METHOD TO START A PROCESS FOR HYDROCARBON SYNTHESIS

Abstract: Method to start a steady state process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons from synthesis gas in at least two conversion reactors, which process comprises the steps of: (i) providing the synthesis gas; and (ii) catalytically converting the synthesis gas of step (i) at an elevated steady state temperature and a steady state pressure to obtain the normally gaseous, normally liquid and optionally normally solid hydrocarbons; the method comprising using in at least one conversion reactor an initial pressure for the catalytic conversion of the synthesis gas lower than the steady state pressure.
METHOD TO START A PROCESS FOR HYDROCARBON SYNTHESIS

The present invention relates to a method to start a catalytic process for producing normally gaseous, normally liquid and optionally solid hydrocarbons from synthesis gas, generally provided from a hydrocarbonaceous feed, for example a Fischer-Tropsch process. In particular the present invention relates to a method to start an integrated, low cost process for the production of hydrocarbons, especially normally liquid hydrocarbons, from natural gas or associated gas, in particular at remote locations as well as at off-shore platforms.

Many documents are known describing processes for the catalytic conversion of (gaseous) hydrocarbonaceous feedstocks, especially methane, natural gas and/or associated gas, into liquid products, especially methanol and liquid hydrocarbons, particularly paraffinic hydrocarbons. In this respect often reference is made to remote locations and/or off-shore locations, where no direct use of the gas is possible. Transportation of the gas, e.g. through a pipeline or in the form of liquefied natural gas, is not always practical. This holds even more in the case of relatively small gas production rates and/or fields. Reinjection of gas will add to the costs of oil production, and may, in the case of associated gas, result in undesired effects on the crude oil production. Burning of associated gas has become an undesired option in view of depletion of hydrocarbon sources and air pollution.
The Fischer-Tropsch process can be used for the conversion of hydrocarbonaceous feed stocks into liquid and/or solid hydrocarbons. Generally the feed stock (e.g. natural gas, associated gas and/or coal-bed methane, peat, biomass, residual oil streams (e.g. tar sands, coal) is converted in a first step into a mixture of hydrogen and carbon monoxide (this mixture is often referred to as synthesis gas or syngas). The synthesis gas is then fed into a reactor where it is converted in one or more steps over a suitable catalyst at elevated temperature and pressure into paraffinic compounds ranging from methane to high molecular weight modules comprising up to 200 carbon atoms, or, under particular circumstances, even more.

Numerous types of reactor systems have been developed for carrying out the Fischer-Tropsch reaction. For example, Fischer-Tropsch reactor systems include fixed bed reactors, especially multi-tubular fixed bed reactors, fluidised bed reactors, such as entrained fluidised bed reactors and fixed fluidised bed reactors, and slurry bed reactors such as three-phase slurry bubble columns and ebulated bed reactors.

The Fischer-Tropsch reaction is very exothermic and temperature sensitive, with the result that careful temperature control is required to maintain optimum operation conditions and desired hydrocarbon product selectivity. Indeed, close temperature control and operation throughout the reactor are major objectives.

Starting up such a process will involve new and fresh catalyst material. However, catalyst material when new is often more active than once it has achieved a steady state activity under reaction conditions. In chemical reactions such as the Fischer-Tropsch reaction, which is
very exothermic and temperature sensitive as mentioned above, a higher level of activity of a catalyst at the start up of a reactor is of significant concern. There is required a way of using the initial greater activity of new catalyst material until the reaction process reaches a steady state.

It is one object of the present invention to provide this.

Thus, according to one aspect of the present invention, there is provided a method to start a steady state process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons from synthesis gas in at least two conversion reactors, which process comprises the steps of:

1. providing the synthesis gas; and
2. catalytically converting the synthesis gas of step (1) at an elevated steady state temperature and a steady state pressure to obtain the normally gaseous, normally liquid and optionally normally solid hydrocarbons;

the method comprising using in at least one conversion reactor for a period of at least three days, preferably one week, an initial pressure for the catalytic conversion of the synthesis gas lower than the steady state pressure.

