Abstract: A plant is provided for processing a methane-containing feed gas to form heavier hydrocarbons. The plant comprises: a syngas generation module and a Fischer-Tropsch synthesis module. The syngas generation module is an autothermal reforming module provided with an associated air separation unit. Waste nitrogen from the air separation unit is used to purge or inert the Fischer-Tropsch synthesis reactor.
before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
Processing a Methane-Containing Feed Gas

The present invention relates to improvements in a plant for processing a methane-containing feed gas; it also relates to the management of catalyst, in particular particulate catalyst, in fixed bed reactors for use in the processing of methane-containing gases, and/or synthesis gas.

Many factors influence the selection of a catalyst and reactor geometry and these factors also impact on aspects of the preparation, start-up, operation, shut-down, regeneration and refurbishment of the reactor and/or catalyst. The present invention represents a holistic approach to the overall preparation and operation of a range of processes designed to upgrade methane-containing gases, taking into account the integration of all aspects of the process.

According to the present invention there is provided a plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the plant comprises: at least one syngas generation module, at least one Fischer-Tropsch synthesis module, and an ammonia removal bed positioned between the syngas generation module and the Fischer-Tropsch module and configured to reduce the level of ammonia in the syngas.

The plant may further comprise a scrubber for removing bulk ammonia from the feed gas. This scrubber may be provided upstream of the syngas generation module.

The ammonia removal bed may be configured to reduce the level of ammonia in the syngas to below 100 ppb, or below 10 ppb or even below 5 ppb.

The plant may further comprise a feed gas conditioning unit through which the feed gases flow prior to entering the syngas generation module. The syngas generation module may comprise an autothermal reformer or a steam methane reformer or a partial oxidation reactor. Additionally, the syngas generation module may comprise a pre-reformer unit. The plant may further comprise a carbonyl trap positioned between the syngas generation module and the Fischer-Tropsch module. The carbonyl trap is configured to reduce the level of metal carbonyls in the syngas.

The Fischer-Tropsch synthesis module may comprise a plurality of Fischer-Tropsch reactors operating in parallel in each of one or more stages. For example, the Fischer-Tropsch module may comprise two stages of Fischer-Tropsch synthesis reactors, with the first stage comprising eight Fischer-Tropsch reactors, mounted on four skids and a second stage comprising six Fischer-Tropsch reactors, mounted on three skids.

The Fischer-Tropsch module may comprise at least one Fischer-Tropsch reactor including flow channels or tubes that have one dimension that is less than 20 mm, less than 10 mm, less than 5 mm, less than 2 mm or even less than 1 mm.
A plant for processing a methane-containing feed gas to form heavier hydrocarbons may comprise a syngas generation module and a Fischer-Tropsch synthesis module; wherein the Fischer Tropsch module comprises a plurality of reactors arranged into two or more stages and wherein the number of Fischer-Tropsch reactors in each stage is less than the number of Fischer-Tropsch reactors in the previous stage.

Furthermore, according to the present invention there is provided a plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the plant comprises: a syngas generation module and a Fischer-Tropsch synthesis module and wherein the syngas generation module is an autothermal reforming module provided with an associated air separation unit and wherein waste nitrogen from the air separation unit is used to purge, or to make inert, the Fischer-Tropsch synthesis reactor.

The nitrogen may be provided directly to the Fischer-Tropsch module or the plant may further comprise a purification unit for purifying the nitrogen from the air separation unit.

Furthermore, according to the present invention there is provided a plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the plant comprises: at least one syngas generation module; at least one Fischer-Tropsch synthesis module; and a refurbishment facility configured to provide one or more of the following: catalyst activation, reactor refurbishment and catalyst regeneration; wherein the refurbishment facility is integrated within the plant; and wherein the refurbishment facility can run at the same time as the syngas generation module and the Fischer-Tropsch module.

The hydrogen for catalyst activation within the refurbishment facility may be obtained from tail gas from the Fischer-Tropsch synthesis module or by the separation of syngas from the syngas generation module. The refurbishment facility may further comprise an ultrasonic bath configured to aid the removal of catalyst from at least a part of either a syngas generation module or a Fischer-Tropsch synthesis module.

The invention also provides a method of filling a reactor with catalyst comprising the steps of: pouring catalyst into more than one channel simultaneously; vibrating the reactor in order to compact the catalyst; wherein vibration is commenced before the pouring is complete. The vibration and pouring steps may occur sequentially or simultaneously.

Furthermore, according to the present invention there is provided a reactor comprising a plurality of coterminous, substantially parallel reaction channels; a particulate catalyst provided in one or more of the reaction channels; and a retainer configured to retain the particulate catalyst within the reaction channels.
An end surface of the reaction channels may be configured to provide a flat surface for engagement with the retainer. Alternatively, or additionally, the retainer may be flexible to conform to an end surface of the reaction channels.

In this context a particulate catalyst is any small catalyst entity, whether supported or unsupported, including extrudates, particles and pellets. The support may be a regular geometrical form, or an amorphous or other irregular form. The particulate catalyst may comprise a plurality of substantially identical catalyst entities, or there may be some planned variance such as catalyst loading, particulate size or size distribution or shape.

In this context a structured catalyst is any catalyst that is provided on a predominantly non-catalytic support. The support may be a regular geometrical form, such as a monolith or honeycomb which may be formed from a stack of alternating substantially flat and curved foils bonded together. Alternatively, the support may be an irregular structure such as a felt, foam or wad. The structured catalyst may be sized to correspond to substantially the full length of the channel or substantially the full volume of the chamber in which the reaction takes place. Alternatively, the structured catalyst may be sized such that two, three, four, five, ten or more catalyst structures are including within a reaction chamber or channel.

Fixed bed reactors have a stationary catalyst which is intended to remain substantially fixed within the reactor during operation. The catalyst may be provided within channels or tubes that are configured to be in thermal contact with a heat exchange medium which may, in turn, be provided within adjacent channels or tubes. The channels or tubes may have a high surface area to volume ratio to ensure heat can be rapidly transferred into and out of the channels. In order to achieve these heat transfer characteristics, the channels may extend up to 20 mm in a direction perpendicular to the direction of flow of process fluid, in use. Further examples of fixed bed reactors may have channels that extend up to 15 mm, or 10 mm, or 5 mm or 2 mm or 1 mm in the direction perpendicular to the intended direction of flow of fluid. The channels may be formed from corrugated or castellated sheets with separator plates interposed between them. The resulting channels may therefore have a sinusoidal, trapezoidal, or rectangular shape when viewed in cross section. Alternatively they may be circular in cross section. The aspect ratio of the height to width for any of the aforementioned shaped channels may be less than 1.0 or more than 1.0. Indeed, the aspect ratio may exceed 2.0, 3.0, 4.0 or even 5.0; or it may be less than 0.5, 0.33, 0.25 or even 0.2. Adjacent channels, separated by separator plates, can have different fluids flowing through them. For example, in a steam methane reforming fixed bed reactor, adjacent channels are provided with steam methane reforming and combustion catalysts respectively. Furthermore, in a Fischer-Tropsch fixed bed reactor, the process channels are provided with Fischer-Tropsch catalyst whilst coolant fluid is caused to flow through the adjacent channels in use.

Furthermore, according to the present invention there is provided a plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the
The plant comprises: a desulphurisation unit; at least one syngas generation module; at least one Fischer-Tropsch synthesis module, and characterised by the provision of a reforming unit upstream of the desulphurisation unit, wherein the reforming unit is configured to reform methanol, alcohol or other hydrocarbons to generate hydrogen during plant start up.

