catalyst compositions contain in excess of about 5 weight percent, preferably about 5 to about 40 weight percent molybdenum and/or tungsten, and at least about 0.5, and generally about 1 to about 15 weight percent of nickel and/or cobalt determined as the corresponding oxides. The noble metal (such as platinum) catalyst contains in excess of 0.01percent metal, preferably between 0.1 and 1.0 percent metal. Combinations of noble metals may also be used, such as mixtures of platinum and palladium.

Isomerization Chemistry

Isomerization of the paraffinic products from the Fischer-Tropsch reaction provide the products with more branched paraffins, thus improving their octane values and lowering the pour point. Isomerization processes are generally carried out at a temperature between 200E F and 700EF, preferably 300EF to 550EF, with a liquid hourly space velocity between 0.1 and 2, preferably between 0.25 and 0.50. The hydrogen content is adjusted such that the hydrogen to hydrocarbon mole ratio is between 1:1 and 5:1. Catalysts useful for isomerization are generally bifunctional catalysts comprising a hydrogenation component, (preferably selected from the Group VIII metals of the Periodic Table of the Elements, and more preferably selected from the group consisting of nickel, platinum, palladium and mixtures thereof) and an acid component. Examples of an acid component useful in the preferred isomerization catalyst include a crystalline zeolite, a halogenated alumina component, or a silica-alumina component. Such paraffin isomerization catalysts are well known in the art.

The Paragon Process

The Paragon process is well known to those of skill in the art, and is described, for example, in U.S. Patent Nos. 4,502,945; 4,436,614; 4,390,413; 4,282,085; and 4,251,348, the contents of which are hereby incorporated by reference.

The Paragon Process is capable of producing olefins from normal paraffins, slightly branched paraffins and mixtures thereof. This is accomplished by contacting a paraffinic feedstock with a catalyst under conditions which convert the paraffins to predominantly C_{3-5} olefins.

An example of a typical conversion is shown below with respect to a C_{40} paraffin. Similar conversions occur for other paraffins of different molecular weights.

$$C_{40}H_{82} \quad 2C_3H_6 + 4\ C_4H_8\ + 3\ C_5H_{10}\ + C_3H_8$$

The products from the reaction are in a distribution that is determined mainly by thermodynamics. The products tend to include traces of ethylene (it is not thermodynamically favored), propylene, butenes, and C_5+ olefins. As the pressure drops, the yield of light olefins increases. The yield and types of olefins can be adjusted by varying the temperature and pressure of the reaction. Since the olefin product stream is an equilibrium mixture, undesired olefins can be recycled to the reactor and converted to desired olefins. For example, if the desired product stream is propylene, butenes and higher olefins can be recycled, optionally to extinction, to yield additional propylene. Any light paraffins in the reaction mixture will be largely inert, and it may be desirable to separate paraffins from olefins at some point in the overall process.

The catalyst typically includes an intermediate pore size, silicaceous crystalline molecular sieve having a silica:alumina mole ratio from about 25:1 to about 500:1 and which preferably has little or no hydrogenation activity. The reaction is conducted under olefin-producing reaction conditions, which typically involve pressures between about 30 psia and 1000 psia. The temperatures typically range between about 290 and 5951C, more preferably between about 340 and 4801C. The liquid hourly space velocities typically range between about 0.1 and 50 v/v/hr, preferably between about 0.5 and 25 v/v/hr.

The feedstock for the Paragon Process is primarily the waxy (i.e., C_{20}+) fraction from the Fischer-Tropsch reaction. However, this fraction can be combined with hydrocarbons from other sources, such as gas oils, lubricating oil stocks, high pour point polyalphaolefins, foots oils, synthetic waxes such as normal alpha-olefin waxes, slack waxes, deoiled waxes and microcrystalline waxes. Foots oil is prepared by separating oil from the wax, where the isolated oil is referred to as foots oil. Preferably, the boiling point of the feedstocks is above that of distillate fuel and below about 12001F.

The presence of nitrogen compounds in the feed tends to lead to a reduction of the catalyst's activity and a shortening of the run life. For this reason, it is preferred that the total feed nitrogen be reduced to less than about 50 ppm by weight, and more preferably less than about 10 ppm by weight total nitrogen. It is also preferred that the feed have a sulfur content of less than about 1000 ppm by weight organic sulfur, and preferably less than about 500 ppm by weight organic sulfur. The products from the Fischer-Tropsch reaction are an ideal feedstock for the Paragon Process, since it contains relatively low levels of organonitrogen and organosulfur compounds.

