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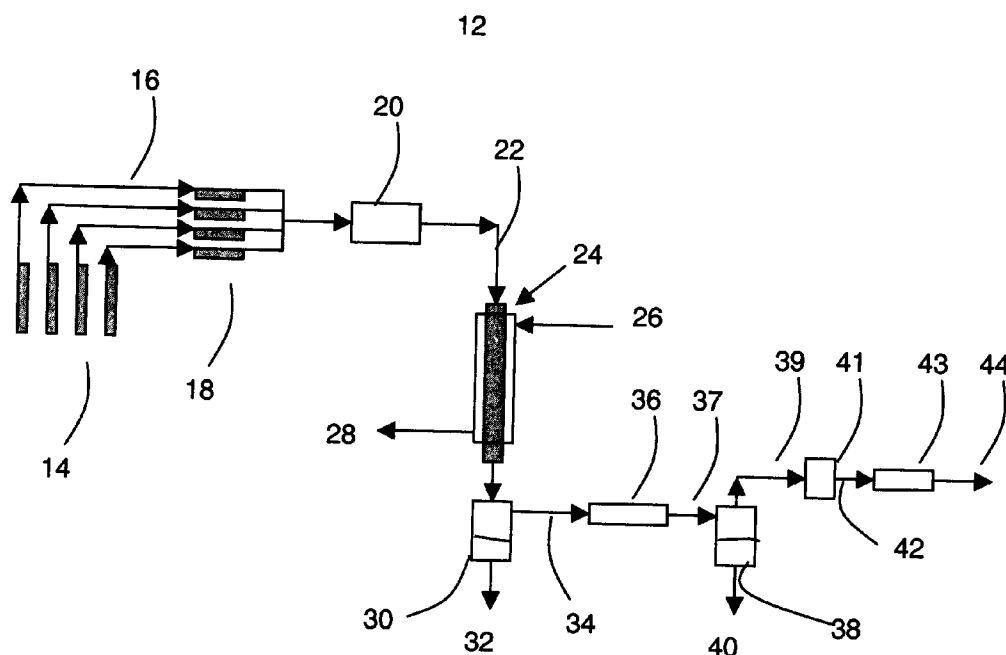
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(54) Title: LOW PRESSURE FIXED BED FISCHER-TROPSCH PROCESS AND APPARATUS



Low-Pressure Fischer-Tropsch Process and Apparatus

Field of Invention

This invention relates generally to a process and apparatus for converting carbon monoxide and hydrogen to liquid fuels and/or waxes, and particularly to a low
5 pressure Fischer-Tropsch process and apparatus for performing same.

Background

The Fischer-Tropsch (FT) process is a catalyzed chemical reaction known since the 1920's in which carbon monoxide and hydrogen are converted into wax and liquid hydrocarbons of various forms. One purpose of this process is to produce
10 a synthetic petroleum substitute, typically from coal or natural gas, for use as synthetic motor fuel.

During the Second World War, synthetic diesel was manufactured in Germany using coal gasification to supply a 1:1 ratio of hydrogen and carbon monoxide for conversion to fuel hydrocarbons. Because of trade sanctions and the paucity of
15 natural gas, South Africa further developed coal gasification to synthesize gas and employed a fixed-bed iron Fischer-Tropsch catalyst. Iron catalysts are very active for the water-gas shift reaction which moves the gas composition from a deficiency of hydrogen and closer to the optimum H_2/CO ratio of around 2.0. When large natural gas supplies were developed, steam and autothermal
20 reformers were employed to produce synthesis gas feedstock for slurry-bed FT reactors that use cobalt or iron catalysts.

The catalytic hydrogenation of carbon monoxide to produce a variety of products ranging from methane to heavy hydrocarbons (up to C_{80} and higher) as well as oxygenated hydrocarbons is usually referred to as Fischer-Tropsch synthesis.
25 The high molecular weight hydrocarbon product primarily comprises normal paraffins which can not be used directly as motor fuels because their cold properties are not compatible. After further hydroprocessing, Fischer-Tropsch

hydrocarbon products can be transformed into products with a higher added value such as diesel, jet fuel or kerosene. It is desirable to maximize the production of high value liquid hydrocarbons directly so that component separation or hydrocracking are not necessary.

- 5 Catalytically active group VIII, in particular, iron, cobalt and nickel are known to be used as Fischer-Tropsch catalysts; cobalt/ruthenium is a known catalyzing combination. The catalyst usually contains a support or carrier metal as well as a promoter, e.g., rhenium. Metal oxides, e.g., silica, alumina, titania, zirconia or mixture thereof, have been utilized as catalyst supports in Fischer-Tropsch
- 10 hydrocarbons synthesis. For example, U.S. Pat. No. 4,542,122 disclosed a cobalt or cobalt thoria on titania as a hydrocarbon synthesis catalyst. U.S. Pat. No. 4,088,671 disclosed a cobalt-ruthenium catalyst where alumina was used as a support. European Pat. No. 142,887 described a silica-supported cobalt catalyst together with zirconium, titanium, ruthenium and/or chromium.
- 15 In Gas-To-Liquids (GTL) plants, compromises must be made between liquid product yield and plant operating and capital costs. For example, if there is a market for electricity, a steam reformer design may be chosen because this technology produces a large amount of waste heat: flue gas heat can be converted to electricity using an 'economiser' and a steam turbine. If
- 20 conservation of natural gas feedstock and low capital cost are paramount, autothermal or partial oxidation reformers using air are favored. Another factor in selecting the best reformer type is the nature of the reformer hydrocarbon feed gas. If the gas is rich in CO₂, this can be advantageous because the desired H₂/CO ratio can then be achieved directly in the reformer gas without the need to
- 25 remove excess hydrogen, and some of the CO₂ is converted to CO, increasing the potential volume of liquid hydrocarbon product that can be produced. Additionally, the volume of steam that is required is reduced, which reduces the process energy requirements.

The present market for FT processes is concentrated on large "world-scale" plants with natural gas feed rates of greater than 200 million scfd because of the considerable economies of scale. These plants operate at high-pressure, about 450 psia, and use extensive recycling of tail gas in the FT reactor. For, example, the Norsk Hydro plant design has a recycle ratio of about 3.0. The emphasis is on achieving a maximum wax yield. In terms of product slate, these large plants strive for the maximum yield of FT waxes in order to minimize the formation of C₁-C₅ products. The waxes are then hydrocracked to primarily diesel and naphtha fractions. Unfortunately, light hydrocarbons are also formed in this process. The reformers use some form of autothermal reforming with oxygen produced cryogenically from air, an expensive process in terms of operating cost and capital cost. The economies of scale justify the use of high operating pressure, the use of oxygen natural gas reforming, extensive tail gas recycling to the FT reactor for increasing synthesis gas conversion and controlling heat removal and product wax hydrocracking. To date, an economical FT plant design has not been developed for small plants with capacities of less than 100 million scfd, nor for low pressure applications.

Fischer-Tropsch synthesis performed at relatively low pressure, e.g. 250-300 psia, and relatively high temperature, usually produces short chain hydrocarbons of a 0.6-0.7 chain growth probability factor. This is shown in U.S. patent 7,109,248, which describes a Fischer-Tropsch process performed at an elevated temperature between 230-280°C, for example 240°C and at elevated pressure typically between 1.7MPa and 2.1MPa, for example 1.8MPa, using a compact reactor. The disclosed reactor comprises metal plates coated on one side thereof with a catalyst comprising a coating of gamma alumina support with 10-40% cobalt (by weight compared to the alumina) and with a promoter such as ruthenium, platinum or gadolinium which is less than 10% of the cobalt weight. The support comprises very fine particles in a layer of about 100 microns thick; such a coating would be very expensive and of questionable durability. The gas hourly space velocity was very high, for example 20000hr⁻¹ and the produced

hydrocarbon liquid consisted of saturated linear alkanes of chain lengths range between about 6-17 wherein a significant proportion of the hydrocarbons are gaseous at ambient temperature” and therefore the product can not be used directly as motor fuel. Additionally, the selectivity to the production of C_5^+ hydrocarbon was less than 65%, which means that C_1 - C_4 hydrocarbons constitute 35% of the hydrocarbon product and this is burned to generate electricity. Also, the process has low efficiency, with the conversion of carbon monoxide no greater than 75%. The reactor operates using a very small feed gas travel time and compensates by using a very high temperature to promote molecule formation.

Hence, there is still a great need to identify other Fischer-Tropsch processes which can be used to directly produce different types of fuel such as diesel fuel (C_9 - C_{23} , Chevron definition).

Summary of the invention

According to one aspect of the invention, there is provided a low pressure fixed-bed FT reactor for producing a liquid hydrocarbon with a high diesel fraction yield without hydro-cracking. The operating pressure is preferably less than 200 psia and the diesel fraction yield is preferably greater than 55% by weight. The FT reactor has a catalyst assembly comprising a: catalyst support particles having an average particle size between 800 and 5,000 microns, and catalyst on the catalyst support particles and having a metallic cobalt loading of between 5 and 35 % by weight of the catalyst assembly. More particularly, the average particle size of the support particles can be between 1000 and 2500 microns. The catalyst support particles can be alumina, zirconia, or silica. The cobalt catalyst loading can be between 10 and 35 % by weight. The catalyst assembly can further comprise promoters selected from the group consisting of ruthenium, rhenium, nickel zirconium and titanium. The FT reactor can be operated at a pressure

between 50 and 175 psia, and more particularly between 70 and 175 psia. The FT reactor can be operated at a temperature between 170 and 240 Celsius.

According to another aspect of the invention, there is provided a FT process comprising: supplying a feed gas to a fixed bed FT reactor having a catalyst assembly comprising catalyst support particles with an average size between 800 and 5,000 microns and catalyst on the support particles having a metallic cobalt loading between 5 and 35 % by weight of the catalyst assembly; and operating the FT reactor at under 200 psia to produce FT products including a liquid hydrocarbon with a diesel cut greater than 55 wt. % without hydro-cracking.

It has been discovered that this catalyst is very effective at low pressures in converting synthesis gas into diesel in high yield.

The present invention is particularly well suited to conversion of low pressure gases containing low molecular weight hydrocarbons into FT liquids. Examples of applications are landfill gas, oil field solution gas and low pressure gas from de-pressured gas fields. In all these cases, a multiple-stage gas and air compression would be required in traditional FT plants. The high efficiency of the FT catalyst according to this aspect of the invention enables high CO conversion and produces a product stream containing up to 90+ wt. % diesel in a single pass. The use of air in a natural gas reformer provides a synthesis gas containing approximately 50% nitrogen, which facilitates heat removal in the FT reactor as sensible heat and increases gas velocity and heat transfer efficiency, so that tail gas recycling is not needed. Naphtha can be partially separated from the hydrocarbon product by flash distillation at low cost to generate a more pure diesel product. This also serves to provide some product cooling. The liquid hydrocarbon product is excellent for blending with petroleum diesel to increase cetane number and reduce sulfur content.