In general, a methane-containing feed may arise as associated gas harvested as part of oil production; it may be stranded gas, shale gas, coa bed methane or it may be obtained from gasification of biomass or waste products. In order to prepare the methane-containing gas for processing, there is provided a feed gas conditioning unit which removes unwanted contaminants such as sulphur, mercury, heavy metals, inorganic compounds and chlorides which may damage the catalysts. The gas conditioning unit also includes a cooling system which may operate by Joule Thomson cooling, mechanical cooling or refrigeration in order to remove Natural Gas Liquids and Light Petroleum Gases to leave a predominantly methane feed.

All of the processes include the synthesis of heavier hydrocarbons from syngas, which is a mixture of H₂ and CO, typically using the Fischer-Tropsch process. In this context, heavier hydrocarbons are predominantly C₅, which are liquid at ambient temperature, although it may also include waxes in the region of C₁₀ and up to C₉₀ which are solid at ambient temperature. The output from the Fischer-Tropsch synthesis reaction may subsequently be subject to further upgrading of the synthetic crude to produce refined products such as naphtha, diesel and distillate or partial upgrading to improve the flow characteristics of the Fischer-Tropsch product by reducing the wax content. The preparation of syngas may be by steam methane reforming, dry reforming, gasification, autothermal reforming or partial oxidation. The upgrading includes hydrocracking and/or hydroisomerisation at a temperature in the range of 350°C-390°C. The improvements in catalyst management outlined as part of the present invention may be applied to one or more stages of the overall process.

The output of the upgrading unit may be supplied to a product stripper column where naphtha and light end components are removed using steam stripping. These components can be redeployed as liquid fuel elsewhere in the plant or recycled to the syngas generation module. The remaining output may then be provided to a product fractionator which is a s Ow pressure, refluxed column that is designed to separate the unconverted oil, diesel and naphtha.

The present invention will now be described by way of example only with reference to the accompanying drawings in which:
Figure 1 is a schematic illustration of a production plant for processing a methane-containing gas feed;
Figure 2 shows an exemplary temperature and concentration profile over the duration of an activation procedure;
Figure 3 is a schematic of an exemplary activation process; and
Figure 4 shows the typical activity flows for reactor refurbishment of the Fischer-Tropsch reactors.

The major technologies are shown in Figure 1 which illustrates schematically an overview of an example of a production plant for processing a methane-containing gas feed. The production plant 10 is broadly divided between a syngas production unit 20, Fischer-Tropsch synthesis unit 30 and synthetic crude product upgrading unit 40.

Each of these units 20, 30, 40 may be made up of one or more reactors configured to undertake the relevant processes. For example reactors may be grouped, e.g. in pairs, onto a skid which is also provided with the relevant connectivity to slot the skid of reactors into the production plant 10 in a "plug and play" operation. Groups of one or more skids may be referred to as a module, where a module is a group of reactors configured to perform substantially the same processes in use. Each of the units 20, 30, 40 therefore comprises at least one module configured to carry out the relevant process.

In this example the syngas production occurs in an autothermal reformer 22 once the feed gas 12 has flowed through a desulphurisation unit 24, a pre-reformer 26 and optionally a natural gas liquids (NGL) recovery and/or a liquid petroleum gas (LPG) unit (not shown).

The autothermal reformer 22 also requires a source of oxygen-rich gas. In this case an air separation unit 14 is used to supply oxygen. Associated with the syngas production unit 20 are a steam generator 28 and a unit 29 in which the syngas can be cooled and cleaned. The steam generator 28 and the heat exchanger and syngas cleaning unit 29 interface with a water treatment unit 16.

The Fischer-Tropsch synthesis unit 30 includes a nickel carbonyl trap 32 and two stages of Fischer-Tropsch synthesis modules 34, 36. There may also be provided an ammonia adsorption bed (not shown) and/or a cyanide removal bed (not shown). To protect the Fischer Tropsch catalyst it is required to reduce the amount of ammonia and cyanide that may be present in the syngas to very low levels. The levels required may be below 100 parts per billion (ppb), or they may be below 10 ppb, or they may be below 5 ppb. The two Fischer-Tropsch synthesis modules 34, 36 are provided with a cooling system 37. The cooling system 37 may include a phase change in the coolant or it may be pressurised such that the coolant remains in the liquid phase throughout.

Following the first and second stage of Fischer-Tropsch synthesis 36, the product is separated in separator 38. The separator 38 may be a combined separator serving both first and second stage Fischer-Tropsch synthesis modules 34, 36 but preferably a separate separator may be provided to treat the output from each stage. A further separation stage may also be included to further enhance recovery of the C5+ hydrocarbon product. The tail gas 31 that is separated from the desired products in the separator 38 is recycled within the production plant to provide a recycle back to the
Fischer-Tropsch reactors or the syngas generator or as fuel gas or for electricity generation.

There may additionally be provided NGL and/or LPG recovery of the gas feed prior to the sulphur removal. The pre-reformer 26 and autothermai reformer 22 may be integrated.

There may be the same number of first stage Fischer-Tropsch modules 34 and second stage Fischer-Tropsch modules 36. Alternatively there may be more first stage Fischer-Tropsch modules 34 than there are second stage Fischer-Tropsch modules 36. Alternatively, there may be only a single stage of Fischer-Tropsch modules 34. Alternatively there may be more than two stages of Fischer Tropsch modules. In the case where there are more than two stages, the numbers of modules in each stage may be the same, or alternatively they may be different. The configuration of the Fischer Tropsch modules may be intended to maximise CO conversion and/or productivity of C5+ hydrocarbon product. Alternatively, the configuration may be configured to minimise Capex or the configuration may be a compromise between these two factors.

The synthetic crude product upgrading unit 40 receives a feed of separated product from the separator 38 and may, in addition, receive some of the recovered liquids from the NGL recovery unit upstream of the autothermai reformer 22. The upgrading unit yields LPG, diesel and naphtha.

Plant integration

The syngas generation route - steam methane reforming, dry reforming, gasification, autothermai reforming or partial oxidation - may be selected based on a number of different factors including the location of the plant, capacity of the plant and feed gas composition.

Furthermore, the presence of an air separation unit within the plant provides some additional integration opportunities. The air separation unit has a considerable amount of nitrogen as waste gas. The level of purity of the nitrogen varies depending on the operation of the air separation unit. The lower purity nitrogen is sufficiently pure to purge a Fischer-Tropsch reactor prior to catalyst change out because under these circumstances the quality of the catalyst is not critical. However, for a purge under any circumstances where it is intended that the reactor will be brought back on line with the same catalyst, the nitrogen must have a high purity of 10 ppm or less of oxygen. In this case, the air separation unit may be able to provide high purity nitrogen directly.

If further purification of the nitrogen is required it may be possible to further reduce the oxygen content below 10 ppm through use of oxygen scavengers such as zirconium.
Integration of ATR and Fischer-Tropsch synthesis

The feed gas is subject to desulphurisation prior to syngas generation and hydrogen may be added to the feed gas prior to desulphurisation for example if the feed gas contains mercaptans. The hydrogen can be obtained via a recycle of syngas produced in the ATR. Alternatively, the hydrogen can be obtained from the Fischer-Tropsch tail gas or from an independent source of hydrogen such as a small dedicated steam methane or methanol reforming unit. Regardless of the source of the hydrogen, it can be introduced upstream of at least one of the compressors that are configured to raise the pressure of the feed to the level required for the ATR.