There is a relationship between the pressure in the reaction zone and the aluminum content of the molecular sieve which gives a region of highly preferred olefin-producing activity. The conditions in the reaction zone can include standard hydroprocessing temperatures and flow rates. The pressure, however, can range from about 30 psia to about 1000 psia, preferably from about 45 psia to about 90 psia, and most preferably from about 55 psia to about 75 psia.

It is preferred that the pressure in the Paragon Process step is close to that used in the subsequent oligomerization step (about 100 psig), to avoid compression of the gases.

When operated at atmospheric pressure, the paragon reactor=s catalysts last a long time (1000=s of hours of operation). When operated above atmospheric pressure, the olefin products can react by hydrogen transfer to form coke that can foul the catalyst. To avoid this reaction, the silica:alumina mole ratio of the (molecular sieve) catalyst is kept high, either by performing the synthesis at this value, or by post-synthesis modification (steaming and acid leaching). Steaming and acid leaching can reduce hydrogen transfer, providing higher olefin yields and lowering fouling. If the catalyst fouls, it can be regenerated by oxidation burn using standard methods. Typically, volatile gases are removed in a stream of an inert gas such as nitrogen, the bed is heated, and oxygen is slowly introduced to the inert gas feed while monitoring the exotherms, at temperatures between about 800 and 10001F.

The silica:alumina mole ratio of the molecular sieve, as will be described, can range from about 150:1 to about 1000:1, more preferably from about 175:1 to about 300:1, most preferably from about 210:1 to about 270:1. Within these ranges, long run lives and high olefin production rates can be achieved.

By "intermediate pore size silicaceous crystalline molecular sieve," as used herein, is meant two classes of silica-containing crystalline materials. The first class includes materials that, in addition to silica, contain significant amounts of alumina. These crystalline materials are usually called "zeolites," i.e., crystalline aluminosilicates. The second class of materials is essentially alumina-free silicates. These crystalline materials can include crystalline silica polymorphs, e.g., silicalite, chromia silicates, e.g., CZM, and ferrosilicates, which are described, for example, in U.S. Pat. No. 4,238,318, the contents of which are hereby incorporated by reference. ZSM-5 and ZSM-11 are preferred materials. The zeolites should be substantially in the H+ ion exchange form, that is, substantially free of sodium, potassium and other alkali metal and alkali earth ions.

All of these materials have the ability to sort molecules based on their size and/or shape. The larger pore size materials will admit larger molecules than the smaller pore size materials. Intermediate pore size silicaceous crystalline molecular sieves have the unique characteristics of being able to differentiate between large molecules and molecules containing quaternary carbon atoms on the one hand, and smaller molecules on the other hand. Thus, the intermediate pore size materials have surprising catalytic selectivities by reason of their effective pore apertures, as well as highly desirable and surprising catalytic activity and stability when compared to the larger pore size crystalline molecular sieves.

By "intermediate pore size" as used herein is meant an effective pore aperture in the range of about 5 to 6.5 Angstroms when the molecular sieve is in the H-form. Molecular sieves having pore apertures in this range tend to have unique molecular sieving characteristics. Unlike small pore size zeolites such as erionite and chabazite, they will allow hydrocarbons having some branching into the molecular sieve void spaces. Unlike larger pore size zeolites such as the faujasites, they can differentiate between n-alkanes and slightly branched alkanes on the one hand and larger branched alkanes having, for example, quaternary carbon atoms.

The effective pore size of the molecular sieves can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See Breck, Zeolite Molecular Sieves, 1974 (especially Chapter 8) and

Anderson et al., *J. Catalysis,* Vol. 58, p. 114 (1979), both of which are incorporated by reference.

Intermediate pore size molecular sieves in the H-form will typically admit molecules having kinetic diameters of 5.0 to 6.5 Angstroms with little hindrance. Examples of such compounds (and their kinetic diameters in Angstroms) are: n-hexane (4.3), 3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds having kinetic diameters of about 6 to 6.5 Angstroms can be admitted into the pores, depending on the particular sieve, but do not penetrate as quickly and in some cases are effectively excluded. Compounds having kinetic diameters in the range of 6 to 6.5 Angstroms include: cyclohexane (6.0), 2,3-dimethylbutane (6.1), m-xylene (6.1), and 1,2,3,4-tetramethylbenzene (6.4). Generally, compounds having kinetic diameters of greater than about 6.5 Angstroms do not penetrate the pore apertures and thus are not absorbed into the interior of the molecular sieve lattice. Examples of such larger compounds include: hexamethylbenzene (7.1), 1,3,5-trimethylbenzene (7.5), and tributylamine (8.1). The preferred effective pore size range is from about 5.3 to about 6.2 Angstroms. Among the materials falling within this range are the zeolite ZSM-5, the crystalline silica polymorph silicalite, RE 29,948 organosilicates, and the chromia silicate, CZM.