By using an initial pressure lower than the steady state pressure, no lowering of reaction temperature, to otherwise compensate for the initial greater activity of the catalyst, is required. A reduction in reaction temperature also influences the quality and selectivity of products provided by the reaction. One such product could be steam. Low quality steam cannot be used to assist in either providing start-up energy or power for
one or more other reactions or processes, or as feed material for same, or both. In this way, it is desired to minimise the period of time at the start of catalytic conversion reactors before they are at a suitable temperature of producing steam of sufficient quality which is usable in other parts for the process, or other (preferably integral) apparatus or units involved with the process.

It is observed that the present invention does not relate to the activation of the catalyst. In many cases a catalyst is made by impregnation, precipitation, drying, calcination, etc. by which method a catalyst is obtained in which the catalytic metal is in the oxidic state. In the case of nickel or cobalt, such a catalyst is first reduced with hydrogen. See e.g. EP 861,222, EP 533,227 and EP 533,228. In the case of iron the activation (or conditioning) is often done with CO or CO/H2 mixtures. Activation is usually done with a period up till one or two days. During activation with hydrogen no product is formed. When CO/H2 mixtures are used, some hydrocarbon will be made, usually less than 25% of the steady state production. After activation a highly active catalyst is obtained. Using the steady state (or design) conditions (GHSV, pressure, CO-conversion) a reaction temperature is needed which is relatively low. It is observed in this respect that a major design parameter of a plant is the overall capacity. Based on a certain feed a specific amount of product is to be made. In order to get the desired amount of product to be made a selection is made with respect to GHSV, pressure, CO-conversion, temperature, etc.. Based on these figures a specific reactor size, distillation equipment, pump size, etc. is used.
In the design of a FF plant the temperature is a parameter that can be varied fairly easily. Thus, given a certain capacity, a pressure is selected to carry out the reaction, and the temperature is used to control the reaction. In this way the process is carried out at constant pressure.

The method of the present invention is usable for processes involving one, but preferably at least two hydrocarbon conversion reactors, optionally 2-10 reactors. Such reactors may be in an arrangement or system with one or more other conversion reactors.

In the method of the present invention, at least the conversion reactors to which the invention applies are preferably connected, either in parallel, in series, or both.

In the present invention, the method of using an initial pressure lower than the steady state pressure is preferably used in all the conversion reactors to which the invention applies. The method could be applied to each conversion reactor in a simultaneous manner. This arrangement may be suitable where the catalyst in the conversion reactor(s) is pre-activated, and does not require activation in situ.

In another embodiment of the present invention, each conversion reactor to which the invention applies is started at a different time. In one way, the method is therefore applied sequentially to each relevant conversion reactor. Preferably, each conversion reactor undergoes catalyst activation in situ. This arrangement is particularly suitable where start up resources are only able or only suitable for providing catalyst activation of one or two conversion reactors at a time.
Generally, a conversion reactor takes a number of weeks from its start up before it reaches a steady state. Such period can be between 1 and 12 weeks, preferably in the range 1-8 weeks or longer, more usually 2-5 weeks especially 3-4 weeks. Where the arrangement is for applying the method of the present invention to a number of conversion reactors sequentially, then there will be a cumulative time period before all the conversion reactors have reached a steady state, such that the initial pressure of the synthesis gas can then be raised in all the conversion reactors to the steady state pressure.

In another embodiment of the present invention, the lower initial pressure used in the at least one conversion reactor is increased to the steady state pressure once the process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons has reached a steady state in said at least one conversion reactor.

The term "steady state" as used herein is a term well known in the art, and relates to a constant or regular, relative to the matter involved, value or position over a period of time. Minor variation in all chemical reactions is common even for a steady state process, but a steady state process is well known in the art wherein the expected output or result is relatively predictable over time. Such conditions may or may not also be optimal, or to provide optimum results. Occasionally the "steady state" is also called the "design state" or indicated as "line out conditions". It is the intention to use the plant for a prolonged period of time (e.g. at least 6 months, preferably at least 1 year, more preferably at least two or three years. It is closely related to the "name plate capacity" of the plant.
Another definition of "steady state" relates to the overall and individual conditions, including pressures and temperatures, of the hydrocarbon synthesis plant design. Such conditions are fundamental conditions set for the plant, and their selection would be known to a person skilled in the art.