Brief Description of the Drawings

Figure 1(a) is a low pressure FT process flow diagram for one particular embodiment of the invention.

5

Figure 1(b) is a schematic diagram of the components of an experimental FT reactor assembly.

Figure 2 is a flow diagram for flash separation of naphtha and diesel hydrocarbon fractions as a subsequent step to the Fischer-Tropsch process of the embodiment shown in Figure 1.

10

Figure 3 is a graph showing the effect of pressure on catalyst performance, for a catalyst of Example 4 at 202.5°C;

15

Figure 4 is a graph showing the effect of carbon number on the % weight production of liquid fuels and/or waxes, at 190°C, 70 psia, using a CSS-350 alumina support (i.e. Example 7), for a catalyst of Example 4 at 202.5°C.

Figure 4a is a graph showing the effect of catalyst support particle diameter on wax cut in a Fischer-Tropsch product (i.e. Example 8).

20

Figure 5 is a graph showing the effect of carbon number distribution on the % weight production of liquid fuels and/or waxes, at 220°C and 70 psia, using an LD-5 alumina support (i.e. Example 8).

25

Figure 6 is a graph showing the effect of carbon number distribution on the % weight production of liquid fuels and/or waxes, at 190°C at 70 psia using an F-220 alumina support (i.e. Example 9);

30

Figure 7 is a graph showing the effect of carbon number distribution on the % weight production of liquid fuels and/or waxes, for the catalyst of Example 3 at 190 °C.

5 **Figure 8** is a graph showing the effect of carbon number distribution on the % weight production of liquid fuels and/or waxes, for the catalyst of Example 10 using a ruthenium promoter and LD-5 alumina support.

10 **Figure 9** is a graph showing the effect of carbon number distribution on the % weight reduction of liquid fuels and/or waxes, for the Catalyst of Example 11, using rhenium promoter and using Aerolyst 3038 silica catalyst support instead of alumina.

15 **Figure 10** is a graph showing a comparison of Example 9 carbon distribution with a known Anderson-Shultz-Flory distribution.

Detailed Description of Embodiments of the Invention

According to one embodiment of the invention, there is provided an apparatus and process for producing a liquid hydrocarbon having a relatively high diesel
20 fraction yield in a small FT plant operating at a relatively low pressure. This embodiment is suitable for use in FT plants using less than 200 million scfd, and particularly suitable for small FT plants using less than 100 million scfd.

Referring to Figure 1 (a), a process flow diagram shows a low pressure FT plant. Raw hydrocarbon-containing process feed gas **A** (also known as “synthesis gas”
25 or “syngas”) is fed into gas conditioning equipment **B**. The feed gas **A** can be from a wide variety of sources, such as a natural gas field, a land-fill facility (biogenic gas), and a petroleum oil processing facility (solution gas). The pressure of the gas for the present process can vary widely, from atmospheric pressure to 200 psia.

Single-stage or two-stage compression may be required, depending on the source pressure and the desired process operating pressure. For example, for landfill gas, the pressure is typically close to atmospheric pressure and blowers are used to transmit the gas into combustion equipment. Solution gas, which is normally flared, must also be compressed to the process operating pressure. There are also many old exploited and late-life natural gas fields with pressures too low for acceptance into pipelines that could make possible feedstock for the present process. Other natural gas sources, which may or may not be stranded (no access to a pipeline) may already be at or above the desired process operation pressure and these are also candidates. Another candidate is natural gas that is too high in inert materials such as nitrogen to meet pipeline specifications.

The hydrocarbon gas conditioning equipment **B** serves to clean up and remove components in the feed gas **A** that would damage a reformer or a FT catalyst. Such components to be removed include mercury, hydrogen sulfide, silicones and organic chlorides. Organic chlorides, such as found in land-fill gas, produce hydrochloric acid in the reformer, which can cause severe corrosion. Silicones form a continuous silicon dioxide coating on the catalyst, blocking pores. Hydrogen sulphide is a powerful FT catalyst poison and is usually removed to 1.0 ppm or lower. Some gas, from sweet-gas fields, may not require any conditioning (clean-up). Suitable gas conditioning equipment is known in the art and thus not described in detail here.

The hydrocarbon concentration in the raw feed gas affects the economics of the process. Feed gas containing high levels of nitrogen or carbon dioxide will not make as much hydrocarbon liquid compared with the same volume of hydrocarbon-rich feed gas. Nevertheless, the process can operate with 50% or lower methane concentration, for example, using land-fill gas. There may even be reasons to operate the process even at a financial loss: for example to meet greenhouse gas government or corporate emission standards. The process can operate with feed gases containing only methane hydrocarbon or containing

natural gas liquids by the application of known reformer technologies. The presence of carbon dioxide in the feed gas is beneficial because it can enable the production of the desired H₂/CO ratio of about 2 directly from the reformer.

Downstream of and coupled to the gas output of the gas conditioning equipment **B** is a reformer **C**. The reformer **C** is operable at low pressures and may be one of several types depending on the composition of the feed gas. A significant benefit of low pressure reformer operation is the lower rate of the Brouard reaction and diminution of metal dusting. The reformer **C** can be a partial oxidation reformer, a steam reformer, or an autothermal reformer.

- Partial oxidation reformers normally operate at very high pressure i.e. 450 psia or greater, and so are not optimum for a low-pressure FT process. It is energetically inefficient, and can easily make soot, however, it does not require water, and makes a syngas with a H₂/CO ratio near 2.0, optimum for FT catalysts. In spite of these limitations, partial oxidation reformers can still be employed in the present process.

- Steam reformers are capital expensive and require flue gas heat recovery to maximize efficiency in large plants. Because the synthesis gas contains relatively low levels of inerts such as nitrogen, temperature control in the FT reactor can be difficult without tail gas recycling to the FT reactor. However, the low level of inerts enables recycling of some tail gas to the reformer tube-side, supplementing the natural gas feed, or to the shell side to provide heat. Keeping in mind that FT tail gas must be combusted before venting in any event, this energy can be used for electrical generation or, better yet, to provide the reformer heat which would otherwise be provided from burning natural gas. Steam reformers are a viable choice in the present process.

Autothermal reforming is an efficient process of relatively low capital cost that uses moderate temperatures and modest steam concentrations to produce a soot-free synthesis gas with H₂/CO around 2.5 using low-CO₂ natural gas feed, which is closer to the desired ratio than by steam reforming. However some

hydrogen removal is still required for most natural gas feeds. If the feed gas contains greater than about 33 % CO₂, as is the case with land-fill gas feed, then an H₂/CO ratio of 2.0 can be achieved without any recycle streams, and the water use can also be diminished. This is a particularly suitable type of reformer for the low-pressure FT processes of the present embodiment.

Water **D** can be optionally injected as steam into the reformer **C**. All reformer technologies except partial oxidation require the injection of steam.

An oxidizing gas **E** such as air, oxygen or oxygen-enriched air is also provided to the reformer **C** in all cases except the steam reformer.

A cooler **F** is coupled downstream to the reformer **C** and serves to reduce the temperature of tail gas exiting the reformer **C** from a reformer outlet temperature of greater than 800 °C to close to ambient temperature. The cooling may be done in several stages, but preferably in a single stage. The cooling may be achieved with shell-and-tube or plate-and-frame heat exchangers and the recovered energy may be utilized to pre-heat the reformer feed gases, as is well known in the industry. Another way of cooling the reformer tail gas is by direct injection of water into the stream or by passing the stream through water in a vessel.

A separator **G** is coupled downstream of and to the outlet of the cooler **F** and serves to collect condensed water from the tail gas, so as to minimize the amount of water entering downstream equipment.

Certain reformer processes produce a synthesis gas too rich in hydrogen, some of which must be removed to achieve optimum FT reactor performance. An ideal H₂/CO ratio is 2.0-2.1, whereas the raw synthesis gas may have a ratio of 3.0 or higher. High hydrogen concentrations give rise to larger CO loss to producing methane instead of the desired motor fuels or motor fuel precursor such as naphtha. Therefore, optional hydrogen removal equipment **H** can be coupled

downstream of and to the outlet of separator **G**. Such equipment **H** can be provided by Air Products (Prism™ membranes), or Natco (Cynara membranes).

An FT reactor assembly **I** is coupled to the outlet of the separator **G** (or hydrogen removal equipment **H** if present). The reactor assembly **I** receives the separated reformer synthesis gas and converts this gas into wax and liquid hydrocarbons of various forms. The FT reactor assembly **I** preferably is of the fixed-bed type because the required catalyst particle size is too large for suspension in a slurry bed. The shell-and-tube fixed-bed type is particularly suitable because of its simplicity of operation and ease of scale-up.

A back-pressure controller **J** sets the process pressure and in this embodiment is located downstream of the FT reactor assembly **I**, but may be placed in other locations depending on the product recovery and possible partial separation process employed.

Product cooling and recovery equipment **K** receives and cools the converted products from the reactor assembly **I**. Product cooling is typically accomplished by heat exchange with cold water and serves to pre-heat the water for use elsewhere in the FT plant or to make steam. Separation is accomplished in a separator vessel designed for oil/water separation. However a second alternative is to flash-cool the FT reactor product before the aforementioned cooler-separator as shown in Figure 2. This serves two purposes: firstly to reduce the product temperature and secondly to enable partial separation of the naphtha component in the produced hydrocarbon product, enriching the remaining liquid in the diesel component.

Referring now to Figure 2, the FT reactor assembly **I** is described in more detail.

The FT reactor assembly **I** in this embodiment comprises:

- a fixed-bed Fischer Tropsch reactor 1;
- a conduit 2 for carrying a mixture of gases, water, naphtha, diesel and light waxes at ca.190-240 °C and pressure greater than atmospheric;

- a pressure let-down valve 3;
- a second conduit 4 for carrying the mixture stream at reduced temperature due to gas expansion and at c.a.14.7 psia;
- a flash drum vessel 5;
- 5 ○ a third conduit 6 for carrying the mixture stream in a vapour phase and minus diesel and light waxes;
- a cooler 7;
- a fourth conduit 8 for carrying the mixture stream in conduit 6 but with naphtha and water in the liquid phase;
- 10 ○ a vessel 9 to retain naphtha and water; and
- a waste tail-gas stream 10 consisting mainly of inert gases and light hydrocarbons and including un-reacted hydrogen and carbon monoxide.