In performing adsorption measurements to determine pore size, standard techniques are used. It is convenient to consider a particular molecule as excluded if it does not fill at least 80% of the zeolite pore volume in less than about one hour (p/po=0.5; 25°C).

Examples of intermediate pore size silicaceous crystalline molecular sieves include zeolites such as members of the ZSM series, e.g., ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-23, ZSM-35, ZSM-38, and ZSM-48. ZSM-5 is described in U.S. Pat. Nos. 3,702,886 and 3,770,614; ZSM-11 is described in U.S. Pat. No. 3,709,979; ZSM-12 is described in U.S. Pat. No. 3,832,449; ZSM-21 and ZSM-38 are described in U.S. Pat. No. 3,948,758; ZSM-23 is described in U.S. Pat. No. 4,076,842; ZSM-35 is described in U.S. Pat. No. 4,016,245; ZSM-48 is disclosed in EP No. 15,132, published Sept. 3, 1980. These patents and specifications are incorporated herein by reference. The intermediate pore size materials can include "crystalline admixtures" which are thought to be the result of faults occurring within the crystal or crystalline area during the synthesis of the zeolites. The "crystalline admixtures" are themselves zeolites but

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Other examples of intermediate pore size silicaceous crystalline molecular sieves include silicalite, as disclosed in U.S. Pat. No. 4,061,724, and "U.S. Pat. No. Re. 29,948 organosilicates," as disclosed in U.S. Pat. No. Re. 29,948. Intermediate pore size silicas, ferrosilicates and galliosilicates are disclosed in U.S. Pat. No. 4,238,318. All of these patents are incorporated by reference.

The most preferred molecular sieves are those that have the crystal structure and exhibit the X-ray diffraction pattern characteristic of ZSM-5, ZSM-11, and their crystalline admixtures, silicalite, organosilicates, and the chromia silicate, CZM. These materials will have silica:alumina mole ratios of from about 150:1 to about 500:1, preferably from about 175:1 to about 300:1, and more preferably from about 210:1 to about 270:1. It can be appreciated that these mole ratios are higher than the typical "ZSM-5 zeolite" and lower than the typical "silicalite silicate."

The molecular sieve can be in any convenient form for ordinary fixed bed, fluidized bed or slurry use. It is preferably used in a fixed bed reactor and in a composite with a porous inorganic binder or matrix in such proportions that the resulting product contains from 1 to 95 percent by weight and preferably from 10 to 70 percent by weight of molecular sieve.

The terms "matrix" and "porous matrix" include inorganic compositions with which the molecular sieve can be combined, dispersed, or otherwise intimately admixed. The matrix should not be catalytically active in a cracking sense, i.e., it should contain substantially no acid sites, and it should have substantially no hydrogenation activity. The porosity of the matrix can either be inherent in a particular material or it can be caused by a mechanical or chemical means. Representative matrix materials include pumice, firebrick, diatomaceous earth and inorganic oxides. Representative inorganic oxides include alumina, silica, naturally occurring and conventionally processed clays, for example, attapulgite, sepiolite, bentonite, and kaolin. The preferred matrices have few, if any, acid sites and little or no cracking activity. Silica and alumina are especially preferred.

The compositing of the molecular sieve with the inorganic oxide matrix can be achieved by any suitable method wherein the sieve is intimately admixed with the oxide. Typical compositing procedures known to the art include co-gelling and co-mulling.

The use of a non-acidic matrix is highly preferred for maximizing olefin production. The olefins produced in the Paragon Process can be converted to distillate fuels in an oligomerization reaction, as discussed in more detail below. Alternatively, the olefins can be used in other processes. For example, propylene can be purified and used to form polypropylene or propylene oxide. Isobutylene can be used, for example, to form polymers or MTBE.