The term "steady state" is similarly used herein in relation to pressure and temperature and catalyst activity. In a conversion reactor, pressure is usually related to that at the top of the reactor.

In relation to catalyst activity, fresh or new catalyst when first used can have as much as 70% or higher greater activity of the expected or design or steady state activity. This heightened activity naturally reduces as the catalyst is used from the start up. Thus, the initial catalyst activity can be in the range 120-170%, preferably in the range 135-140%, of the steady state catalyst activity.

In the present invention the H2/CO ratio of the syngas is suitably around the same as the H2/CO ratio of the syngas in the steady state condition. The value may be e.g. 10% higher or lower, preferably 5%, but is preferably the same.

In the present invention, at least two of the conversion reactors involved in the method of the present invention could have a product recycle system or arrangement, more preferably a common gas recycle. With a common recycle, preferably all the conversion reactors to which the method applies have the same pressure, such that the lower initial pressure used is increased to the steady state pressure once the process for producing the hydrocarbons has reached a steady state in all the
conversion reactors started at the lower initial pressure.

The lower initial pressure used in at least one conversion reactor could be any suitable amount lower than the steady state pressure which suits other start up conditions, or the reactor conditions and/or products being provided by such reactor. The present invention is particularly suitable for integrated processes. One other usual product of the Fischer-Tropsch reaction is the provision of steam, and one effect of the present invention is to provide in minimal time steam of sufficient quality for use in other parts of the process, or ancillary or other connected processes, units or apparatus, such as an air separation unit (ASU). ASUs are often powered by steam generators, which generally require steam of sufficient quality, generally pressure, as a power source.

The lower initial pressure used in at least one conversion reactor could be 5-50% lower than the steady state pressure, preferably 10-40% lower.

In another embodiment of the present invention, the method starts with using in at least one conversion reactor an initial temperature for the catalytic conversion of the synthesis gas lower than the steady state temperature.

The initial lower temperature could then be raised above the steady state temperature for a period, in order to compensate for the lower initial pressure in terms of producing desired types and proportions of hydrocarbon products as soon as possible. The temperature could then be adjusted to the steady state temperature once the process for producing hydrocarbons in the conversion reactor reaches a steady state, preferably in co-
ordination with the increase of the pressure in such conversion reactor from the initial lower pressure to the steady state pressure.

In any such conversion reactors, any initial temperature used could in the range >0-30 °C lower than the steady state temperature, preferably 5-15 °C lower, and the subsequent raise in temperature could be in the range >0-50 °C above the steady state temperature, preferably 5-15 °C above.

Preferably, the temperature regime used in each conversion reactor to which the method of the present invention applies is wholly or substantially the same or similar. Also preferably, the or each conversion reactor to which the invention applies has the same space time yield (STY, hydrocarbon produced/1 catalyst/hour, hydrocarbon including C$_{3-}$-hydrocarbons inclusive olefin, oxygenates etc., but excluding CO2. The STY is usually between 50 and 300, especially 100-150 (fixed bed) or 50-100, especially 60-90 (slurry, hydrocarbon/1 gasified slurry/hour).

The synthesis gas can be provided by any suitable means, process or arrangement. This includes partial oxidation and/or reforming of a hydrocarbonaceous feedstock as is known in the art.

Where the catalytic conversion of synthesis gas in step (ii) provides steam, the present invention includes the provision of using the steam obtained in step (ii) for generating power in the provision of the synthesis gas for step (i), once the temperature in the at least one conversion reactor using an initial lower pressure is approximately the same as or above the steady state temperature.
As mentioned above, the process to which the present start up invention applies could involve a number of conversion reactors. In one embodiment, an initial pressure for step (ii) lower than the steady state pressure is used in at least two but not all of the conversion reactors, optionally between 25-75% of the reactors, preferably between 40-60% of the reactors, and the method to start with an initial pressure for step (ii) lower than the steady state pressure is not used in the remaining conversion reactors.