The waste water produced in the ATR can be treated to attain sufficient purity to be used as boiler feed water. The waste water produced in the ATR will have ammonia and other gases dissolved in it, but these may be removed using ion exchange. This reuse of the water reduces the plant's overall water requirement.

The syngas produced by the ATR is intended for introduction into the Fischer-Tropsch synthesis reactor. The ATR is typically controlled to provide a syngas ratio that meets the Fischer-Tropsch unit requirements. However, the percentage of hydrogen present in the syngas may be greater than is required for Fischer-Tropsch synthesis. This may be the case if alternative syngas generation technologies, such as steam methane reforming, are used. Under these circumstances, hydrogen can be recovered from the syngas in order to lower the hydrogen to CO ratio of the syngas that is introduced to the Fischer-Tropsch synthesis reactor. The hydrogen that is removed can be recycled to the product upgrading unit, the desulphurisation unit or to the refurbishment facility to aid passivation, regeneration or activation of the catalyst. The provision for altering the H₂:CO ratio in the syngas is also advantageous during start-up because the optimum H₂:CO ratio can be achieved more quickly without relying on the tail gas recycle from the Fischer-Tropsch reactor and the associated time to establish the correct ratio via the chemistry of the syngas generation step.

The Fischer-Tropsch tail gas contains unconverted syngas, light hydrocarbon components, hydrogen and some oxygenates produced in the Fischer-Tropsch synthesis reactor. This tail gas can be recycled, in whole or in part, to provide fuel gas to other parts of the overall plant, including recycle to the ATR for improved carbon efficiency and also to optimise the hydrogen to CO ratio in the ATR. This recycle is advantageous because it retains carbon within the system.

However, as a further alternative that is applicable in circumstances when there is more Fischer-Tropsch tail gas than is required to meet the fuel demand, the tail gas can be treated to remove CO₂ prior to recycle to ATR in order to improve the carbon efficiency of the plant as a whole. This will increase the gas recycled and reduce the tail gas that is routed to provide fuel gas. The CO₂ can be removed using liquid or solid adsorption processes or membrane separation.
Hydrogen can be separated from the Fischer-Tropsch tail gas and recycled separately. Whilst the hydrogen may be recycled to the ATR as described above, it may alternatively or additionally be recycled directly to the Fischer-Tropsch unit in order to improve the conversion and performance of the Fischer-Tropsch reactors. Where the plant operates two or more stages of Fischer-Tropsch synthesis, the recycle is particularly beneficial when recycled to an intermediate position.

In order to improve the overall energy efficiency of the plant, heat recovery can be incorporated into the plant. For example steam derived from the ATR can be used to generate power for the ASU. Some of the steam will be used in the ATR unit and the remainder will be exported to the steam system of the plant as a whole where it can be used in sulphur removal, heating and/or electricity generation and/or ASU drivers. Alternatively or additionally some of the heat from the Fischer-Tropsch process may be recovered as steam for power generation or heating. The use of steam in electricity generation may be direct or indirect as the steam may be deployed directly to drive a steam turbine or a steam turbine generator.

Integration of crude product upgrading

The crude product upgrading unit is configured to take the syncrude feed from the Fischer-Tropsch synthesis reactors and upgrade it to provide naphtha and diesel (distillate) products. Alternatively, the upgraded product may be an improved syncrude with a reduced pour point or wax appearance temperature to transport and storage properties or to improve blendability with the conventional crude oil. In this case, the upgrading unit will have a reduced level of hydrocracking and a simplified product fractionation section. Also included in this potentially blendable improved syncrude, may be a Natural Gas Liquids stream separated from the feed gas conditioning unit upstream of the ATR. These Natural Gas Liquids may have been extracted using Joule-Thomson cooling or similar refrigeration or cryogenic technologies.

The syncrude product may be provided directly to the upgrading unit or it may alternatively be routed to an intermediate storage location via a product stripper or a vacuum flash system which is configured to reduce the levels of non-condensable gases and light hydrocarbons in the feed stream that is subsequently provided to the upgrading unit.

As a further alternative the output of the Fischer-Tropsch synthesis reactors may be divided into a hot, waxy liquid stream and a colder, oil hydrocarbon product. These two streams may then be introduced to different parts of the upgrading unit as their upgrading routes may differ. This may provide an improved diesel yield and may therefore be economically preferable.

The plant will also be provided with storage locations for products that do not comply with the desired specification. These may be especially useful when at least a part of the plant has to be shut-in as a result. The provision of such storage locations
allows the unsatisfactory product to be stored until it can be re-routed into the process at the relevant stage to complete the processing to create the desired end product.

Refurbishment Facility

The plant may also include a refurbishment facility which is configured to perform the activation, passivation and refurbishment of reactors, and optionally the replacement and/or regeneration of the catalyst. In this context, therefore, the term plant refers to the production plant for processing the methane containing gas and the refurbishment facility. To be included in the overall plant, the refurbishment facility is physically located close to or adjacent to the production plant such that supplies of nitrogen, hydrogen, power and other utilities and infrastructure that are required by the various operations that make up the plant as a whole can be shared. Provision of such a facility on site also eliminates some of the transport issues that arise if refurbishment takes place at a remote location. By providing a dedicated location within or adjacent to the production plant for these activities, the production processes themselves are not affected by the running of activation, regeneration or refurbishment cycles. So, in order to be refurbished, a spent reactor is removed from the process location and replaced in a "plug and play" operation. The spent reactor is rendered inert, and is then moved to the refurbishment facility for the catalyst to be regenerated or replaced. The provision of a refurbishment facility also enables improved management of catalyst life as catalyst will only be replaced when it has been degraded sufficiently that it can no longer be regenerated, rather than replacement being dictated at least in part by down-time in the production plant as a whole, for example as dictated by maintenance schedules.

Depending on the operations undertaken within the production plant, the refurbishment facility may be configured to accept any modular reactor including SMR reactors, Fischer-Tropsch reactors and product upgrade reactors.

The refurbishment facility is configured to take one or more reactor units, skids or modules. It would be convenient to run refurbishment cycles on a complete skid or module although reactor units may alternatively be removed from the skid or module and the headers removed in order to access the catalyst. If the headers are welded, this requires the headers to be cut off and then subsequently re-welded. If the headers are flanged, then they can be removed and subsequently replaced.

The refurbishment facility may further be provided with the means to regenerate catalyst within the reactor.

The refurbishment facility includes specialist catalyst removal equipment. The refurbishment facility may be provided within a building to isolate the activities of the refurbishment facility from those in the production plant, as well as from the climatic extremes and area classification constraints in which the hydrocarbon production plant operates.
The refurbishment facility is configured to receive nitrogen from the air separation unit for use in passivation and de-waxing and regeneration operations. For example, it may be required to dilute oxidising air for high temperature oxidation to remove carbon as part of a regeneration cycle.

Loading of Fischer-Tropsch particulate catalyst into a reactor

In circumstances where the Fischer-Tropsch catalyst is a particulate catalyst, the following represents an example of how the catalyst may be loaded into the reactor. The aim of the loading procedure is to obtain a uniform loading density along the length of each channel. It is also an aim to provide uniform catalyst bed density in each channel or group of channels. The channels may be filled individually, although this is very time intensive. Alternatively, the channels may be filled in groups. A group of channels may consist of a row, or small number of rows of channels that extend across the whole or part of the reactor. Alternatively, a group of channels may consist of a square or rectangular portion of the reactor that corresponds in size and shape to the filling apparatus.

When catalyst is changed as part of a reactor refurbishment cycle, it is loaded into the reactor within a refurbishment facility which is on site within the production plant or adjacent to it, but separate from the process location itself. This means that the refurbishment facility can share utilities with the plant as whole, but the activities of the refurbishment facility should not affect the production process.