The olefins may need to be purified for sale, particularly if high purity olefins are desired. The olefins tend to contain small amounts of paraffins, and tend to contain very small quantities of heteroatom impurities. The acetylene and diolefin impurities are also relatively low, compared with FCC, cokers and ethane and EP crackers because of the relatively low temperature in the Paragon reactor. Methods for purifying olefins, as well as specifications for different grades for olefin products, are well known to those of skill in the art. Purification methods include fractional distillation, for example, using propane/propylene splitters to purify propylene. Methods for removing diolefins and acetylenes are also well known to those of skill in the art, and include hydrogenation, adsorption and extraction.

The Oligomerization Conditions

Catalysts and reaction conditions for oligomerizing olefins such as the C_{3-5} olefins primarily produced in the Paragon process, as well as similar olefins produced in the Fischer-Tropsch reaction, are well known to those of skill in the art. Such catalysts and conditions are described, for example, in U.S. Patent Nos. 6,013,851; 6,002,060; 5,942,642; 5,929,297; 4,608,450; 4,551,438; 4,542,251; 4,538,012; 4,511,746; 4,465,788; 4,423,269; 4,423,268; 4,417,088; 4,414,423; 4,417,086; and 4,417,087, the contents of which are hereby incorporated by reference.

Any of the conditions known in the art for oligomerizing olefins can be used. In a particularly preferred embodiment, a fraction rich in C_{3-5} olefins is converted in a two-stage multiforming reaction to tetramers over a nickel-containing HZSM-5 zeolite catalyst. C_{3-5} tetramers are very useful petrochemical feeds for making detergents such as alkylbenzene sulfonates, and for making high quality middle distillates such as jet fuel.

Other olefin dimerization, oligomerization and polymerization processes are well known in the art and can also be used.

The preferred oligomerization process involves a high once-through conversion of the olefins from the Paragon Process to the corresponding tetramer by contacting the olefins in the liquid form with Ni-HZSM-5 in a two-stage process. The first stage of the process converts the olefin feed to dimers, and the second stage of the process converts the dimer

from the first stage to tetramer products with high selectivity. The product contains mostly olefin tetramers, and contains a relatively small amount of cracked products or paraffins.

The reaction conditions in the first reaction zone cause the olefins in the liquid state to oligomerize about 90% to 99% of the olefin to form an effluent which contains at least about 70% by weight dimer and preferably from about 75% to 80% by weight dimer. The first reaction zone can be operated at temperatures from about 80-200°F, pressures from about 400 psig to 1600 psig, and hourly space velocities of from about 0.5 to 2.

The feed to the second step of the process contains the normally liquid dimer olefins produced by the first step. The second step is operated so that the dimers produced in this second step are liquids under the conditions in that reaction zone. The second reaction zone can be operated at temperatures of from about 250-450°F, pressures from about 200 psig to 800 psig, and hourly space velocities from about 0.5 to 4. The once-through conversion to tetramer, based on starting olefins, can be 60% or more.

The tetramers are highly useful for both fuels and chemicals. As a fuel, the tetramers serve as extremely high quality mid-barrel fuels, such as jet fuel. These tetramers can also undergo chemical reactions to produce surfactants that can be used as additives in products such as lubricating oils. Among the most used surfactants prepared from the tetramers are alkyl sulfonates and alkyl benzene sulfonates.

Preferably, the olefin feed is in the liquid phase when it is contacted with the nickel-HZSM-5 crystalline molecular sieve. In this embodiment, the pressures and temperatures employed must be sufficient to maintain the system in the liquid phase. The pressure will therefore be a function of the feed olefin and the temperature.

The two-stage multi-forming process described herein may be carried out as a batch type, semi-continuous or continuous operation utilizing fixed or moving bed catalyst system.

Nickel-containing HZSM-5 is described in U.S. Pat. Nos. 3,702,886 and 3,770,614. The preferred nickel-containing HZSM-5 zeolite is a silicaceous crystalline molecular sieve of intermediate pore size. By "intermediate pore size" as used herein is meant an effective pore aperture in the range of about 5 to 6.5 Angstroms when the molecular sieve is in the H-form. Molecular sieves having pore apertures in this range tend to have unique molecular sieving characteristics. Unlike small pore zeolites such as erionite and chabazite, they will allow hydrocarbons having some branching into the molecular sieve void spaces. Unlike larger pore zeolites such as the faujasites and mordenites, they can differentiate between n-alkanes and slightly branched alkanes on the one hand and larger branched alkanes having, for example, quaternary carbon atoms.

The effective pore size of the molecular sieves can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See Breck, <u>Zeolite Molecular Sieves</u>, 1974 (especially Chapter 8) and Anderson et al, *J. Catalysis* Vol. 58, p. 114 (1979), both of which are incorporated by reference.