In such a situation, the start up of at least one of the remaining conversion reactors for step (ii) could involve using the steady state pressure, and an admixture stream of the synthesis gas of step (i) and one or more inert gases. The one or more inert gases could be, or could be part of, one or more selected from the group comprising: methane, nitrogen, ethane, propane, offgas, carbon dioxide, and post-conversion reactor syngas; preferably methane, offgas and/or post-conversion reactor syngas.

The term "inert gas" as used herein can be 100% inert in itself for a Fischer-Tropsch process or reaction. The invention also covers a gas stream containing one or more such inert gases. That is offgas or post-conversion reactor syngas, which gas streams can include one or more Fischer-Tropsch 'inert' gases.

In such an arrangement, the amount of inert gas(es) in the admixture stream could be in the range >0-99%, more suitably 5-50%, more suitably 20-40%, and more suitably 30-40%, of the combination of the inert gas(es) and the synthesis gas of step (i).

The admixture stream could be used in more than one of the remainder conversion reactors, preferably all.
Each remainder conversion reactor using such an admixture stream could be started simultaneously, or sequentially. Preferably, the remainder conversion reactors using an admixture stream are started after the conversion reactors to which the start up method of the present invention applies, and are started up simultaneously. As each remaining conversion reactor using the admixture stream proceeds towards a steady state of synthesis gas conversion, the amount of inert gas(es) in the admixture stream could be reduced, either incrementally, continuously, or a combination of both, to zero. The use of the admixture stream allows the conversion reactor to be started directly at a steady state temperature and steady state pressure, as the use of inert gas provides a lower partial pressure of the syngas and a lower possible water pressure.

The method of the present invention could further comprise:

step (iii) catalytically hydrocracking higher boiling range paraffinic hydrocarbons produced in step (ii).

In another way, the present invention provides a method to start a process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons from a synthesis gas in at least two conversion reactors, which method comprises the steps of:

(i) providing the synthesis gas; and
(ii) in at least one conversion reactor, catalytically converting the synthesis gas of step (i) at elevated steady state temperature and a first pressure to obtain the normally liquid, normally gaseous, and optionally normally solid hydrocarbons; and
(iii) subsequently increasing the pressure in step (ii) to a second pressure.
The present invention also provides a process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons from a hydrocarbonaceous feed using the method hereindescribed, as well as hydrocarbons whenever provided by such a process. In the steady state process the catalysts used in step (ii) for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide into hydrocarbons are known in the art and are usually referred to as Fischer-Tropsch catalysts. Catalysts for use in the Fischer-Tropsch hydrocarbon synthesis process frequently comprise, as the catalytically active component, a metal from Group VIII of the previous IUPAC version of the Periodic Table of Elements such as that described in the 68th Edition of the Handbook of Chemistry and Physics (CPC Press). Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal.

The hydrocarbonaceous feed suitably is methane, natural gas, associated gas or a mixture of C\(_4\) hydrocarbons. The feed comprises mainly, i.e. more than 90 v/v%, especially more than 94%, C\(_4\) hydrocarbons, especially comprises at least 60 v/v percent methane, preferably at least 75 percent, more preferably 90 percent. Very suitably natural gas or associated gas is used. Suitably, any sulphur in the feedstock is removed.

The hydrocarbons produced in the process and mentioned in the present description are suitably C3-200 hydrocarbons, more suitably C4\(_1\)-50 hydrocarbons, especially C5\(_1\)-90 hydrocarbons, or mixtures thereof. These hydrocarbons or mixtures thereof are liquid or solid at temperatures between 5 and 30 °C (1 bar),
especially at about 20 °C (1 bar), and usually are paraffinic of nature, while up to 30 wt%, preferably up to 15 wt%, of either olefins or oxygenated compounds may be present.

Depending on the catalyst and the process conditions used in a Fischer-Tropsch reaction, normally gaseous hydrocarbons, normally liquid hydrocarbons and optionally normally solid hydrocarbons are obtained. It is often preferred to obtain a large fraction of normally solid hydrocarbons. These solid hydrocarbons may be obtained up to 85 wt% based on total hydrocarbons, usually between 50 and 75 wt%.