Particulate catalyst is loaded into the reactor by pouring. The equipment may need to be configured to reduce the possibility of the particles becoming statically charged during the filling operation. The catalyst may be poured directly into the channels or it may be poured onto an outer face of the reactor and then encouraged to move into the channels either under gravity alone or with vibration to assist and speed up the process. The pour rate should be between one particle per second and a rate equivalent to filling a channel per second. It may also be uniform across all channels being filled at the same time. The weight of catalyst provided to each channel or group of channels is measured by measuring the catalyst before it is poured into the reactor and then weighing any surplus catalyst that is not required. The weight is required to be correct to within 1-3% accuracy.

Once the catalyst has been at least partially loaded, vibration can be used to optimise the packing density of the catalyst. The optimisation of the timing and extent of the vibration is influenced by the ratio of the particle size and the hydraulic diameter of the channel.

The average diameter of the particles may be greater than or equal to 50 pm or 100 pm or 200 pm or 300 pm or 400 pm or 500 pm or 600 pm and less than or equal to 900 µm or 1000 µm. The term “diameter” is used to mean, for example, an equivalent spherical diameter. The average diameter may be a mass median diameter, a volume equivalent diameter, or hydraulic diameter or any other suitable average diameter. The
diameter may be measured using standing sifting techniques or in any other suitable way.

The vibration is either commenced once the catalyst fills the channel or when the channel is only part-filled with catalyst.

If the catalyst particles are small, for example less than 300 \( \mu \text{m} \), 200 \( \mu \text{m} \) or 100 pm or 50 \( \mu \text{m} \) in diameter, then the vibration can be applied once the catalyst has filled the channel. This is because simultaneous filling and vibration of such small particles can result in unwanted agitation of the catalyst rather than the desired catalyst compaction.

Simultaneous filling and vibration can be effective for larger particles, for example with diameters of 200 pm or more. When the catalyst has been suitably compacted by the vibration, the catalyst filling can be completed. If the channel was filled with the catalyst prior to the application of vibration, then the channel is subsequently "topped up" with additional catalyst to take into account the compaction of the catalyst. Alternatively, for larger particulate catalysts, the vibration may be provided continuously throughout the pouring of the catalyst.

The frequency and amplitude of the vibration are selected to optimise the compaction of the catalyst. The frequency will be low, typically less than 100 Hz, for example between 5 Hz and 45 Hz, for example 30 Hz and the amplitude high, for example 0.01 mm, 0.1 mm, 1 mm, 2 mm or even up to 10 mm. The vibration may be in the vertical plane and/or the horizontal plane, for example it may comprise an elliptical motion. The vibration may continue for 30 s, or in the region of 2 hours, possibly even up to 10 hours. The vibration may be provided by a sonic or ultrasonic process or device, for example a sonic or ultrasonic head applied to the channel ends. The sonic or ultrasonic head may be provided to the bottom end of the channels whilst the catalyst is filled from the top of the channels in order to enable simultaneous filling and vibrating of the reactor. Alternatively the vibration can be provided by either a vibration table or vibration pads. The vibration table can be provided with an off-centred motor in order to provide vibration in two planes of motion.

Alternatively, where the entire process volume of one part of a reactor, for either SMR or Fischer-Tropsch, has flow paths defined in part by corrugated or castellated sheets ("fin form") with separator plates interposed between them, and those corrugated or castellated sheets are perforated, it may be possible to provide the catalyst to the outer face of the reactor and then optionally to provide vibration and the catalyst will move through the fin form to provide an even distribution throughout the reactor.

Once the catalyst has been loaded into the reactor, the reactor will be checked in order to provide quality control. The differential pressure across the bed is measured either in each individual channel or across a group of channels. The measurement can be achieved by feeding a fixed flowrate of clean air fed from the top or bottom of the reactor. This can be achieved via a nozzle or head that is adapted to engage with either
an individual channel, each layer or a group of channels and then measuring the back pressure. The optimum group of channels is configured as a row of channels so that the quality control check can be carried out on a row-by-row or layer-by-layer basis. An anemometer is used at the channel exit to measure the flow rate of the air in order to effect the differential pressure testing. As an alternative, the air is fed into the channels and both the back pressure and the flow rate at the bottom of the reactor are measured.

If any particular channels or groups of channels do not meet the required quality control standard then the catalyst can be withdrawn from the top face of the reactor.

One method of achieving this is using a vacuum device.

Catalyst retention

Although it is intended for the catalyst to remain stationary in a fixed bed, in use the orientation of the reactor and the flow of fluids through the reactor channels may result in the catalyst moving. It is therefore important to provide a retainer to prevent the catalyst from unintentionally exiting the reactor during operation. For a reactor that is configured to have channels that are orientated vertically in use, a catalyst retainer is provided at both the top and the bottom of the channels. The retainer can be a wedge wire screen, which may be a screen such as a Johnson® Screen or it may be a mesh, perforated sheet, sintered metal or high porosity metal fibre felt or a combination of these. The retainer may therefore have either a regular geometry, as provided by the Johnson® Screen, mesh, or perforated sheet, or it may have an irregular geometry, as provided by a high porosity metal fibre felt or sintered metal. The screen must have a sufficient voidage to ensure that it does not unduly impede the flow of the process fluids, but conversely the openings must be sufficiently small to prevent the catalyst particles from exiting the reactor. The screen must also have sufficient mechanical strength to withstand a depressurisation of the reactor which may be required during a process upset.

The retainer may be configured to include predominantly a series of parallel dividers, rather than a mesh-like design in which dividers extend in both directions orthogonal to the fluid flow. This is because multiple substantially parallel dividers, such as those provided in a Johnson® Screen, ensure a lower pressure drop than a mesh of the same voidage.

The catalyst retainer must conform as closely as possible to the end of the reactor, in other words, any space between the end of the channel and the retainer must be minimised or preferably eradicated completely. This may be achieved by providing a retainer that is flexible or by treating the reactor block, for example, by grinding the end face of the reactor block to ensure that catalyst cannot exit the channel, be caught by the retainer and held adjacent to the end of the reactor. This is important because if any catalyst is trapped in this location, there is no adjacent cooling provision and therefore heat generated when this catalyst catalyses an exothermic reaction cannot be removed and this could contribute to, or even potentially initiate, a local hotspot which could damage the catalyst.
in order to facilitate the monitoring of the reaction, the retainer may be modified to include holes sized to accommodate temperature sensors that are placed within some of the channels to monitor the temperature and/or pressure of the fluids that pass through the respective channels. The holes are provided in the retainer at either the top or the bottom of the reactor. The position and size of the holes provided in the retainer must closely conform to the size and optimum position of the temperature sensors to be inserted therethrough. Sub-optimal positioning of the temperature sensor may result in the wrong part of a channel being monitored or even the temperature sensor entering a different channel from that which was intended. The size of the hole is also critical in ensuring the retention of all of the catalyst particles which could escape from the reactor if the hole were to be too large. The required accuracy and tolerances can be achieved through use of laser of other similar techniques. Alternatively, a self sealing support may be designed using a combination of metal felt and supported wire mesh, so that thermocouples may be pushed through the felt but the felt compressibility prevents particles from escaping through a gap.