Intermediate pore size molecular sieves in the H-form will typically admit molecules having kinetic diameters of 5.0 to 6.5 Angstroms with little hindrance. Examples of such compounds (and their kinetic diameters in Angstroms) are: n-hexane (4.3), 3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds having kinetic diameters of about 6 to 6.5 Angstroms can be admitted into the pores, depending on the particular sieve, but do not penetrate as quickly and in some cases are effectively excluded. Compounds having kinetic diameters in the range of 6 to 6.5 Angstroms include: cyclohexane (6.0), 2,3-dimethylbutane (6.1), m-xylene (6.1), and 1,2,3,4-tetramethylbenzene (6.4). Generally, compounds having kinetic diameters of greater than about 6.5 Angstroms do not penetrate the pore apertures and thus are not absorbed into the interior of the molecular sieve lattice. Examples of such larger compounds include: o-xylene (6,8), hexamethylbenzene (7.1), 1,3,5-trimethylbenzene (7.5), and tributylamine (8.1).

In performing adsorption measurements to determine pore size, standard techniques are used. It is convenient to consider a particular molecule as excluded if it does not reach at least 95% of its equilibrium adsorption value on the zeolite in less than about 10 minutes (p/po=0.5; 25°C).

When synthesized in the alkali metal form, the ZSM-5 zeolite may be conveniently converted to the hydrogen form by well-known ion exchange reactions. This can involve intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form, as disclosed in U.S. Pat. No. 4,211,640, or by treatment with an acid such as hydrochloric acid as disclosed in U.S. Pat. No. 3,702,886.

Nickel is incorporated into the silicaceous crystalline molecular sieve according to techniques well known in the art, for example, impregnation and cation exchange. For example, typical ion exchange techniques would be to contact the particular sieve in the hydrogen form with an aqueous solution of a nickel salt. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates. The amount of nickel in the zeolites range from 0.5% to 10% by weight and preferably from 1% to 5% by weight.

Representative ion exchange techniques are disclosed in a wide variety of patents including U.S. Pat. Nos. 3,140,249; 3,140,251; 3,960,978; and 3,140,253.

Following contact with the salt solution, the zeolites are preferably washed with water and dried at a temperature ranging from 150°F to about 500°F and thereafter heated in air at temperatures ranging from about 500°F for periods of time ranging from 1 to 48 hours or more.

The nickel-containing HZSM-5 zeolite catalyst can be made substantially more stable for oligomerization by including from about 0.2% to 3% by weight and preferably 0.5% to 2% by weight of the Group IIB metals, zinc or cadmium and preferably zinc. A primary characteristic of these substituents is that they are weak bases and are not easily reduced. These metals can be incorporated into the catalysts using standard impregnation, ion exchange, etc., techniques. Strongly basic metals such as the alkali metals are unsatisfactory as they poison substantially all of the polymerization sites on the zeolite. For this reason, the alkali metal content of the zeolite is less than 1%, preferably less than 0.1%, most preferably less than 0.01%. The feed should include less than 100 ppm, more preferably less than 10 ppm, water. It should include less than 100 ppm, preferably less than 10 ppm, sulfur. Further, it should include less than 0.5%, preferably less than 0.05%, most preferably less than 0.01%, diolefins. Still further, it should include less than 5 ppm, preferably less than 1 ppm, most preferably less than 0.2 ppm, nitrogen.

The polymerization process is more efficient with small crystallite sieve particles than with larger crystalline particles. Preferably, the molecular sieve crystals or crystallites are less than about 10 microns, more preferably less than about 1 micron, most preferably less than about 0.1 micron in the largest dimension. Methods for making molecular sieve crystals in different physical size ranges are known to the art.

The molecular sieves can be composited with inorganic matrix materials, or they can be used with an organic binder. It is preferred to use an inorganic matrix since the molecular sieves, because of their large internal pore volumes, tend to be fragile, and to be subject to physical collapse and attrition during normal loading and unloading of the reaction zones as well as during the oligomerization processes. Where an inorganic matrix is used, it is preferred that the matrix be substantially free of hydrocarbon conversion activity.

Once the effluent from the oligomerization reaction zone is recovered, a number of further processing steps can be performed. If it is desired to use the long chain compounds directly as fuels, the tetramers can be hydrogenated.