The partial oxidation of gaseous feedstocks, producing mixtures of especially carbon monoxide and hydrogen, can take place according to various established processes. These processes include the Shell Gasification Process. A comprehensive survey of this process can be found in the Oil and Gas Journal, September 6, 1971, pp 86-90.

The oxygen containing gas for the partial oxidation can be air (containing about 21 vol. percent of oxygen), oxygen enriched air, suitably containing up to 70 percent, or substantially pure air, containing typically at least 95 vol.%, usually at least 98 vol.%, oxygen. Oxygen or oxygen enriched air may be produced via cryogenic techniques, but could also be produced by a membrane based process, e.g. the process as described in WO 93/06041. A gas turbine can provide the power for driving at least one air compressor or separator of the air compression/separating unit. If necessary, an additional compressing unit may be used between the separation process and step (i), and the gas turbine in that case may also provide at the (re) start power for
this compressor. The compressor, however, may also be
started at a later point in time, e.g. after a full
start, using steam generated in steps (i) and/or (ii).

To adjust the H2/CO ratio in the syngas, carbon
dioxide and/or steam may be introduced into the partial
oxidation process. Preferably up to 15% volume based on
the amount of syngas, preferably up to 8% volume, more
preferable up to 4% volume, of either carbon dioxide or
steam is added to the feed. Water produced in the
hydrocarbon synthesis may be used to generate the steam.
As a suitable carbon dioxide source, carbon dioxide from
the effluent gasses of the expanding/combustion step may
be used. The H2/CO ratio of the syngas is suitably
between 1.5 and 2.3, preferably between 1.8 and 2.1. If
desired, (small) additional amounts of hydrogen may be
made by steam methane reforming, preferably in
combination with the water shift reaction. Any carbon
monoxide and carbon dioxide produced together with the
hydrogen may be used in the hydrocarbon synthesis
reaction or recycled to increase the carbon efficiency.
Additional hydrogen manufacture may be an option.

The gaseous mixture, comprising predominantly
hydrogen, carbon monoxide and optionally nitrogen, is
contacted with a suitable catalyst in the catalytic
conversion stage, in which the hydrocarbons are formed.
Suitably at least 70 v/v% of the syngas is contacted with
the catalyst, preferably at least 80%, more preferably at
least 90%, still more preferably all the syngas.

The catalytically active metal is preferably
supported on a porous carrier. The porous carrier may be
selected from any of the suitable refractory metal oxides
or silicates or combinations thereof known in the art.
Particular examples of preferred porous carriers include
silica, alumina, titania, zirconia, ceria, gallia and mixtures thereof, especially silica and titania.

The amount of catalytically active metal on the carrier is preferably in the range of from 3 to 300 pbw per 100 pbw of carrier material, more preferably from 10 to 80 pbw, especially from 20 to 60 pbw.

If desired, the catalyst may also comprise one or more metals or metal oxides as promoters. Suitable metal oxide promoters may be selected from Groups UA, IIIB, IVB, VB and VIB of the (same) Periodic Table of Elements, or the actinides and lanthanides. In particular, oxides of magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, cerium, titanium, zirconium, hafnium, thorium, uranium, vanadium, chromium and manganese are most suitable promoters. Particularly preferred metal oxide promoters for the catalyst used to prepare the waxes for use in the present invention are manganese and zirconium oxide. Suitable metal promoters may be selected from Groups VIIB or VIII of the (same) Periodic Table.

Rhenium and Group VIII noble metals are particularly suitable, with platinum and palladium being especially preferred. The amount of promoter present in the catalyst is suitably in the range of from 0.01 to 100 pbw, preferably 0.1 to 40, more preferably 1 to 20 pbw, per 100 pbw of carrier.