A protective open-ended guide tube may be provided within each channel that is designated to include a temperature sensor. The tube may extend from the top or the bottom of the channel, usually from the top. The protective tube prevents the temperature sensor from being damaged by the catalyst as it is moved into position in the channel. It also defines the intended position of the temperature sensor as the temperature differs between the channel walls and the centre of the channel in use and data from a temperature sensor is more useful if its position within the channel is known. The temperature sensor will preferably be positioned in the centre of the channel so that it provides an indication of the temperature of the process gases flowing through the channel rather than the temperature of the channel wall. As the channel is loaded with catalyst, the protective tube will be removed from the channel.

The temperature sensor may be a thermocouple or, alternatively, it may comprise a fibre optic wire configured to provide distributed temperature sensing. Distributed temperature sensing provides monitoring of temperature profiles along the entire channel, as the mean temperatures of successive lengths of the sensor can be monitored. The temperature monitoring may be continuous or intermittent.

The temperature sensors may be located in either the channels or tubes of the reactor or in the case of a channel based reactor these may be located in the separator plate.

Once the catalyst has been loaded and the retainer fitted, then the reactor header will be welded or bolted into place and the reactor subject to a final test to check for leaks. This test may be either a pneumatic or hydraulic test. However a pneumatic test is preferred in order to avoid any damage to the catalyst.
The reactors are then installed onto a skid and the catalyst activated. Activation takes place at the refurbishment facility located within or adjacent to the production plant. The refurbishment facility includes a dedicated pressure test facility.

Activation

The Fischer-Tropsch catalyst is usually supplied in its relatively inactive cobalt oxide form. To act as an effective catalyst, the cobalt must be reduced into its metallic form. This can be achieved as a single stage reduction or an ROR (reduction-oxidation-reduction) cycle.

It is preferable for the activation to take place when the catalyst is in the reactor because activated catalyst is pyrophoric and therefore loading it into a reactor could be too dangerous. A particulate catalyst can be activated but then coated with a protective wax layer, but once such a layer has been applied it can be difficult to load the catalyst into the channels of the reactor without being heated to a temperature in the region of 70°C which is above the melting point of the wax. Alternatively, the particulate catalyst can be activated and passivated with Fischer-Tropsch product oil which has a carbon chain length in the region of up to C₂₀ and is predominantly liquid at 20-30°C.

The location of the reactor during activation is open to selection. It may take place on site, either with the reactor in situ or in the refurbishment facility that is provided on the same site as the production plant, preferably adjacent to the production plant, whilst not forming a part of the production plant. The provision of a specific refurbishment facility is particularly useful for activation of new catalyst once the plant as a whole is running because activation at the refurbishment facility minimises the down-time of the production plant, or group of reactors, for reactor change out. A refurbishment facility also has the advantages of improved safety provision as the stored gases required for activation and regeneration, including oxygen-containing gases, are segregated from the production plant. A further advantage of separation from the production plant is that the refurbishment cycle may be carried out in a more controlled environment than the production plant and also it is not subject to the time pressure that would drive decisions if the reactor were still to be within the production plant.

The activation conditions such as temperature and pressure selected are a compromise between time taken and the gas volume required to achieve the reduction. If the temperature is raised only to around 150-250°C, then the reduction cycle may take in excess of 12 hours, for example the region of 12 to 120 hours. In contrast, if the temperature is raised to 350-450°C then the required time to obtain the necessary level of reduction may be considerably shorter.

The reducing gas may be pure hydrogen or it may be a mixture of hydrogen and an inert gas such as nitrogen. A mixed gas may more appropriate for a longer, lower temperature reduction. The reducing gas may also be recycled via a gas recycle loop.
The pressure also alters the reaction rate. The pressure may be atmospheric pressure or the pressure may be increased to 6 bar or even 10 bar. A higher pressure may allow a lower temperature or shorter duration to be utilised to achieve the required level of reduction.

For example, the activation of the Fischer-Tropsch catalyst can proceed via the following reduction reactions:

<table>
<thead>
<tr>
<th>Initial</th>
<th>Co$_3$O$_4$ + H$_2$ $\rightarrow$ 3CoO + H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final</td>
<td>CoO + H$_2$ $\rightarrow$ Co + H$_2$O</td>
</tr>
</tbody>
</table>

The water concentration in the reactor effluent correlates with the reaction rate and therefore measurement of the water concentration provides an indication of the reaction rate. Typical temperature and concentration profiles over the duration of an activation procedure are shown in Figure 2.

This shows the temperature, T, within the reactor and also the concentration, C, of water vapour in the reactor effluent over time, t. In this example the total activation cycle takes around 24 hours, although the majority of the reduction takes place over a 3-4 hour period as the temperature in the reactor reaches a sufficient level to initiate the reduction reactions. The reactor is maintained at the maximum temperature of 390°C for an extended period in the region of 10 hours to ensure full activation of the catalyst.

The minimum hydrogen make-up rate is dictated by the peak reaction rate. In the example above this occurs as the temperature in the reactor exceeds 250°C for the first time. In other examples this temperature may be as low as 150°C, depending on other conditions such as pressure. On Figure 2 this occurs at around t = 8 hours. There are several alternative methods of activating the Fischer-Tropsch catalyst including the above mentioned reduction and alternatively using a reduction-oxidation-reduction cycle and the optimum method is a balance between reliability, cost efficiency, and the stability and life of the Fischer-Tropsch catalyst.

The exact nature of the re-use of gas streams by the refurbishment facility will depend on the identity of the different constituent parts of the production plant. Where syngas generation takes place through autothermal reforming this will provide a hydrogen stream, and the associated air separation unit will provide a nitrogen stream. In addition, electrical power, instrument and plant air from the production plant may be deployed within the refurbishment facility.

Reduction under hydrogen, a hydrogen containing gas, or other reducing gas at a high temperature in the region of 350-400°C and a medium pressure will be executed on site using a dedicated refurbishment facility, separate from the main process, which includes a gas recycle circuit, gas conditioning, heating and cooling equipment.

The heat for activation can be introduced into the Fischer-Tropsch process channels via the coolant side of the reactor. The intention is to minimise the temperature gradients through the reactor to ensure that the catalyst is uniformly
activated to provide the same initial level of activity throughout the reactor. The fluid provided on the coolant side is unlikely to be a commercially available specialised heat transfer fluid as very few such fluids are capable of operating at the high temperatures required during activation. One commercially available heat transfer fluid, Dowtherm A, is capable of operation at the required temperatures. However, there may be issues with respect to the incompatibility with the normal water-based Fischer-Tropsch coolant and the consequential requirement to remove the Dowtherm A fully from the reactor prior to installation of the reactor within the process block.

In order to avoid the temperature limitations associated with liquid phase heat transfer fluids, gas heating may be used. Unlike liquid phase heat transfer fluids, gas heating has effectively no temperature limitations and it also eliminates the requirement for reactor clean-up and the subsequent management and treatment of effluents.

The most straightforward adaption of a gas heated system is to utilise a common gas recycle circuit for both the reduction circuit and the heat transfer circuit, which will contribute to both heating and cooling of the fluids in the process channels at different points within the activation cycle. The gas used is high purity hydrogen that is heated before being introduced into the cooling channels thus providing the required heat.

The activation rig, within the refurbishment facility, can be sized to accommodate either single or multiple Fischer-Tropsch reactors, skids or modules. The size is influenced by capital expenditure, the number of activation cycles and associated duration required to process a group of Fischer-Tropsch skids or modules. By increasing the number of activation cycles, the overall gas conditioning demand is increased which has a negative impact on the cost of operation. For example, the rig can be sized to allow parallel activation of one, two, four or up to eight Fischer-Tropsch reactors, skids or modules.