The FT reactor 1 is a shell-and-tube heat exchanger with catalyst and promoter material on catalyst support particles (collectively, "catalyst assembly") placed

15 inside the tube. The catalyst support particles can be one of alumina, zirconia or silica with an average particle size greater than 800 microns and less than 20,000 microns, preferably between 800 and 5000 microns and more preferably between 1000 and 2500 microns. For irregularly-shaped catalyst support

20 particles the above dimensions refer to the shortest dimension. For the larger particles, the desired diesel cut will continue to be obtained, however, the CO conversion will suffer. The catalyst has a metallic cobalt loading of between about 5% and 35% by weight of the catalyst assembly and preferably between about 10% and 35% by weight. This wt. % refers to final weight of the metal cobalt. The promoter material can be rhenium, ruthenium, nickel, zirconium or

25 titanium with a loading of between about 0.01 – 2 % by weight of the catalyst

assembly. The FT reactor 1 can be preferably operated at pressures between about 15 psia and 200 psia and more preferably between 50 psia and 175 psia.

In the reactor 1, the synthesis gas is converted into inert gases, gaseous lower-boiling hydrocarbons, water vapour, naphtha gas, liquid diesel, and waxes ("FT products"). The FT products 2 flow through a pressure let-down valve 3 and into a flash drum 5. The inert gases and lower-boiling hydrocarbons, water and naphtha go overhead as vapour out of the flash drum and through cooler 7. The diesel and light waxes collect in vessel 5. The water and naphtha condense in cooler 7 and are collected in vessel 9. The remaining gases exit overhead in stream 10 and are typically combusted, sometimes with energy recovery, or are used to generate electricity.

In order to operate the FT process at high conversions with oxygen-blown reformer synthesis gas, the approach has been to recycle tail gas in a high proportion: typically at a ratio of 3.0 or greater based on fresh gas feed. A secondary benefit is that the fresh gas is diluted in carbon monoxide, which reduces the required rate of heat removal from the FT reactor, reduces hot-spotting and improving the product slate. However, tail gas recycling is a very energy and capital expensive activity. The separation of oxygen from air is also an energy and capital expensive activity.

The preferable approach taken in the present process is to use air in the reformer, which gives a synthesis gas containing approximately 50 % nitrogen as inert diluent, eliminating the need for tail gas recycling to moderate FT reactor heat removal requirements. Others employing air-blown synthesis gas in FT processes have achieved the desired high CO conversions by using multiple FT reactors in series, which entails high capital costs and complex operation. The present process achieves high CO conversion in a simple single pass and a high diesel cut by using a special catalyst assembly.

In this embodiment, the catalyst assembly employs an alumina support with high cobalt concentration, along with a low level of rhenium to facilitate catalyst

reduction. The high cobalt concentrations increase catalyst activity, enabling high single-pass synthesis gas conversion.

The Anderson-Shultz-Florey theory predicts the FT hydrocarbons to cover a very wide range of carbon numbers, from 1-60, whereas the most desirable product is diesel fuel (C₉-C₂₃, Chevron definition). In order to reduce the 'losses' of CO to making C₁-C₅ hydrocarbons, a prior art approach is to strive to make mostly wax in the FT reactor and then, in a separate operation, to hydrocrack the wax to produce mostly diesel and naphtha. Surprisingly, the process and catalyst of the present embodiment makes diesel in high yield (up to 90 wt%) directly in the FT reactor 1, obviating the need for expensive and complex hydrocracking facilities.

Because of the elimination of oxygen purification, high-pressure compression, tail gas recycling and hydrocracking, the present process can be applied economically in much smaller plants than hitherto considered possible for FT technology. A comparison of the present embodiment against existing FT technologies is provided below:

Existing FT Technologies

Present Embodiment

Large plants, > 250MMscfd

Small plants, < 100MMscfd

High pressure, > 200 psia

Low pressure, < 200 psia

Oxygen to reformer

Air to reformer

Extensive recycling to FT reactor or reformer

No recycling ("once-through" process)

Low single-pass FT CO conversion (< 50%)

High single-pass conversion (> 65%)

Deliberate and extensive wax formation

Less than 10% wax formation

Hydrocracking waxes

No hydrocracking operations

Multiple-pass FT reactors

Single-pass-FT reactor

Low FT diesel yield (<50 %)

High diesel yield (55-90 % of hydrocarbon liq

Examples

Referring to Figure 1 (b), a number of experiments were carried out by an experiment scale FT reactor assembly 12.

- 5 The assembly 12 comprises compressed gas cylinders 14 each respectively containing CO, H₂, N₂ and CO₂. These gases together represent the feed gas supplied to a FT reactor assembly I in a commercial scale FT plant. Each gas cylinder 14 is connected to a gas conduit 16 that conveys gas from the cylinder 14, through a mass flow controller 18 coupled to each conduit 16, and to an
- 10 electrical feed gas pre-heater 20 wherein the gases are mixed to form a feed gas mixture. The pre-heater 20 operates to bring the feed gas mixture to a suitable reactor temperature, which for the purposes of these experiments was in the range of 170-240 °C.

- After the feed gas mixture has been suitably heated, a feed gas conduit 22
- 15 conveys the feed gas mixture from the pre-heater 20 to a shell-and-tube FT reactor 24 for processing. A number of experiments were conducted with different catalyst assemblies in the tube of the reactor 24 within the catalyst assembly parameters described above. The results of these experiments are discussed in examples 1 to 11 below. The catalyst assemblies used in these
- 20 experiments used one of the supports described in Table 1:

Table 1. Physical characteristics of catalyst supports.

| | | | | | |
|---------------------------------|--------------------------|-----------------------------|---------------------------|--------------------------------|--|
| catalyst support | Alcoa LD-5 Alumina | Alcoa CSS-350 Alumina | Alcoa F-220 Alumina | Sasol (Trilobes) Alumina | DeGussa Aerolyst. 3038 Silica |
| Surface Area, m ² /g | 300 min | 350 | 360 | 248 | 270 |

| | | | | | |
|---|----------|------|-------|-----------|-----------|
| Average Particle size, microns | various | 2120 | 2000 | 1670x4100 | 2500x7600 |
| Pore Volume, cc/g | 0.63 | 0.57 | 0.5 | 0.82 | 0.9-1.0 |
| Bulk Density, g/cc | 0.645 | 0.72 | 0.769 | 0.42 | 0.40-0.46 |
| Al ₂ O ₃ , %wt | Diff. | 99.6 | 93.1 | Diff. | < 0.2 |
| SiO ₂ , %wt | 0.40 max | 0.02 | 0.02 | 0.015 | 99.8 |
| Fe ₂ O ₃ , %wt, max | 0.04 | - | 0.02 | 0.015 | - |
| Na ₂ O, %wt, max | 0.2 | 0.35 | 0.3 | 0.05 | - |
| LOI (250-1100°C), %wt | 23-30 | 3.5 | 6.5 | - | - |

The FT reactor 24 is cooled by heat-exchange oil coolant introduced into the annular cavity between the shell and tube by coolant feed line 26, and discharged from the reactor 24 by coolant discharge line 28. The coolant is used to control the reactor temperature as is known in the art.

After the feed gas mixture is processed in the FT reactor 24, the reactor products consisting of inert gases, gaseous lower-boiling hydrocarbons, water vapour, naphtha gas, liquid diesel, and waxes, are conveyed to a separator 30. The separator operates to separate hot liquid, which is discharged via liquid conduit 32, and gas which is discharged via gas conduit 34. The liquid collecting in separator 30 is made up of hydrocarbons which are in the liquid state at the reactor temperature and pressure, all the waxes and some of the diesel. The gas conduit 34 conveys the product gases, that include some diesel, inert gases

naphtha and water vapor to a cooling unit 36 for condensing the diesel, naphtha and water vapour. product gases, including water vapour.

The cooled product gases and liquids from the cooling unit 36 are conveyed by the conduit 37 to a second separator 38 which separates the remaining diesel naphtha and liquid water from the product gases via a discharge conduit 40. The separated product gases are conveyed by the conduit 39 through a back-pressure valve 41 and via the gas conduit 42 to a gas chromatograph 43, which is used to analyze the cold produced gas which is vented through discharge conduit 44.

- Each of the aforementioned components (shell-and-tube reactor, separator, cooling unit, second separator, back pressure control valve, gas chromatograph) are known in the art and thus not described in detail here.

Experiments were carried out under different operating conditions and with different catalyst assembly parameters and the results of these experiments are discussed in examples 1 to 11:

Example 1

Catalyst synthesis was conducted by ordinary means as practiced by those knowledgeable in the art. The catalyst support was alumina trilobe extrudate obtained from Sasol Germany GmbH (hereafter referred to as 'trilobe'). Trilobes are cylindrical extrudates having 3 fluted ribs, 1670 microns in diameter and 4100 microns long. The support was calcined in air at 500 °C. for 24 hours. A solution mixture of cobalt nitrate and perrhenic acid was added to the support by the method of incipient wetness to achieve 5 wt% cobalt metal and 0.5 wt.% rhenium metal in the finished catalyst. The catalyst was dried slowly and then heated in a convection oven at the rate of 1.0 °C. per minute to 350 °C. and held at that temperature for 12 hours. A volume of 29 cc of oxidized catalyst was placed in a ½ inch OD tube that had an outer annular space through which temperature-control heat-exchange oil was flowed in order to remove the heat of reaction. In

effect, the FT reactor was a shell-and-tube heat exchanger with catalyst placed in the tube side. The inlet gas and coolant were both at the targeted reaction temperature. Catalyst reduction was accomplished by the following procedure:

Reduction- gas flow rate (cc/min)/H₂ in nitrogen (%) /temperature (°C.) /time (hours):

1. 386/70/200/4, pre-heat stage
2. 386/80/to 325/4, slow heating stage
3. 386/80/325/30, fixed- temperature stage

During Fischer-Tropsch catalysis, total gas flow to the FT reactor 24 was at a GHSV of 1000 hr⁻¹. Gas composition was representative of an air-autothermal reformer gas: 50% nitrogen, 33.3% H₂ and 16.7 % CO. A seasoning of the catalyst was used to reduce methane production in the early stages. This was accomplished by holding the reactor temperature at 170 °C. for the first 24 hours. Presumably, this process causes carbonylation of the cobalt surface and increased FT activity. CO conversion and liquid production were measured at a variety of temperatures between 190 °C. and 220 °C.

Example 2

The same process as described in Example 1 was carried out except with a cobalt metal loading of 10 wt%.

Example 3

The same process as described in Example 1 was carried out except with a cobalt metal loading of 15 wt%.

Example 4

The same process as described in Example 1 was carried out except with a cobalt metal loading of 20 wt%.