All or part of the effluent of the second zone can be contacted with the molecular sieve catalyst in further reaction zones to further react the olefin tetramers with themselves to form still longer chain materials. Of course, the longer the carbon chain, the more susceptible the compound is to being cracked. Therefore, where successive oligomerization zones are used, the oligomerization zones must be operated under conditions that will not cause the oligomers to crack or engage in hydrogen transfer reactions. The most convenient, and preferred, method of operation where multiple reaction zones are used is to operate each zone under reaction conditions less severe than the preceding oligomerization zone. Operating with oligomerization zones in series with decreasing severity makes process control of the exothermic oligomerization reactions much easier.

Unreacted olefins from the first stage can be separated and recycled. In the same way, unreacted dimers from the second stage can also be recycled.

The products from the oligomerization reaction include highly branched iso-olefins with a size range of between C_{12} and C_{20} along with unconverted C_{3-5} paraffins. Iso-olefins (and/or reduced iso-olefins) in the naptha range from the oligomerization reaction will have a good octane number. Material in the jet and diesel ranges will have high smoke and cetane values. In addition, the jet freeze point and diesel cloud points will be low. The values for these properties are preferably within ATSM standards, for example, ASTM D 975 or diesel and D 1655 for jet fuel. The products should meet these standards due to their relatively high levels of isoparaffins.

If the distillate fuels are to be saturated to reduce the olefins, syngas can be used, rather than hydrogen, to avoid the need for building a separate hydrogen plant on site. The carbon oxides remaining after the reduction can be recycled through the Fischer-Tropsch reactor. The hydrogenation (saturation) of the olefins can be done at several stages, including after the oligomerization step, after the products are isolated via distillation, or after the products are optionally blended with other components.

Optional Process Steps for the C3-5 Paraffins

The low molecular weight (C_{3-5}) paraffins from isolated from the demethanization/deethanization of natural gas, from the Fischer-Tropsch reaction, the Paragon Process and/or oligomerization reaction can be dehydrogenated to form olefins and combined with the feedstock to the oligomerization reactor. Catalysts and methods for dehydrogenating paraffins are well known to those of skill in the art, and are described, for example, in U.S. Patent Nos. 4,420,649; 4,476,344; 4,827,066; 4,482,646; 4,686,316; 4,7516,342; 4,777,319; 4,778,942; and 4,798,911, the contents of which are hereby incorporated by reference.

The dehydrogenation catalyst usually will include a Group VIII metal, which includes iron, cobalt, nickel, palladium, platinum, rhodium, ruthenium, osmium, and iridium. Platinum and palladium or the compounds thereof are preferred, and platinum or a compound thereof is particularly preferred.

The process conditions selected for carrying out the dehydrogenation step will depend upon the dehydrogenation catalyst used. In general, the pressure is less than about 1000 psig. The temperature is typically between about 200°C to about 800°C with and LHSV of between 0.1 and 5.

Alternatively the paraffins can be subjected to molecular redistribution as described, for example, in U.S. Patent No. 3,856,876 to Burnett, the contents of which are hereby incorporated by reference. The molecular redistribution reaction involves dehydrogenation of the paraffins to form olefins, methathesis of the olefins, and hydrogenation of the metathesized olefins. Dehydrogenation catalysts include those listed above. Olefin metathesis catalysts typically include one or more of a metal or the compound of a metal from Group VIB or Group VIIB of the Periodic Table of the Elements, which include chromium, manganese, molybdenum, rhenium and tungsten. Molybdenum, rhenium, tungsten, and compounds including these metals are preferred, and tungsten and compounds including tungsten are particularly preferred. The chemistry does not require using hydrogen gas, and therefore does not require relatively expensive recycle gas compressors. The chemistry is typically performed at mild pressures (100-5000 psig). The chemistry is typically thermoneutral and, therefore, there is no need for expensive internal reactor quench systems or interstage reheaters to control the temperature.

The product of the molecular redistribution of the C_{3-5} paraffins includes ethane, unconverted C_{3-5} paraffins and C_6+ products, each of which can be separately isolated.

Molecular redistribution is very sensitive to sulfur impurities in the feedstock, and these must be removed prior to the reaction. The presence of excess olefins and hydrogen in the disproportionation zone are also known to affect the equilibrium of the disproportionation reaction and to deactivate the catalyst. Since the composition of the fractions may vary, some routine experimentation will be necessary to identify the contaminants that are present and identify the optimal processing scheme and catalyst to use in carrying out the invention.