An example activation process schematic, corresponding to a plant 50, is shown in Figure 3. In this example the activation plant 50 is designed to circulate hot hydrogen gas to the installed Fischer-Tropsch reactors, skids or modules, at the required flow-rate and temperature. Hot gas is arranged to flow to both the process side, where it provides heating and reduces the synthesis catalyst, and the coolant side, where it provides additional heating. In this example, during the activation phase, hydrogen leaves the conditioning gas compressor 51 at approximately 9 bara and is cooled in the compressor discharge cooler 52 and any water condensing is removed in the compressor discharge knockout drum 53, in order to protect the conditioning gas drier 55. The gas, which may contain up to ca. 1% water vapour, then passes to the conditioning gas drier 55, which contains molecular sieve type adsorbent. Dry hydrogen then passes to the conditioning gas interchanger 56, where it is pre-heated by hot hydrogen leaving the Fischer-Tropsch reactors 34, 36. This gas then reaches the conditioning gas heater 57 where it is heated to the required temperature for the Fischer-Tropsch reactor activation. After passing through the reactors 34, 36, the gas is recycled through the conditioning gas interchanger 56 and a recycle cooler 58 and a recycle knockout drum 59 to the compressor 51.
The hydrogen gas is initially heated to 120°C, and is held at this temperature for 4 hours, and it is confirmed that no further water leaves any reactor 34, 36, as measured at the outlet of each reactor 34, 36. After this phase, gas is then heated at 1°C/min to achieve a peak 390°C reactor temperature. These conditions are then held for approx. 4 hrs and until the cumulative water evolved at each reactor 34, 36 indicates that reduction of the catalyst in the reactors 34, 36 is complete. During the cooling phase the temperature to the skids is controlled by the conditioning gas interchanger 56, with the electric heater of the heater 57 switched off. Gas temperature to the reactors is reduced at 2°C/min until the skids reach 60°C. The activation of the reactor catalyst is then complete. Once isolated and purged with an inert gas the skids are ready for de-coupling from the activation plant within the refurbishment facility and removal from the refurbishment facility and incorporation into the process plant.

Reactor geometry

The Fischer-Tropsch reactors 34, 36 have process channels with a height and width, perpendicular to the direction of flow of process fluid, of up to 20 mm. More particularly, the height may be up to 10 mm, 5 mm or 2 mm and the width may be up to 10 mm, 5 mm or 2 mm. The width and height may be the same, such that the aspect ratio is 1.0. Alternatively, the height may exceed the width or vice versa to give an aspect ratio greater or less than 1.0, for example 0.33, 0.5, 0.75 or 2.0 or 3.0.

Adjacent to the process channels is a coolant side through which coolant fluid flows, in use. The coolant side of the reactor may be divided into discrete channels or it may comprise a "fin form" structure that enables the coolant fluid to take a tortuous path through the reactor, rather than being confined to a substantially linear channel. Each reactor unit comprises a reactor block, headers and associated piping. Each reactor block may consist of multiple cores welded together, where each reactor core is a single brazed entity. A skid comprises one or more reactor units and associated piping. The piping may configure the one or more reactor units on a skid to be in parallel or in series. The term module may also refer to a group consisting of one or more skids joined together that is capable of producing 50 to 1000 bpd, for example 200 bpd or 500 bpd.

Production plant start-up

Overall production plant start-up can be summarised in the following major steps: start up of steam and power generation systems; start up of Air Separation Unit (ASU) 14 where required; start up syngas production unit 22 including desulphurisation unit 24 and prereformer 26; optional H₂:CO adjustment; start up of the Fischer-Tropsch cooling system 37; nickel carbonyl trap 32 start up; Fischer-Tropsch synthesis 34, 36 start up, and product upgrading 40 start up.

An Air Separation Unit is required if the syngas production unit is an autothermal reformer. If it is a steam/methane reformer, then an ASU is not required. The nature of
the syngas production unit will also dictate to an extent the likely requirements in terms of \( \text{H}_2: \text{CO} \) adjustment.

It is therefore apparent that the desuiphurisation unit is started up before the Fischer-Tropsch synthesis unit from which the desuiphurisation unit obtains its hydrogen during steady state operation. Depending on the levels of mercaptan, COS and other non \( \text{H}_2\text{S} \) sources of sulphur contamination, it may be possible to start up the system without the desuiphurisation unit being operable until the Fischer-Tropsch synthesis unit has been started up. If this is the case, then the quantity of pre-reformer catalyst may be increased in a partially sacrificial manner. If the level of sulphur contamination exceeds the safe threshold for operation of the various parts of the GTL process, then an alternative source of hydrogen is required during start up. Hydrogen may be generated from methanol, implemented through the provision of an additional bed or reformer catalyst upstream of the desuiphurisation unit to enable the reforming of methanol to provide hydrogen for the desuiphurisation unit. Alternatively, the hydrogen may be stored hydrogen or syngas generated by steam/methane reforming or hydrogen from electrolysis.

During the initial start-up, when the syngas production is low and no Fischer-
Tropsch tail gas for recycle is available, the \( \text{H}_2: \text{CO} \) ratio in the syngas will be higher than ideally required for the Fischer-Tropsch operation. The \( \text{H}_2: \text{CO} \) ratio in the syngas will typically be higher than 2.2 and therefore higher than the \( \text{H}_2: \text{CO} \) usage ratio for the Fischer-Tropsch reaction, where the usage ratio is defined as the ratio of \( \text{H}_2 \) consumption to CO consumption in the Fischer-Tropsch reaction. Feeding the syngas with a \( \text{H}_2: \text{CO} \) ratio above the usage ratio to the Fischer-Tropsch reactors will typically result in a Fischer-Tropsch tail gas with a \( \text{H}_2: \text{CO} \) ratio that is higher than the \( \text{H}_2: \text{CO} \) in the syngas feed. In contrast, in normal operation when using an ATR, the \( \text{H}_2: \text{CO} \) ratio in the syngas is lower than the usage ratio and therefore results in a reduction in \( \text{H}_2: \text{CO} \) of the Fischer-Tropsch tail gas.

One start-up mode is to reduce the \( \text{H}_2: \text{CO} \) ratio of the syngas generated to-be in line with the \( \text{H}_2: \text{CO} \) ratio of the Fischer-Tropsch feed gas during normal operation, or as a minimum, to below the \( \text{H}_2: \text{CO} \) usage ratio for the Fischer-Tropsch reaction. The benefit of this start-up mode is that operating conditions for the Fischer-Tropsch reactors and the syngas generation unit are more in line with normal operation and this mode therefore results in a smoother start-up. The disadvantage of this start-up mode is that the design of the GTL facility must provide the additional facilities or means to achieve the reduction in \( \text{H}_2: \text{CO} \) ratio. This may include providing a hydrogen removal membrane between syngas generation unit and Fischer-Tropsch section, recycling of an alternative \( \text{CO}_2 \)-containing stream to the syngas generation unit, altering of operating conditions around ATR (e.g. reactor temperature or steam to carbon ratio) or a combination of these options according to the capacity or design of the equipment and syngas generation technology.

If the syngas production unit is a steam methane reformer, hydrogen removal will be required for start-up and normal operation. If the syngas production unit is a POX-
based piani, the $H_2:CO$ ratio may be lower than ideally required for the operation of the Fischer-Tropsch reactor and some upwards adjustment to the $H_2:CO$ ratio, i.e. some additional hydrogen may be required.