Example 5

The same process as described in Example 1 was carried out except with a cobalt metal loading of 26 wt%.

Example 6

- 5 The same process as described in Example 1 was carried out except with a cobalt metal loading of 35 wt%.

Influence of cobalt loading

- 10 The effect of Co loading on catalyst performance was tested with Examples 1-6 with the results shown in Table 2. Tests were conducted at various temperatures and the temperature that gave the largest amount of hydrocarbon product is listed. Although a 5% cobalt loading produces a very high concentration of diesel (92.5 wt. %), the hydrocarbon liquid rate is quite low. In contrast, the best concentration was 20 wt% Co, which gave 1.03 ml/h. The concentration of diesel
15 range hydrocarbons in the hydrocarbon product was 75.3-92.5 % at cobalt loadings of 5 wt% cobalt or higher. The highest diesel production rate (0.78 ml/h) was achieved with the trilobe support with 20% cobalt at 70 psia.

20 **Table 2. Effect of catalyst loading on performance on Examples 1-6 (trilobes) at 70 psia.**

| Weight % Cobalt | | | | | | |
|-------------------------|--------------|---------------|---------------|---------------|---------------|---------------|
| (Example number) | 5 (1) | 10 (2) | 15 (3) | 20 (4) | 26 (5) | 35 (6) |
| Optimum Temperature, °C | 220 | 210 | 205 | 200 | 200 | 200 |

| | | | | | | |
|----------------------------------|------|------|------|------|------|------|
| Hydrocarbon Liquid Rate, ml/h | 0.09 | 0.54 | 0.74 | 1.03 | 0.77 | 0.86 |
| Naphtha, wt% | 6.4 | 8.8 | 13.9 | 17.9 | 16.4 | 15.8 |
| Diesel, wt% | 92.5 | 82.8 | 78.3 | 75.3 | 76.8 | 76.8 |
| Light wax, wt% | 1.1 | 8.4 | 7.8 | 6.9 | 6.8 | 7.4 |
| Diesel production, ml/h | 0.08 | 0.45 | 0.58 | 0.78 | 0.59 | 0.66 |
| CO Conversion, mol % | 19.4 | 42.0 | 61.2 | 85.1 | 82.8 | 83.1 |
| C5+ Selectivity, % | 28.6 | 80.6 | 71.3 | 68.0 | 65.1 | 64.3 |
| Cetane number | 81 | 79 | 77 | 76 | 74 | 75 |

Influence of pressure

The catalyst in Example 4 was run in the standard testing rig as described above at a temperature of 202.5 °C. and at a variety of pressures. Results in Table 3 and Figure 3 indicate that productivity of the catalyst for production of liquid hydrocarbons is somewhat sensitive to pressure, with the optimum results obtained at pressures between 70 psia and 175 psia. The diesel fraction over that pressure range was fairly constant at 70.8-73.5 weight percent. Surprisingly, the CO conversion decreased as pressure increased in spite of the fact that the gas contact time was greater at higher pressures.

Table 3. Effect of pressure on catalyst performance (Example 4 catalyst, 202.5 °C.).

| | | | | | | | |
|-----------------------|-----------|-----------|------------|------------|------------|------------|------------|
| Pressure, psia | 40 | 70 | 100 | 125 | 140 | 175 | 200 |
|-----------------------|-----------|-----------|------------|------------|------------|------------|------------|

| | | | | | | | |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Hydrocarbon Liquid Rate, ml/h | 0.405 | 1.047 | 1.082 | 1.034 | 1.046 | 1.079 | 0.805 |
| Naphtha, wt% | 8.5 | 19.7 | 24.7 | 23.5 | 23.9 | 26.6 | 23.9 |
| Diesel, wt% | 77.8 | 73.5 | 71.9 | 73.1 | 73.4 | 70.8 | 74.1 |
| Light wax, wt% | 13.7 | 6.8 | 3.4 | 3.4 | 2.7 | 2.6 | 2.0 |
| Diesel production, ml/h | 0.32 | 0.77 | 0.78 | 0.76 | 0.77 | 0.76 | 0.60 |
| CO Conversion, mol % | 59.4 | 90.2 | 84.1 | 83.8 | 74.8 | 73.4 | 65.8 |
| C5+ Selectivity, % | 76.6 | 58.1 | 54.4 | 52.5 | 61.3 | 57.7 | 52.0 |

Example 7

This is identical to Example 1, except that the alumina support was CSS-350, obtained from Alcoa, and the cobalt loading was 20 wt. %. This support is spherical with a diameter of 2120 microns.

As seen in Table 4, the maximum diesel production rate was achieved at 215 °C. and 70 psia. Compared with Catalyst 4, Catalyst 7 gave a lower diesel production rate at its optimum temperature (215 °C.), but a higher diesel fraction. Figure 4 shows the narrow carbon number range in the liquid product at 190 °C., with 89.6% in the diesel range. Cetane number was 81. In all graphs of carbon numbers, naphtha is indicated by large squares, diesel by diamonds and light waxes by small squares.

Table 4. Performance of Example 7 at various temperatures (CSS-350).

| | | | | | |
|-----------------|-----|-----|-----|-----|-----|
| Temperature, °C | 190 | 200 | 210 | 215 | 220 |
|-----------------|-----|-----|-----|-----|-----|

| | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|
| Hydrocarbon Liquid Rate, ml/h | 0.55 | 0.58 | 0.64 | 0.70 | 0.68 |
| Naphtha, wt% | 5.4 | 15.2 | 13.4 | 15.4 | 14.3 |
| Diesel, wt% | 89.6 | 76.8 | 82.0 | 77.4 | 81.3 |
| Light wax, wt% | 5.0 | 8.0 | 4.6 | 7.2 | 4.4 |
| Diesel production, ml/h | 20.1 | 47.2 | 45.2 | 53.8 | 49.5 |
| Average Molecular Weight | 194.9 | 170.2 | 171.2 | 164.8 | 168.3 |
| CO Conversion, mol % | 47.8 | 53.4 | 81.6 | 93.8 | 100.0 |

Examples 8a and 8b and 8c

These are identical to Example 1, except that the alumina support was LD-5, obtained from Alcoa, and the cobalt loading was 20 weight percent. This support is spherical with an average particle size distribution of 1963 microns. Example 8a used the particle size mixture as received. Example 8b used a sieved selection of smaller particles from the same batch in order to assess the impact of catalyst support particle size on the composition of the Fischer-Tropsch product. Example 8c used sieved larger particles of 2500 microns and gave a diesel cut in the hydrocarbon liquid product of only 3.1 wt%. Additionally some of the original catalyst particles were ground to smaller sieve sizes and were tested.

Some of the testing results are shown in Table 5 below. All tests were conducted at 70 psia and 200 °C. The catalyst particles below 800 microns in diameter gave a high wax cut in the FT product of 17.6-19.3 % wax, whereas the larger particles gave a lower wax cut in inverse proportion to the particle diameter. The relationship of wax cut to particle diameter is further illustrated in Figure 4a.

Table 5. Performance of Catalyst 8a and 8b (LD-5) versus catalyst support particle diameter at 70 psia.

| Example | * | * | * | 8a | 8b |
|--------------------------------|------|------|------|------|------|
| Average Particle size, microns | 274 | 359 | 718 | 1593 | 1963 |
| Temperature, °C | 200 | 200 | 200 | 200 | 200 |
| Hydrocarbon Liquid Rate, ml/h | 0.79 | 0.80 | 0.74 | 0.75 | 0.78 |
| Naphtha, wt% | 10.1 | 10.4 | 11.4 | 5.2 | 15.0 |
| Diesel, wt% | 70.9 | 72.0 | 69.3 | 83.9 | 77.6 |
| Light wax, wt% | 19.0 | 17.6 | 19.3 | 10.9 | 7.4 |
| Diesel production, gm/h | 0.43 | 0.43 | 0.38 | 0.47 | 0.61 |
| Average Molecular Weight | 195 | 190 | 193 | 215 | 177 |
| CO Conversion, mol % | 68.8 | 72.7 | 73.7 | 62.9 | 72.6 |

Example 9

- 5 This is identical to Example 1, except that the alumina support was F-220, obtained from Alcoa, and the cobalt loading was 20 weight percent. F-220 is a spherical support with an average particle size of 1963 microns.

Example 9 catalyst was tested at 70 psia. As shown in Table 6 and Figure 6, the 190 °C hydrocarbon product contained 99.1% naphtha plus diesel. Diesel
 10 itself was at 93.6%. There was very little light wax. Cetane number was 81.

Table 6. Performance of Example 9 (F-220) at various temperatures (pressure 70 psia).

| | | | | |
|-------------------------------|-------|-------|-------|-------|
| Temperature, °C | 190 | 200 | 210 | 215 |
| Hydrocarbon Liquid Rate, ml/h | 0.465 | 0.757 | 0.8 | 0.733 |
| Naphtha, wt% | 5.5 | 9.2 | 20.1 | 21.5 |
| Diesel, wt% | 93.6 | 88.5 | 77.0 | 74.7 |
| Light wax, wt% | 0.9 | 2.3 | 2.9 | 3.8 |
| Diesel production, ml/h | 0.41 | 0.62 | 0.53 | 0.47 |
| Average Molecular Weight | 188.2 | 181.4 | 157.7 | 154.1 |
| CO Conversion, mol % | 50.0 | 72.2 | 94.7 | 92.2 |
| Cetane number | 81.0 | 76.0 | 67.0 | 65.0 |

5

Example 3

Figure 7 shows the carbon number distribution for catalyst Example 3 (trilobe) at 190 °C. A very narrow distribution was obtained having no heavy wax. Diesel was 90.8%, naphtha 6.1% and light waxes 3.1%. Cetane number was very high at 88.

10

Example 10

This is identical with Example 4, except that the promoter was ruthenium rather than rhenium.

Data in Table 7 and Figure 8 show that the use of ruthenium catalyst promoter instead of rhenium also provides a narrow distribution of hydrocarbons with
5 85.9% in the diesel range having an overall cetane number of 80.

Table 7. Performance of ruthenium promoter, LD-5 alumina support.

| | |
|---|----------|
| Temperature, °C./Pressure, psia | 210.3/72 |
| Conv CO to CH ₄ , % | 6.43 |
| Conv CO to C ₂ H ₆ , % | 1.47 |
| Conv CO to C ₃ H ₈ , % | 1.74 |
| Conv CO to C ₄ H ₁₀ , % | 2.55 |
| Conv CO to CO ₂ , % | 2.91 |
| CO unreacted, % | 38.28 |
| Total Conv CO, % | 61.72 |
| CO converted to C ₅ +, % | 46.62 |
| Hydrocarbon Liquid Rate, ml/h | 0.731 |
| Diesel production, ml/h | 0.451 |
| Naphtha, % | 3.6 |
| Diesel, % | 85.9 |
| Light waxes, % | 10.4 |

| | |
|---------------|-------|
| Cetane number | 80 |
| Average MW | 199.6 |

Example 11.