Optional Components

The resulting products are useful in distillate fuel compositions. The distillate fuel compositions may optionally include various additives, such as lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives, corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers, anti-wear agents, dispersants, anti-foaming agents, pour point depressants, detergents, rust inhibitors and the like. Examples of suitable lubricants include polyol esters of C_{12}-C_{28} acids. Other hydrocarbons may be blended with the distillate fuel compositions provided that the final blend has the necessary octane or cetane values, flash point, and toxicity properties. The total amount of additives is preferably between 1-30 percent. All percentages listed herein are weight percentages unless otherwise stated.

The process will be readily understood by referring to the flow diagram in Figure 1. In Figure 1, C_{1-6} hydrocarbons from a natural gas well are subjected to demethanization and deethanization (Box 10) to form methane, ethane and C_3+ products. The methane and ethane are combined with oxygen and reacted in a syngas generator (Box 20) to form a mixture of carbon monoxide and hydrogen (syngas). The syngas is then added to a Fischer-Tropsch reactor (Box 30), and various fractions are isolated by distillation (Box 40). A C_{3-5} fraction from the Fischer-Tropsch reactor is optionally sent to an oligomerization reactor (Box 50). Naptha and distillate fuel fractions are collected, and optionally subjected to hydrotreatment (Box 60) and/or isomerization (Box 70). A wax and heavy fraction is isolated and subjected to the Paragon process (Box 80) and the resulting light olefins are oligomerized (Box 50) and optionally hydrogenated (Box 90) to form a distillate fuel composition which is purified via distillation (Box 40). Wax and heavy products from the oligomerization step can be recycled to extinction. C_{3-5} paraffins can be dehydrogenated to form olefins (Box 100) and these olefins can be oligomerized (Box 50). In the flow scheme contained in Figure 1, the process of the present invention is practiced in continuous operation. However, it is possible to practice the present invention in batch operation.

WHAT IS CLAIMED IS:

1. An integrated process for preparing iso-olefins from syngas, the process comprising;

(a) subjecting syngas to Fischer-Tropsch reaction conditions to form a hydrocarbon product stream comprising olefins and paraffins;

(b) isolating wax and heavy products from the Fischer-Tropsch reaction, and

(c) subjecting the wax and heavy products to the Paragon process to form a product stream comprising light (C_{3-5}) olefins,

2. The process of claim 1, further comprising subjecting the light olefins to oligomerization conditions to form iso-olefins.

3. The process of claim 1, wherein the syngas is derived from natural gas.

4. The process of claim 1, wherein a C_{3-5} fraction is isolated from the Fischer-Tropsch reaction in step (a) and combined with the light olefin fraction from the Paragon Process in the oligomerization step.

5. The process of claim 1, wherein a C_{2-} fraction is isolated from the Fischer-Tropsch step and is recycled through a syngas generator.

6. The process of claim 1, wherein a naptha fraction is isolated from the Fischer-Tropsch reaction.

7. The process of claim 6, wherein the naptha fraction is hydrotreated and/or isomerized.

8. The process of claim 6, wherein the naptha fraction is catalytically reformed.

9. The process of claim 1, wherein the products from the oligomerization step are distilled to form a distillate fuel fraction.

10. The process of claim 9, wherein the products are further distilled to form a fraction including wax and heavy products.

11. The method of claim 10, wherein the fraction including wax and heavy products is recycled to extinction.

12. The process of claim 1, wherein a portion of the iso-olefins formed in the oligomerization step is hydrogenated to form isoparaffins.

13. The process of claim 1, wherein the Fischer-Tropsch reaction uses a catalyst which provides high chain growth probabilities.

14. The process of claim 13, wherein the catalyst comprises cobalt.

15. A distillate fuel composition obtained by the steps of:

(a) subjecting syngas to Fischer-Tropsch reaction conditions to form a hydrocarbon product stream comprising olefins and paraffins;

(b) isolating wax and heavy products from the Fischer-Tropsch reaction,

(c) subjecting the wax and heavy products to the Paragon process to form a product stream comprising light olefins,

(d) subjecting the light olefins to oligomerization conditions to form iso-olefins useful in a distillate fuel composition.

16. The composition of claim 15, further comprising one or more gasoline or diesel fuel additives.

17. The composition of claim 15, wherein a portion of the iso-olefins formed in the oligomerization step is hydrogenated to form isoparaffins.