Start up of the Fischer-Tropsch synthesis unit can commence through the nickel carbonyl bed once the Fischer-Tropsch section has been warmed up. As the whole plant is started up, it will be operated at below full capacity. In one alternative, syngas can be introduced to one or more of the stage 1 and stage 2 reactors so that the space velocity through the reactors stays consistent with normal operating space velocity. As the volume of available syngas increases, more of the Fischer-Tropsch reactors can be started-up until the ATR is operating at full capacity and all of the Fischer-Tropsch reactors have been started up. Alternatively, adjustment of the Fischer-Tropsch reactors can be started up simultaneously at a space velocity well below that of normal operating conditions. At the syngas available increases, the space velocity through all of the Fischer-Tropsch reactors can be increased towards steady state levels.

Effective Operation of Fischer-Tropsch reactor

The prevention of process upsets in a Fischer-Tropsch reactor is critical to the effective running of both the reactor itself and the plant of which the Fischer-Tropsch reactor forms a part. Thermal transients can result in the premature deactivation of the catalyst reducing the overall performance of the reactor and thereby the whole plant. A thermal transient, which may lead to a process upset, is characterised by an accelerating reaction rate and is initiated when the rate of heat generation in some part of the Fischer-Tropsch reaction channels exceeds the rate at which heat is removed from that area onto the coolant side. During a process upset methanation tends to be the dominant reaction and, as methanation is more exothermic than Fischer-Tropsch synthesis, this shift in the predominant reaction further increases the imbalance between the heat created and the heat removed onto the coolant side thus exacerbating the problem.

In order to avoid damage to the reaction channels, the catalyst or both, it is imperative that a thermal transient is stopped as soon as possible, preferably via the detection of precursor conditions that exhibit prior to the rate of change of temperature exceeding acceptable levels.

A number of different responses are available including reduction of reactor temperature, reduction of reactor pressure, introduction of inert gases in place of the feed gas and adjustment of the syngas ratio of the feed.

Reduction of reactor temperature is very influential in terms of reaction kinetics. It is acknowledged in the art that a 50% reduction in reaction rate is achieved for a 15°C reduction in reactor temperature. However, temperature reduction in a Fischer-Tropsch reactor cannot be achieved quickly as a result of the thermal inertia of the system as a whole. Practically, the rate of reduction of temperature in a reactor is only likely to be in
the region of 1-2°C per minute, although the rate may be increased up to 5°C per minute under certain circumstances.

The temperature can be reduced by changing the temperature of the coolant fluid flowing through the coolant side of the reactor. Under normal operating conditions, the coolant fluid may be sourced from a plurality of different sources at different temperatures. If the temperature of the reactor needs to be reduced, the coolest source of heat exchange fluid can be selected as the sole source. The flow rate of the heat exchange fluid is also increased in order to maximise the transfer of heat out of the Fischer-Tropsch channels. Reducing the temperature of the heat exchange fluid to 150°C can increase the rate of change of temperature in the reaction channels to 2.5°C/minute. This approach can be adopted on a reactor-by-reactor basis and the reduction of temperature of one reactor has very little effect on the other Fischer-Tropsch reactors in the plant.

Reduction in reactor pressure has a lesser effect on the reaction kinetics than a reduction in temperature, but is effective in reducing syngas inventory and therefore the potential of the reactor or catalyst to exceed certain maximum temperature values. However, it can be achieved more rapidly than a reduction in reactor temperature. It is achieved via a reduction in the partial pressure of the reactants. It can be achieved either upstream or downstream of the reactor. If depressurisation is implemented on a plant-wide basis, then the feed and the reactor syngas inventory will have to be flared as the reactors are purged with an inert gas such as nitrogen.

Introduction of inert gases involves the deployment of high purity nitrogen in order to prevent catalyst oxidation. It results in a plug flow of inert gas through the reactor. The nitrogen purge can be either upstream or downstream of the reactor and the plug flow may therefore travel in the normal direction of flow through the reactor or in the reverse direction. The advantage of the reverse flow is that it reduces the concentration of syngas that is passed over the regions of catalyst that are at the highest temperature. The nitrogen inventory can be significantly reduced if it is associated with a syngas depressurisation prior to nitrogen purging. The inventory is nominally sized for a single volume sweep of the reactor. The purge may take between 0 and 5 minutes depending on the size of the reactor, for example 1-2 minutes.

Syngas ratio reduction does not reduce the reaction kinetics as much as reductions in temperature and/or pressure of the reactor. In a plant generating syngas using ATR, the Fischer-Tropsch tail gas recycle rate may be increased to reduce the H₂:CO ratio. However, this takes a considerable time to propagate through the system, making it less effective in the case of a thermal transient. In a plant generating syngas using SMR the H₂:CO ratio can be reduced via membrane control. Whilst this is more direct than the situation for an ATR based syngas generation, the system volume upstream of Fischer-Tropsch is still sufficiently large to make this a slow transition. As the syngas is from a common source, a change in the H₂:CO ration affects the whole plant. In a plant generating syngas using partial oxidation, syngas ratio adjustment may be more effective as there is naturally a low H₂:CO ratio which is supplemented with
hydrogen. In these circumstances, the supplemental hydrogen can be shut-off or reduced resulting in a rapid change in the overall H₂:CO ratio.

The different responses can be deployed in combination in order to augment the effectiveness. This is especially effective when a reduction in pressure, nitrogen purge and a reduction in temperature are combined.

Fischer-Tropsch reactor shut-down

There are three distinct scenarios in which one or more of the Fischer-Tropsch reactors within the plant need to be shut down. These are firstly, a controlled or scheduled shut down resulting in the reactor being parked at a temperature in the region of 120°C to 180°C, for example 150°C; secondly, an emergency shutdown caused by a trip within the plant; and thirdly, a shutdown of the reactor in order to either enable "plug and play" change out of a skid comprising two reactors as a result of catalyst deterioration or to reduce the number of reactors online as a result of long term reduction in the volume of feed gas. The activity flow for all of the above mentioned scenarios is outlined in Figure 4.

A controlled shut down includes the gradual ramp down of the temperature to a temperature below the reaction temperature. Once the reaction has effectively halted the flow of syngas is halted and the reactor purged with high purity nitrogen. The reactor is depressurised in a controlled manner. The Fischer-Tropsch reactor is then effectively dormant. This state is useful where a problem elsewhere in the plant has required the shut down of the reactor, but there is no actual problem with the Fischer-Tropsch reactor itself. A reactor placed into this dormant state can be brought back on line with relative ease in comparison with a cold start up of a reactor. A dormant reactor has a temperature in the region of 150°C, is at operating pressure in the region of 25 barg and is isolated under high purity nitrogen, which, as an inert gas, prevents any reactions from taking place within the reactor.

An emergency shut down includes substantial depressurisation of the reactor and simultaneously purging with nitrogen, or purging with nitrogen when a minimum pressure is achieved in the reactor following depressurisation.

A shut down preceding change-out of a skid commences in line with the controlled shut down, but then the reactor is dewaxed prior to being shut in under nitrogen. An example of this dewaxing would involve continuing to flow nitrogen through the reactor at a temperature of between 200 and 300°C and at an elevated pressure for a period of between 1 and 50 hours. The space velocity of the nitrogen through the reactor during dewaxing can be between 1000 and 10,000 h⁻¹. Once the dewaxing process is complete the temperature and pressure are further reduced to ambient levels and the skid is isolated and removed from the plant and moved to the refurbishment facility for regeneration of the catalyst.
The steps undertaken, as set out above, are a balance between minimising downtime during change out of a reactor whilst not increasing the cost of the plant unnecessarily by duplicating equipment and utilities. In order to minimise downtime during change out of a reactor, the reactor may be taken to a laydown or storage area within the plant. This area includes a concrete slab optionally with a roof and provides an intermediate location for the reactor between the active location in the plant and a refurbishment facility which may be at a further distinct location within the plant or at a remote location. Once placed in the laydown or storage area, a reactor may be inspected and optionally cleaned prior to transfer to the refurbishment facility.