This was identical with Example 3, except that Aerolyst 3038 silica catalyst support from Degussa was used instead of alumina.

- 5 The hydrocarbon liquid production rate was 0.55 ml/h at 210 °C. The carbon distribution curve shown in Figure 9 demonstrates a narrow distribution with a high diesel cut.

Remarks

- 10 Examples 1-11 in this disclosure show that a narrow distribution of hydrocarbons, mainly in the diesel range, is obtained. Figure 9 compares this result with expectations from the Anderson-Shultz-Flory (A-S-F) carbon number distribution based on chain growth. The liquid hydrocarbon product of the Examples is more valuable than the broad A-S-F type of product because it can be used directly as
15 a diesel-blending stock to increase cetane number and decrease sulphur content of petroleum diesels. Because the present process is a simple once-through process, it entails low capital cost.

- It is theorized that one of the contributing factors to the unique product slate produced by these embodiments of the invention is the use of relatively large
20 catalyst particles in the range of 800 to 20,000 microns and particularly within the range of 800 to 5000 microns. We believe that the larger particle gives rise to longer wax retention times within the particle. The shorter molecules and the

cracked moities of the wax molecules are able to more easily exit the particle and join the product stream and this gives a product containing less wax.

While the present invention has been described herein by the foregoing embodiments, it will be understood to those skilled in the art that various changes
5 may be made and added to the invention. The changes and alternatives are considered within the spirit and scope of the present invention.

Claims:

1. A fixed-bed Fischer-Tropsch (FT) reactor for producing a liquid hydrocarbon with a diesel cut greater than 55 wt. % without hydro-cracking and at under 200 psia, the reactor including a catalyst assembly comprising:
5
catalyst support particles having an average particle size between 800 and 5,000 microns; and,
catalyst on the catalyst support particles and having a metallic cobalt loading between 5 and 35 wt. % of the catalyst assembly.
- 10 2. An FT reactor as claimed in claim 1 wherein the catalyst support particles are selected from the group consisting of: alumina, zirconia, titania, and silica.
3. An FT reactor as claimed in claim 1 wherein the cobalt catalyst loading is between 10 and 35 wt. %.
- 15 4. An FT reactor as claimed in claim 1 wherein the catalyst assembly further comprises a promoter on the support particles, the promoter selected from the group consisting of: ruthenium, rhenium, nickel, zirconium and titanium.
5. An FT reactor as claimed in claim 4 wherein the promoter has a loading of between 0.01 – 2 wt. %.
- 20 6. An FT reactor as claimed in claim 1 having an operating pressure of between 50 and 175 psia.
7. An FT reactor as claimed in claim 6 having an operating pressure of between 70 and 175 psia.
8. An FT reactor as claimed in claim 1 having an operating temperature of
25 between 170-240 °C.

9. An FT reactor as claimed in claim 1 wherein the reactor is a single pass fixed bed reactor.
10. An FT reactor as claimed in claim 9 wherein the reactor is a shell-and-tube reactor with the catalyst support particles and catalyst located in the tube-side of the reactor.
11. An FT reactor as claimed in claim 1 wherein the support particles have an average particle size between 1000 and 2500 microns.
12. An FT reactor as claimed in claim 11 wherein the support particles are generally spherical and the average particle size is the diameter of the particles.
13. An FT reactor as claimed in claim 11 wherein the support particles are generally non-spherical and the average particle size is the shortest dimension of the particles.
14. A Fischer-Tropsch (FT) process comprising:
- supplying a feed gas to a fixed bed FT reactor including a catalyst assembly comprising catalyst support particles with an average size between 800 and 5,000 microns and catalyst on the support particles having a metallic cobalt loading between 5 and 35 wt. % of the catalyst assembly; and
- operating the FT reactor at under 200 psia to produce FT products including a liquid hydrocarbon with a diesel cut greater than 55 wt. % without hydro-cracking.
15. A FT process as claimed in claim 14 wherein the FT reactor is operated at a pressure between 50 and 175 psia.
16. An FT process as claimed in claim 14 wherein the FT reactor is operated at a pressure between 70 and 175 psia.

17. An FT process as claimed in claim 14 wherein the FT reactor is operated at a temperature between 170-240 °C.
18. An FT process as claimed in claim 14 wherein the feed gas is reformer synthesis gas.
- 5 19. An FT process as claimed in claim 18 wherein the feed gas is air-blown reformer synthesis gas.
20. An FT process as claimed in claim in 19 wherein the feed gas contains about 50% nitrogen.
- 10 21. An FT process as claimed in claim 14 wherein the catalyst support particles are selected from the group consisting of: alumina, zirconia, titania, and silica.
22. An FT process as claimed in claim 14 wherein the cobalt catalyst loading is between 10 and 35 wt. %.
- 15 23. An FT process as claimed in claim 14 wherein the catalyst assembly further comprises a promoter on the support particles, the promoter selected from the group consisting of: ruthenium, rhenium, nickel, zirconium and titanium.
24. An FT process as claimed in claim 23 wherein the promoter has a loading of between 0.01 – 2 wt. %.
- 20 25. An FT process as claimed in claim 24 wherein the support particles have an average particle size between 1000 and 2500 microns.

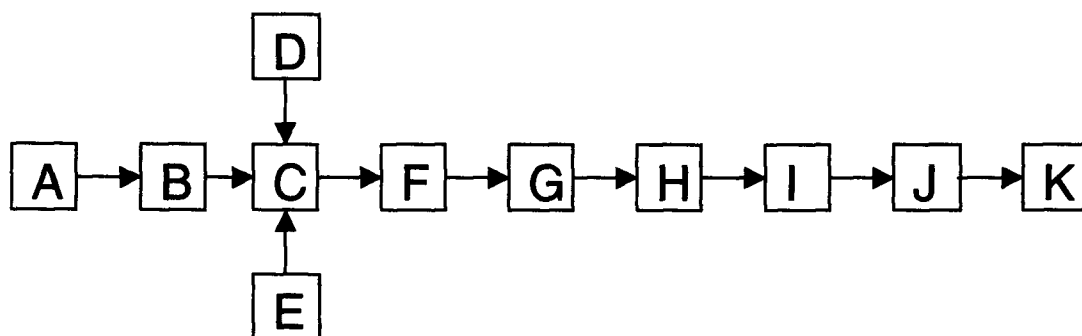
Figure 1 (a)

Figure 1(b)