18. The composition of claim 15, wherein the product is blended with additional gasoline compositions.

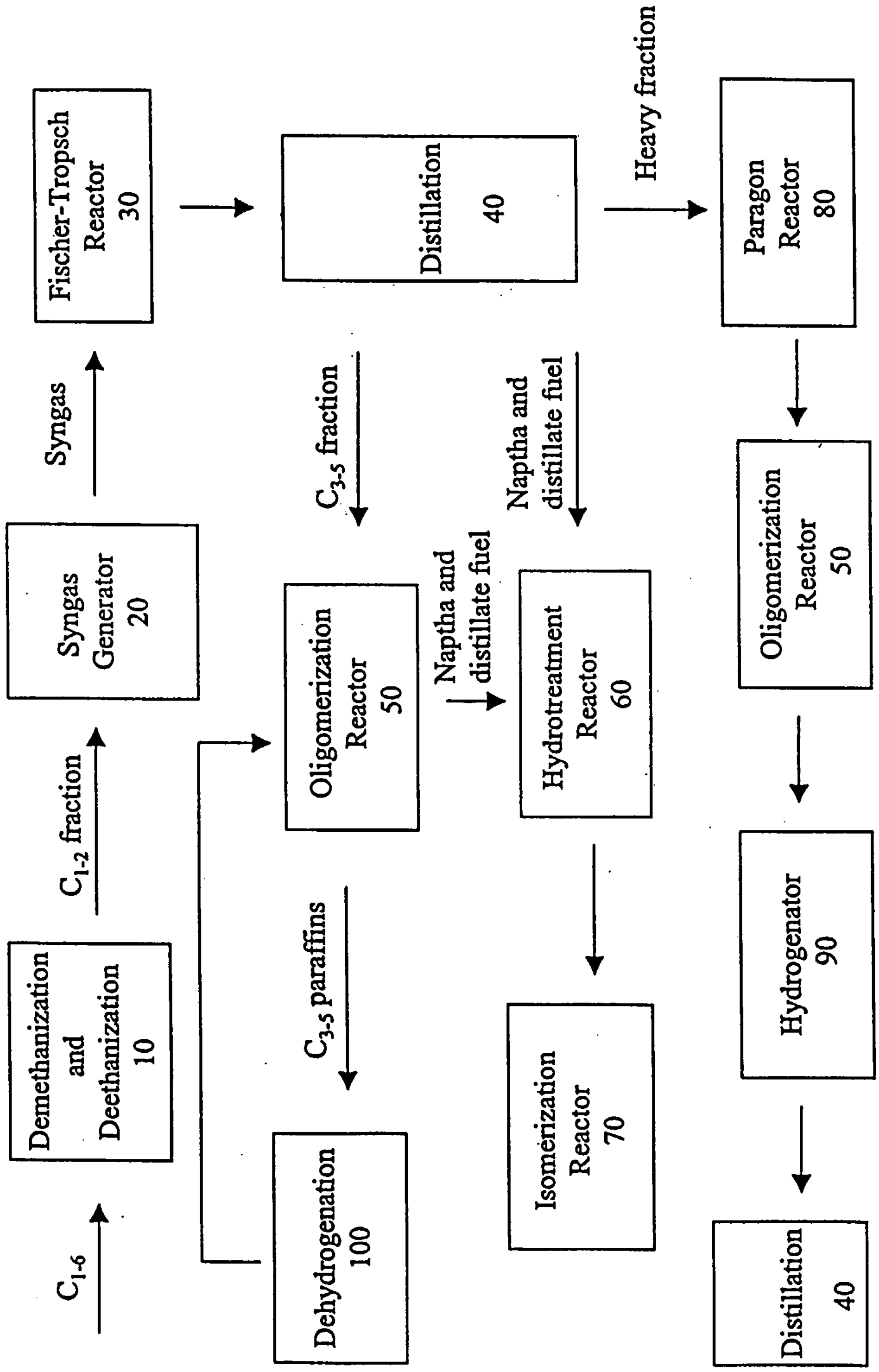
C1-6
Demethanization and Deethanization 10
C1-2 fraction
Syngas Generator 20
Syngas
Fischer-Tropsch Reactor 30
Distillation 40
C3-5 fraction
Oligomerization Reactor 50
C3-5 paraffins
Dehydrogenation 100
Naptha and distillate fuel
Naptha and distillate fuel
Hydrotreatment Reactor 60
Isomerization Reactor 70
Heavy fraction
Paragon Reactor 80
Oligomerization Reactor 50
Hydrogenator 90
Distillation 40

Figure 1