The catalytically active metal and the promoter, if present, may be deposited on the carrier material by any suitable treatment, such as impregnation, kneading and extrusion. After deposition of the metal and, if appropriate, the promoter on the carrier material, the loaded carrier is typically subjected to calcination at a temperature of generally from 350 to 750 °C, preferably a temperature in the range of from 450 to 550 °C. The
effect of the calcination treatment is to remove crystal water, to decompose volatile decomposition products and to convert organic and inorganic compounds to their respective oxides. After calcination, the resulting catalyst may be activated by contacting the catalyst with hydrogen or a hydrogen-containing gas, typically at temperatures of about 200 to 350 °C.

The steady state catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 100 to 600 °C, preferably from 150 to 350 °C, more preferably from 180 to 270 °C. Typical total pressures for the catalytic conversion process are in the range of from 1 to 200 bar absolute, more preferably from 10 to 70 bar absolute. In the catalytic conversion process mainly (at least 70 wt%, preferably 90 wt%) of C5+ hydrocarbons are formed.

Preferably, a Fischer-Tropsch catalyst is used, which yields substantial quantities of paraffins, more preferably substantially unbranched paraffins. A part may boil above the boiling point range of the so-called middle distillates, to normally solid hydrocarbons. A most suitable catalyst for this purpose is a cobalt-containing Fischer-Tropsch catalyst. The term "middle distillates", as used herein, is a reference to hydrocarbon mixtures of which the boiling point range corresponds substantially to that of kerosene and gas oil fractions obtained in a conventional atmospheric distillation of crude mineral oil. The boiling point range of middle distillates generally lies within the range of about 150 to about 360 °C.
The higher boiling range paraffinic hydrocarbons, if present, may be isolated and subjected to a catalytic hydrocracking step, which is known per se in the art, to yield the desired middle distillates. The catalytic hydro-cracking is carried out by contacting the paraffinic hydrocarbons at elevated temperature and pressure and in the presence of hydrogen with a catalyst containing one or more metals having hydrogenation activity, and supported on a carrier. Suitable hydrocracking catalysts include catalysts comprising metals selected from Groups VI B and VIII of the (same) Periodic Table of Elements. Preferably, the hydrocracking catalysts contain one or more noble metals from Group VIII. Preferred noble metals are platinum, palladium, rhodium, ruthenium, iridium and osmium. Most preferred catalysts for use in the hydro-cracking stage are those comprising platinum.

The amount of catalytically active metal present in the hydrocracking catalyst may vary within wide limits and is typically in the range of from about 0.05 to about 5 parts by weight per 100 parts by weight of the carrier material.

Suitable conditions for the catalytic hydrocracking are known in the art. Typically, the hydrocracking is effected at a temperature in the range of from about 175 to 400 °C. Typical hydrogen partial pressures applied in the hydrocracking process are in the range of from 10 to 250 bar.

The process may be operated in a single pass mode ("once through") or in a recycle mode. Slurry bed reactors, ebulliating bed reactors and fixed bed reactors may be used, the fixed bed reactor being the preferred option.
The product of the hydrocarbon synthesis and consequent hydrocracking suitably comprises mainly normally liquid hydrocarbons, beside water and normally gaseous hydrocarbons. By selecting the catalyst and the process conditions in such a way that especially normally liquid hydrocarbons are obtained, the product obtained ("syncrude") may transported in the liquid form or be mixed with any stream of crude oil without creating any problems as to solidification and or crystallization of the mixture. It is observed in this respect that the production of heavy hydrocarbons, comprising large amounts of solid wax, are less suitable for mixing with crude oil while transport in the liquid form has to be done at elevated temperatures, which is less desired.

The off gas of the hydrocarbon synthesis may comprise normally gaseous hydrocarbons produced in the synthesis process, nitrogen, unconverted methane and other feedstock hydrocarbons, unconverted carbon monoxide, carbon dioxide, hydrogen and water. The normally gaseous hydrocarbons are suitably C\(_5\) hydrocarbons, preferably C\(_4\) hydrocarbons, more preferably C\(_3\) hydrocarbons. These hydrocarbons, or mixtures thereof, are gaseous at temperatures of 5-30 °C (1 bar), especially at 20 °C (1 bar). Further, oxygenated compounds, e.g. methanol, dimethyl ether, may be present in the off gas. The off gas may be utilized for the production of electrical power, in an expanding/combustion process such as in a gas turbine described herein, or recycled to the process. The energy generated in the process may be used for own use or for export to local customers. Part of an energy could be used for the compression of the oxygen containing gas.
The process as just described may be combined with all possible embodiments as described in this specification.