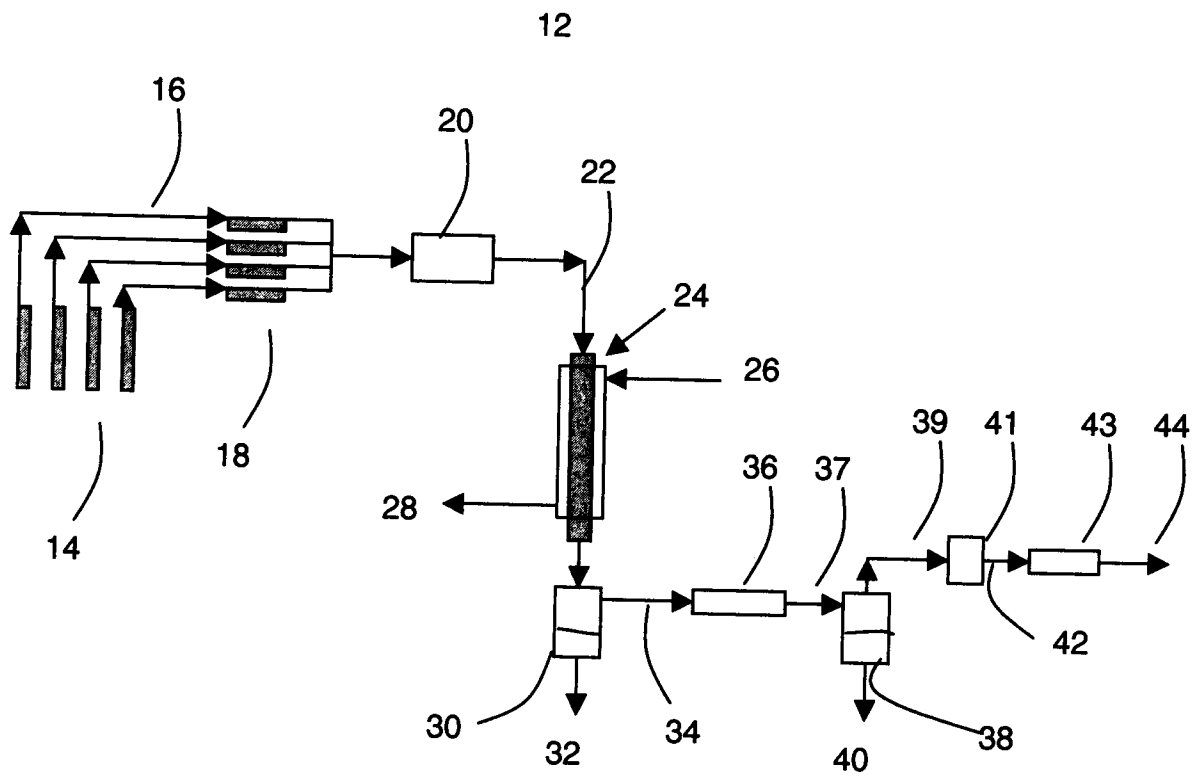


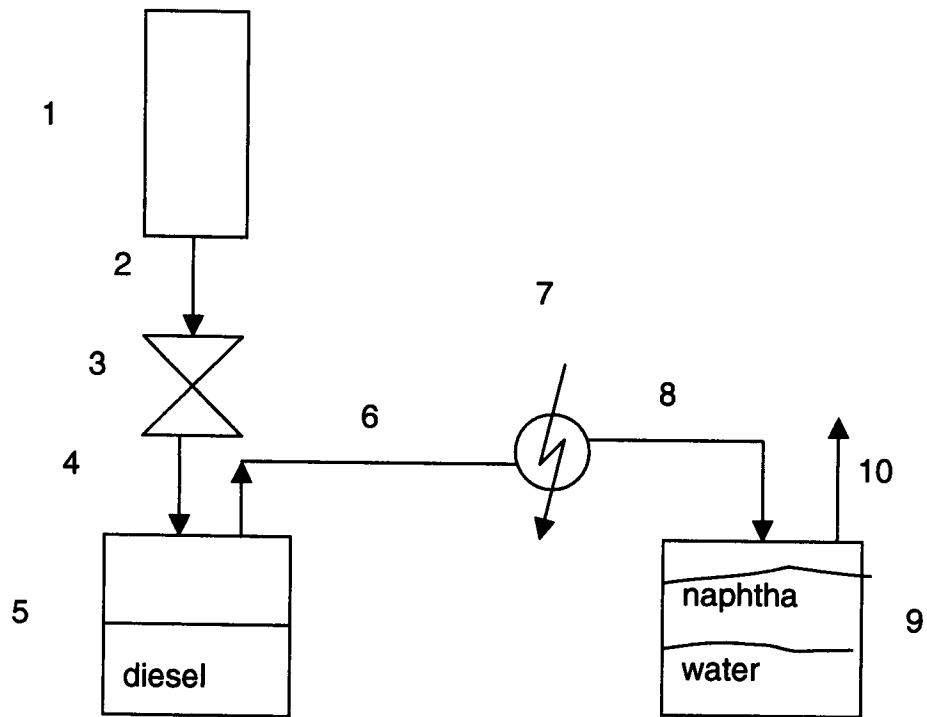
Figure 2

Figure 3

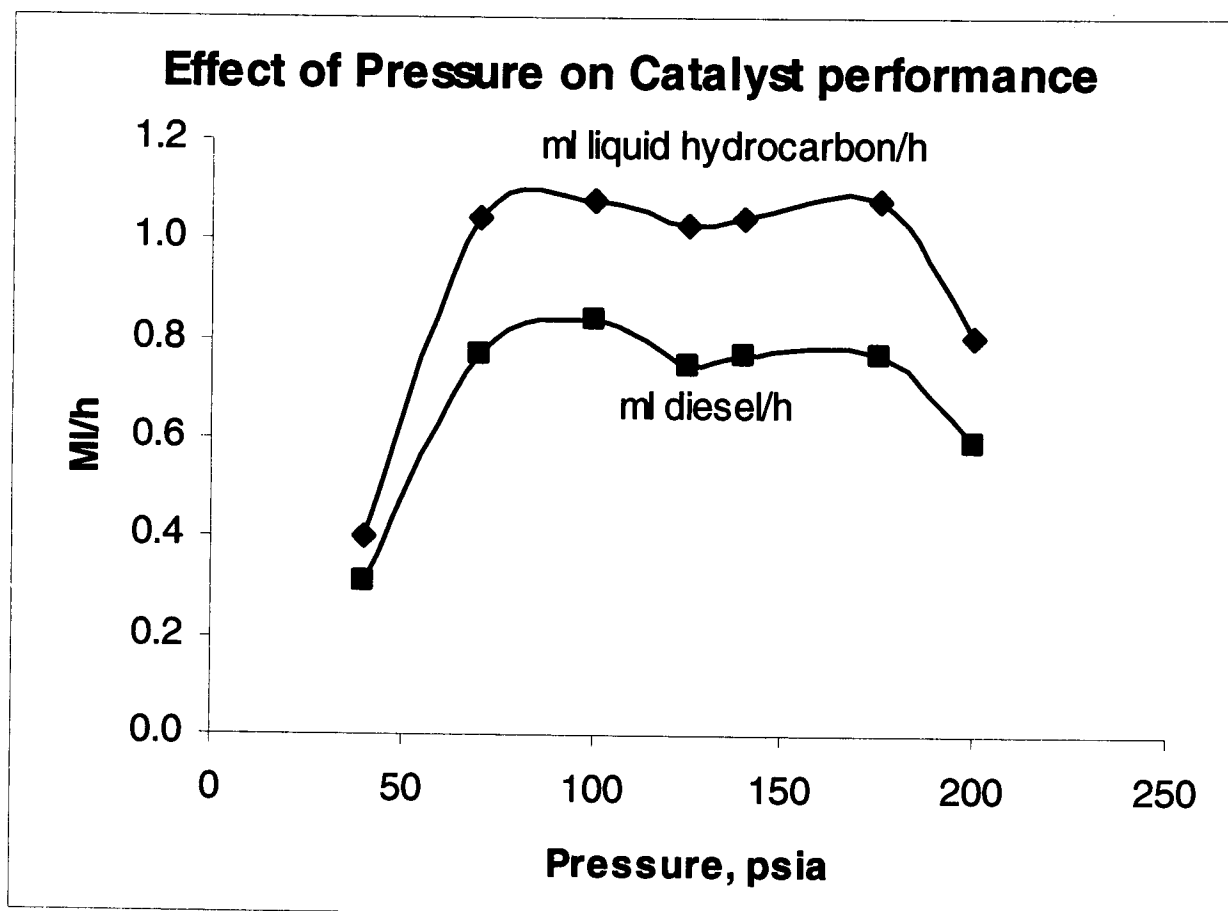


Figure 4

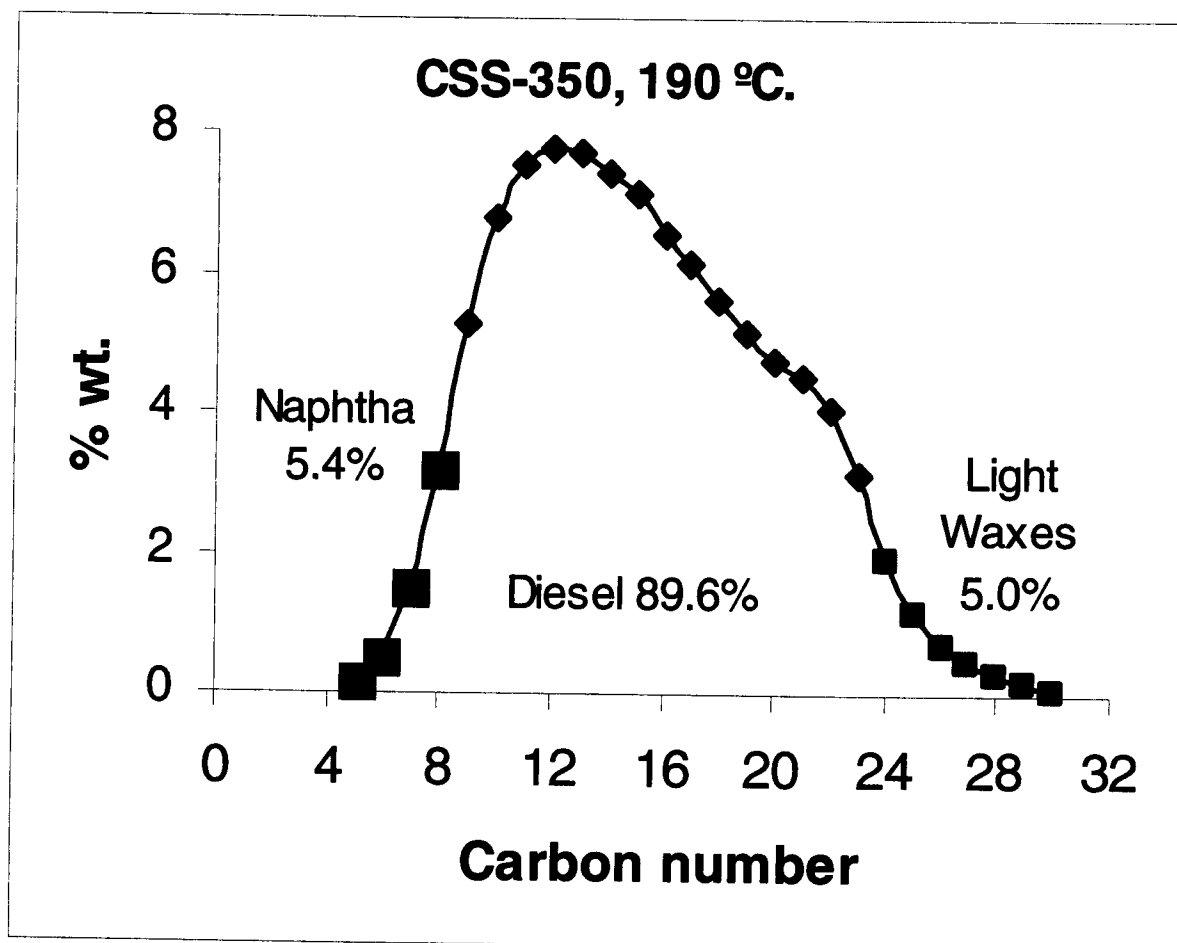


Figure 4a

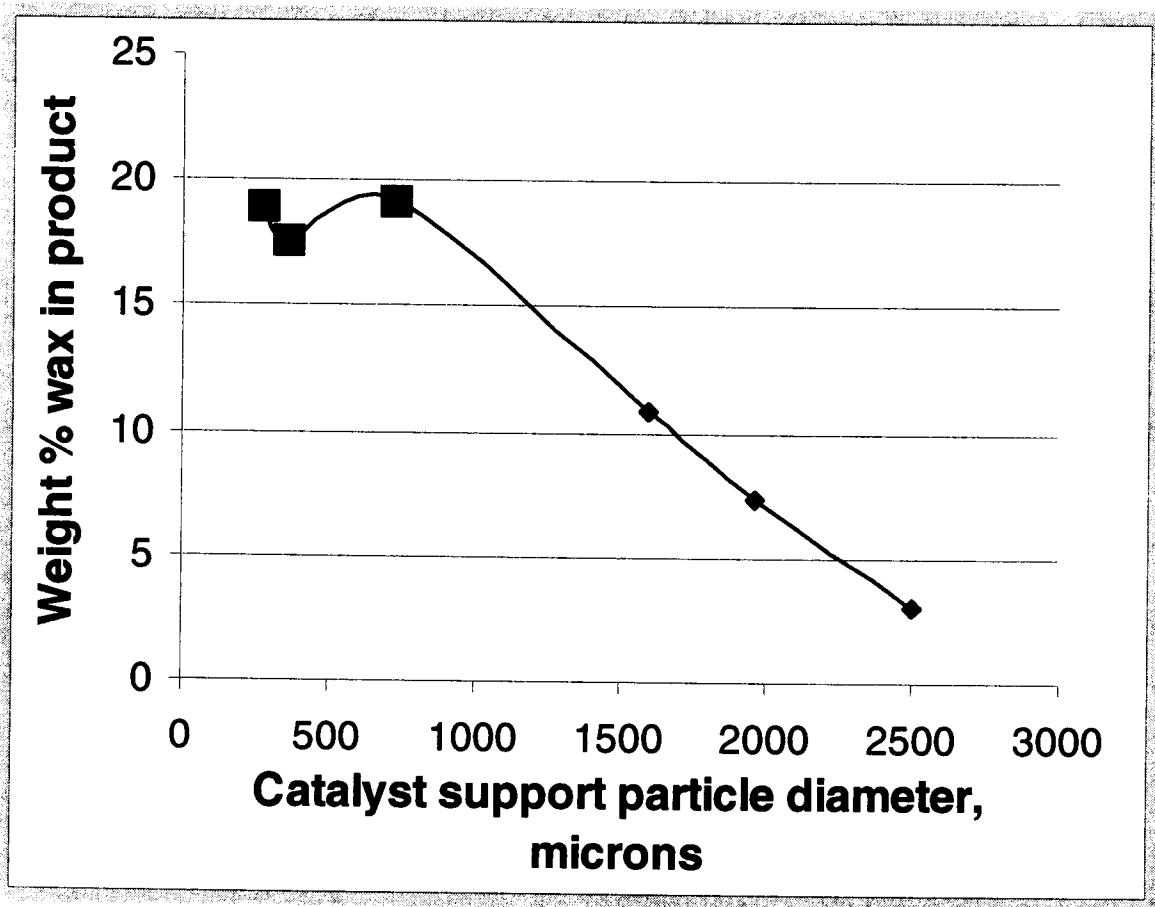


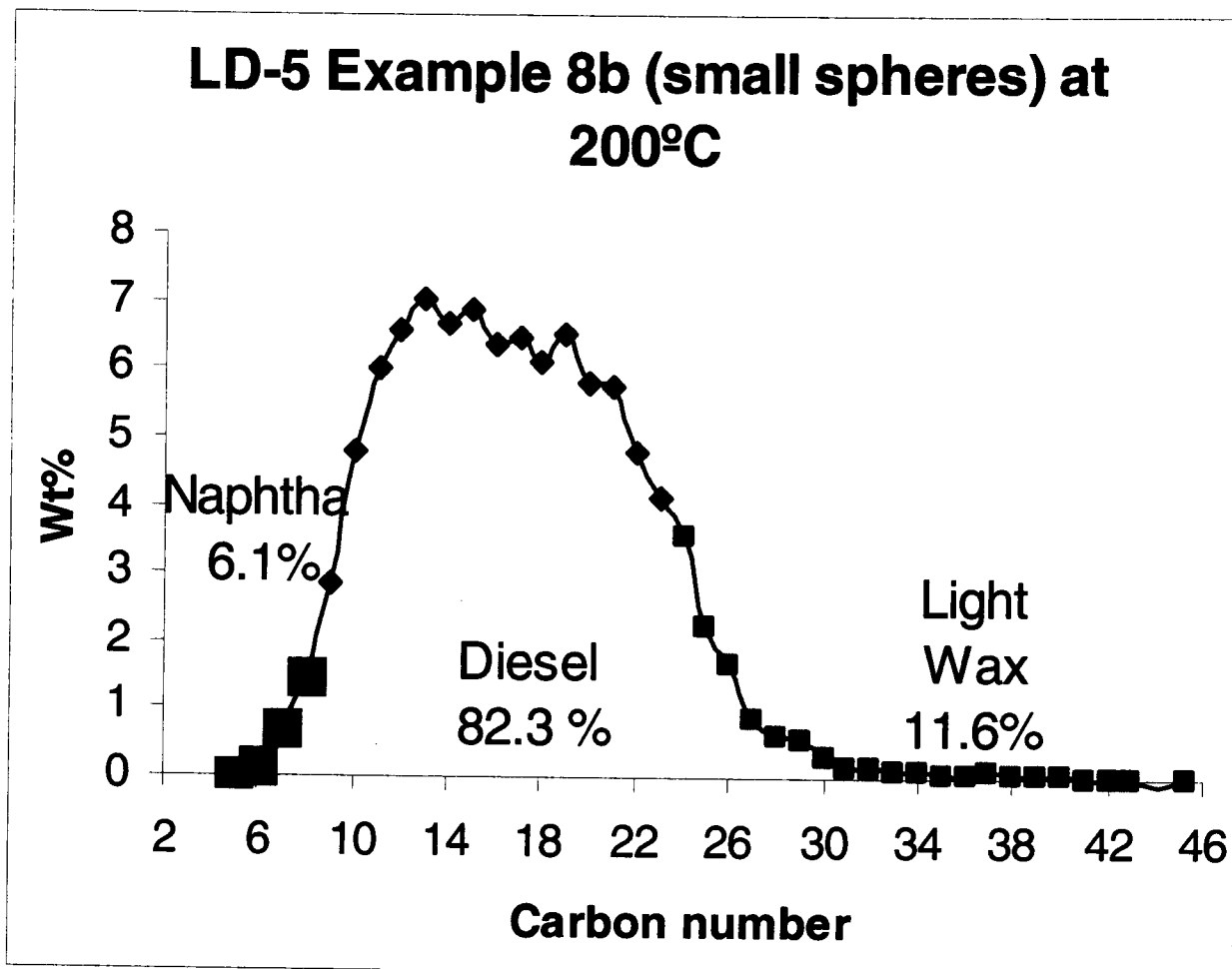
Figure 5

Figure 6

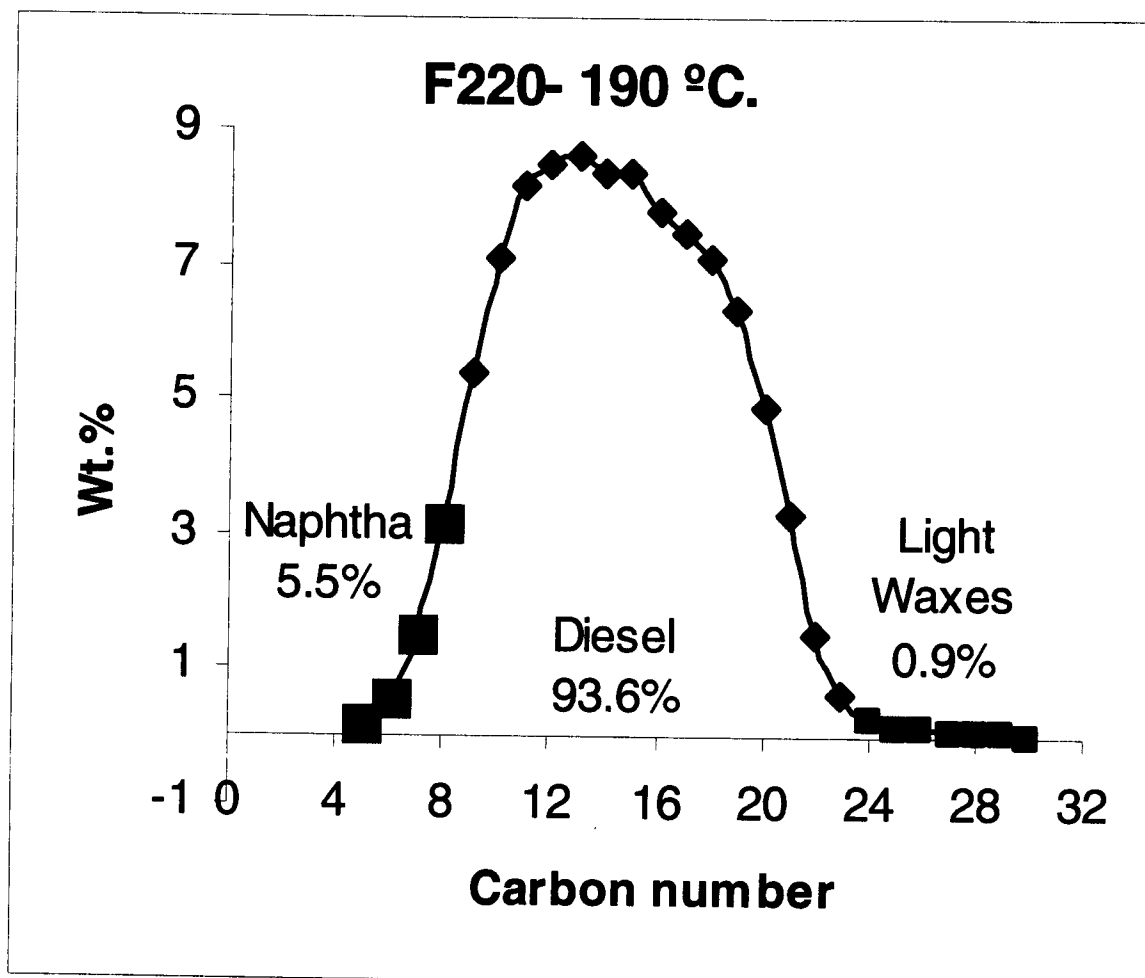


Figure 7

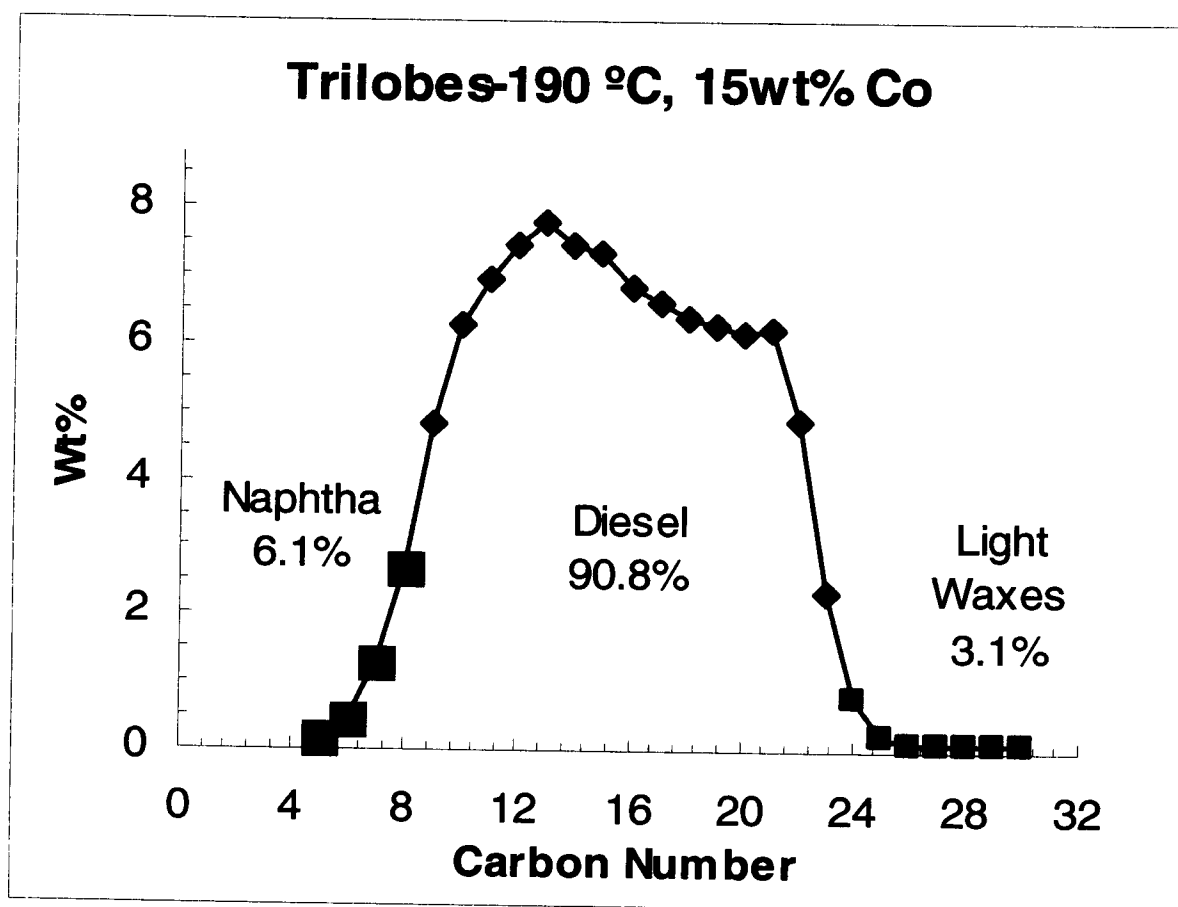


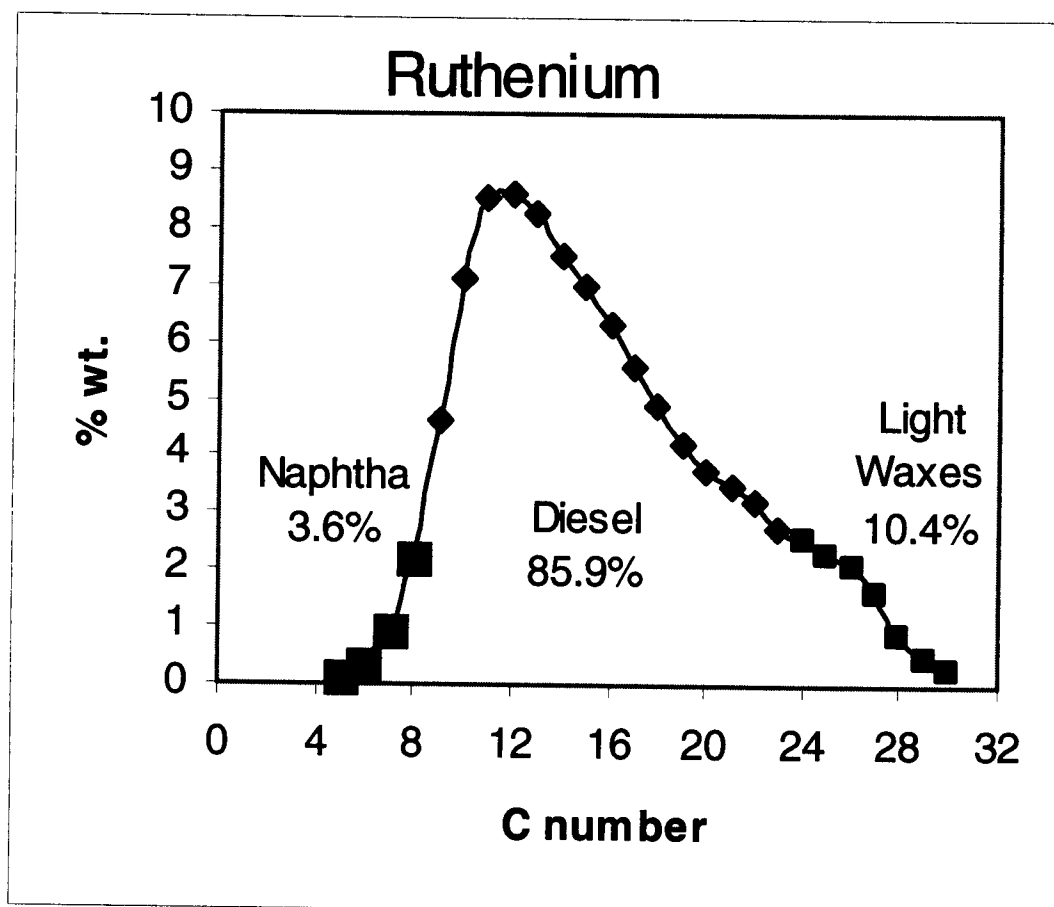
Figure 8

Figure 9

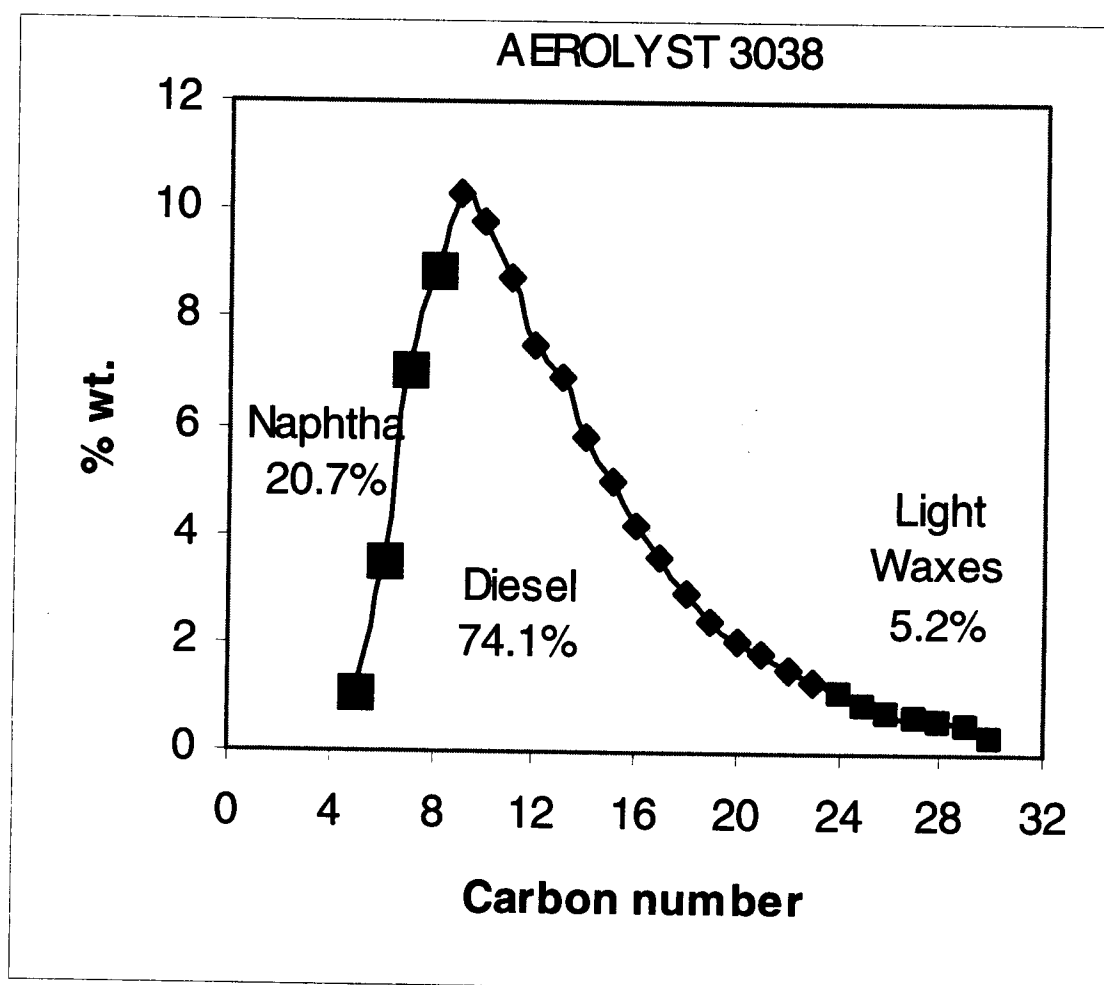