In the process of the invention, hydrogen may be separated from the synthesis gas provided for the first step. The hydrogen is preferably separated after quenching/cooling, and may be separated by techniques well known in the art, as pressure swing adsorption, or, preferably, by means of membrane separation techniques. The hydrogen may be used in a second heavy paraffin synthesis step after the first reactor (provided that a two stage hydrocarbon synthesis is used), or for other purposes, e.g. hydrotreating and/or hydrocracking of hydrocarbons produced in the paraffin synthesis. In this way a further product optimization is obtained (for instance by fine tuning the H2/CO ratios in the first and second hydrocarbon synthesis step), while also the carbon efficiency can be improved. In addition, the product quality may be improved by e.g. hydrogenation and/or hydrocracking.

Steam generated by any start-up gas turbine and/or steam generated in step (i) may also be used to preheat the reactor to be used in step (ii) and/or may be used to create fluidization in the case that a fluidized bed reactor or slurry bubble column is used in step (ii).

Any percentage mentioned in this description is calculated on total weight or volume of the composition, unless indicated differently. When not mentioned, percentages are considered to be weight percentages. Pressures are indicated in bar absolute, unless indicated differently.

It is observed that in the design of a Fischer-Tropsch plant there are usually several so-called steam-
system. Examples are a high pressure steam system, a medium pressure steam system and a low pressure steam system. A large steam system in a Fischer-Tropsch plant is the medium pressure steam system. All Fischer-Tropsch steam (generated in the syngas conversion reactors) is fed to the medium pressure system. A main use of this steam is to drive the compressors in the air separation unit. These compressors, and also other units using the medium pressure steam, are designed for use at a certain pressure. Therefore, in order to be used for the medium pressure steam system, the Fischer-Tropsch steam must have the design steam pressure. For that reason it is important that the Fischer-Tropsch reaction is done at a certain temperature. Due to the high initial activity of the catalyst in the first 4 or 8 or 12 weeks, running at the design pressure would, at the required conversion rate, result in a too low steam pressure. By reducing the pressure, a higher temperature is needed, and thus the steam quality improves and the steam can be introduced at the required pressure to the medium pressure steam system.

The invention is especially useful for fixed bed Fischer-Tropsch reactions, more especially using cobalt catalysts. The term "normally" (unless otherwise defined) relates to STP-condition (0 °C, 1 bar).

Example 1

A process for producing hydrocarbons from syngas prepared from natural gas in two slurry bed reactors using an iron-based catalyst was prepared. The steady state temperature in the conversion reactors was set for 220 °C, and the design of the plant was for a steady state pressure at the head of the reactors of 30 bar.
Using the method of the present invention, the initial temperature of the conversion reactors was 210 °C, and the initial pressure was 20 bar. Thus, the initial pressure for the catalytic conversion of the synthesis gas was lower than the steady state pressure.

After approximately 2 weeks, and as the fresh catalyst material in the conversion reactors started to reduce its catalytic activity towards a steady state, the pressure in the reactor was increased to 25 bar, and the temperature increased to 215 °C. After approximately 5 weeks, it was considered that the catalytic conversion of the synthesis gas had reached a steady state, such that the pressure and temperature in the reactors could be increased to the steady state pressure of 30 bar, and the steady state temperature of 220 °C.
1. Method to start a steady state process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons from synthesis gas in at least two conversion reactors, which process comprises the steps of:

(i) providing the synthesis gas; and

(ii) catalytically converting the synthesis gas of step (i) at an elevated steady state temperature and a steady state pressure to obtain the normally gaseous, normally liquid and optionally normally solid hydrocarbons;

the method comprising using in at least one conversion reactor for a period of at least three days an initial pressure for the catalytic conversion of the synthesis gas lower than the steady state pressure.

2. Method as claimed in claim 1 wherein a lower initial pressure is used in at least two conversion reactors, optionally 2-10 reactors, preferably wherein a lower initial pressure is used in all the conversion reactors.

3. Method as claimed in claims 1 or 2 wherein the start period is between 1 and 12 weeks, preferably 1-8 weeks, more preferably 2-5 weeks.

4. Method as claimed in any one of claims 1 to 3 wherein the H2/CO ratio of the syngas is the same as for the steady state syngas.

5. Method as claimed in any one of the preceding claims wherein the lower initial pressure used in the at least one conversion reactor is increased to the steady state pressure once the process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons has reached a steady state in said at least
one conversion reactor, preferably in all the conversion reactors started at a lower initial pressure.

6. Method as claimed in any one of the preceding claims wherein the lower initial pressure used in at least one conversion reactor is 5-50% lower than the steady state pressure preferably 10-45% lower, more preferably 20-40% lower.

7. Method as claimed in any one of the preceding claims wherein the method starts with using in at least one conversion reactor an initial temperature for the catalytic conversion of the synthesis gas lower than the steady state temperature preferably wherein the temperature in at least one conversion reactor is altered to the steady state temperature once the process for producing hydrocarbons reaches a steady state.

8. Method as claimed in any one of the preceding claims wherein all the conversion reactors have the same initial and steady state pressures.

9. Method as claimed in any one of the preceding claims wherein all the conversion reactors have the same STY.

10. Method as claimed in any one of the preceding claims wherein the activity of the catalyst in step (ii) at start up is 120-170%, preferably 135-140%, of the steady state catalyst activity.

11. Method as claimed in any one of the preceding claims wherein all the conversion reactors have a common gas recycle system

12. Method as claimed in any one of the preceding claims wherein any steam created by step (ii) is used for generating power in the providing of the syngas in step (i), once the temperature in the at least one conversion reactor using an initial lower pressure is
approximately the same as or above the steady state temperature.

13. Method as claimed in any one of the preceding claims wherein the method to start using an initial pressure for step (ii) lower than the steady state pressure is used in at least two but not all of the conversion reactors, optionally between 25-75% of the reactors, and the method to start with an initial pressure for step (ii) lower than the steady state pressure is not used in the remaining conversion reactors, preferably wherein in at least one of the remaining conversion reactors, step (ii) is started at the steady state pressure using an admixture stream of the synthesis gas of step (i) and one or more inert gases, especially wherein the one or more inert gases is or is part of one or more selected from the group comprising: methane, nitrogen, ethane, propane, offgas, carbon dioxide, and post-conversion reactor syngas, preferably methane, offgas and post-conversion reactor syngas.

14. Method as claimed in any one of claims 1 to 13, wherein the process further comprises:

   step (iii) catalytically hydrocracking higher boiling range paraffinic hydrocarbons produced in step (ii) and/or catalytic hydrosomerisation or hydrogenation of these hydrocarbons optionally followed by distillation of the product streams.

15. A process for producing normally gaseous, normally liquid and optionally normally solid hydrocarbons from a hydrocarbonaceous feed as well as, which process includes a method as described in any one of claims 1 to 14.

16. Hydrocarbons whenever provided by a process as claimed in claim 15.
A. CLASSIFICATION OF SUBJECT MATTER

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)

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents

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Date of the actual completion of the international search | Date of mailing of the international search report
----------------------------------------------------------|----------------------------------------------------------

Name and mailing address of the ISA/

European Patent Office, P B 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31651 [po nl,
Fax (+31-70) 340-3016

Authorized officer

Cagnolatti, Michele
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<td>US 4 626 552 A (ARCURI ET AL) 2 December 1986 (1986-12-02) the whole document</td>
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<td>US 2 224 048 A (HERBERT WILHELM) 3 December 1940 (1940-12-03) the whole document</td>
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<td>07-07-1953</td>
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<td>24-03-2005</td>
<td>AU 2004272744 A1</td>
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<td>EP 1668093 A1</td>
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<td>30-09-1941</td>
<td>FR 841043 A</td>
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<td>GB 518614 A</td>
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