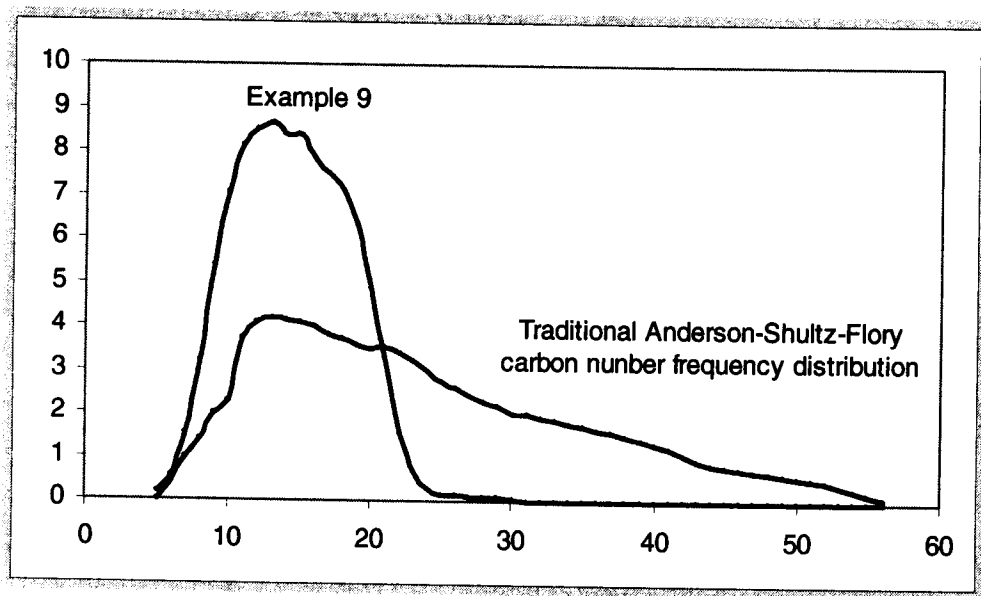


Figure 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2007/002014

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C10G 2/00** (2006.01) , **B01J 21/06** (2006.01) , **B01J 8/06** (2006.01)

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)

C10G (2006.01), B01J (2006.01), C07C (2006.01)

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

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

Delphion, Esp@cenet, Canadian Patent Database

Keywords - Fisher-Tropsch, fixed bed, cobalt, particle size, syn gas, synthesis gas

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search

3 January 2008 (03-01-2008)

Date of mailing of the international search report

19 February 2008 (19-02-2008)

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Stephen Whitarcar 819- 997-7509

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/CA2007/002014

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