There are four or more steps to shutting down a reactor and the order in which they are achieved and the extent of the overlap between them depends on the circumstances under which the reactor is being shut down. The steps are ramp-down of temperature, depressurisation, nitrogen purge and isolation. An additional purge using hydrogen may also be included under certain circumstances.

Ramp down of temperature refers to the reduction in temperature of the reactor from normal operating temperature in excess of 200°C down to a temperature where the Fischer-Tropsch reaction has ceased. This may be 180°C or lower. Once the temperature has been reduced the reactor is considered to be safe as the Fischer-Tropsch reaction will have ceased. The temperature can be further reduced to for example 150°C to place the reactor into a dormant condition. The rate of reduction in temperature is between 0.5°C and 5°C per minute, more preferably between 1°C and 2°C per minute.

Depressurisation of the reactor involves a reduction in the pressure of the reactor from a normal operating pressure of in the region of 15 barg to 35 barg, for example 25 barg, to a pressure in the region of 5 barg to 10 barg. The depressurisation of the reactor may be achieved more quickly than the reduction in temperature although temperature drop is preferred because overly rapid pressure drop can cause damage, possibly even fragmentation, of the catalyst.

The hydrogen purge involves purging with hydrogen at a temperature between 200°C and 270°C, more preferably between 240°C and 250°C, and normal operating pressures at a space velocity (SV) of between 1000 hr⁻¹ and 15000 hr⁻¹, more preferably between 3000 hr⁻¹ and 7000 hr⁻¹ over a period of 10-100 hours, more preferably 30-70 hours although the space velocity can be reduced in order to reduce the gas inventory required.

The nitrogen purge involves the replacement of the syngas feed with high purity nitrogen for a brief period, in the region of a few tens of seconds to a few minutes. This stops any reactions taking place as nitrogen is inert. It also removes any residual reactants from the reactor.

The isolation of the reactor refers to the physical isolation of the reactor from the remainder of the plant by closing the valves that otherwise provide fluid communication.
between the reactor and the plant of which the reactor forms a part. Before being isolated, the reactor would be filled with an inert gas such as hydrogen. Once the reactor has been isolated, it can be removed to the laydown or storage area and a replacement reactor can be installed and started up.

A controlled shut down including a hydrogen purge commences with the hydrogen purge and the reactor is then cooled to a temperature in the range 100°C to 150°C, for example 120°C under hydrogen. The reactor is then depressurised to a pressure of between 1 and 10 barg, for example 5 barg and purged under nitrogen for a time between a few minutes up to several hours after which the temperature is ramped right down to room temperature, and the catalyst may then be passivated by introducing some air into the nitrogen purge gas in order to passivate the catalyst.

Under a controlled shut down without a hydrogen purge, the temperature is ramped down initially and once the temperature reaches a predetermined threshold level, the pressure is also reduced. The threshold level is a temperature where the Fischer Tropsch reaction ceases to occur, for example this can be 180°C or below. Once the pressure reaches 5-10 barg the reactor can be subject to a nitrogen purge for between 1 and 100 hours and then the reactor is isolated.

Alternatively, the pressure may be reduced first and then nitrogen purge may commence whilst the temperature is still in excess of 200°C in order to optimise the removal of volatile hydrocarbons.

In the case of an emergency shut down, the time taken to reduce the temperature is prohibitive and therefore the reactor is first depressurised and then subject to a nitrogen purge and isolation. The temperature will start to ramp down as the reactor is depressurised, but this is a much more time consuming operation and it will continue throughout the depressurisation, nitrogen purge and isolation.

**Purge gases**

The hydrogen purge is a resource-intensive activity because hydrogen is a comparatively scarce resource. The nitrogen that is required may be obtained initially from the air separation unit (ASU) that is associated with the syngas generation part of the plant, where this is fulfilled by an autothermal reforming reactor (ATR). If the purge is prior to a scheduled shut in for reactor change out due to the catalyst being spent, then lower purity nitrogen may be used from the ASU as the purity of the nitrogen is not critical. In contrast, if the purge is during any scheduled shut down or emergency stop where catalyst change-out is not intended then high purity nitrogen from the ASU will be required. In this context, high purity nitrogen has no more than 10 ppm oxygen.

Once the Fischer-Tropsch reactor has been shut down and isolated, and optionally the catalyst passivated, the reactor can be removed to a refurbishment facility. Once the reactor is located within the refurbishment facility, the piping,
instrumentation and insulation is removed and the reactors are removed from their skids.

Catalyst regeneration

In contrast to a slurry reactor, where the catalyst is mobile in use, it is not possible to continuously renew the catalyst in a fixed bed reactor. Therefore, once the quality of the catalyst has degraded past a predetermined threshold level, the catalyst will need to be regenerated. Regeneration of the catalyst may take place whilst the reactor remains online, by providing a pure hydrogen stream, hydrogen diluted with nitrogen, or a high syngas ratio in order to reduce any cobalt that has become oxidised and to methanate any carbon that has been deposited and thus regenerate the catalyst.

Alternatively, the reactor may be purged and filled with nitrogen and then removed from its position within the production plant and moved to the refurbishment facility where the catalyst may be regenerated within the reactor. The first step of the regeneration process is the de-waxing of the catalyst. This can be carried out in the presence of inert gases such as nitrogen with the temperature ramped up to between 200°C and 400°C. The next step of the regeneration process is oxidation to remove carbon that has been deposited on the catalyst. It also converts some of the cobalt to cobalt oxide. This oxidation is achieved by adding either air or steam to the nitrogen with the additional component being carefully managed to avoid a potentially damaging exotherm. The temperature should not exceed 400°C. The final stage of the regeneration is the reduction of the catalyst to convert the cobalt oxide formed during the oxidation step into more active cobalt metal. This reduction step may take place under pure hydrogen at a pressure of 5 barg. The maximum temperature is between 200 and 450°C.

If the catalyst cannot be regenerated whilst remaining within the reactor, then it must be removed and replaced. Provided the catalyst is not irrecoverably damaged, it could be regenerated outside of a reactor, either at a remote location or within the refurbishment facility.

Catalyst removal

If the catalyst has to be removed from the reactor then, providing the catalyst is not waxed, a strong vacuum should be sufficient to suck the catalyst out of the reactor channels.

De-waxing

A de-waxing procedure will be undertaken if there is any indication that at least some of the catalyst is waxed. The de-waxing procedure involves the removal of waxy material to enable the catalyst to move comparatively easily under gravity or in response to a vacuum. De-waxing takes place in the region of 200-400°C for a number of hours. The de-waxing can take place in the presence of inert gases such as nitrogen,
or in the presence of air or diluted air or in a reducing atmosphere, for example, in the presence of hydrogen.

Following the de-waxing procedure, the reactor is purged with nitrogen before opening the reactor.

Passivation

In order to eliminate pyrophoric hazards, the catalyst is passivated for removal and transit. Passivation relates to the re-oxidisation of the cobalt catalyst and results in a catalyst that is more stable for handling and removal. It is achieved by the gradual introduction of air into the nitrogen purge gas in order to oxidise the catalyst. Oxidation is exothermic and heat generated is drawn out of the reactor by the provision of cold water or cold oxidation gases through the coolant side of the reactor. The rate of oxidation is indirectly measureable through measuring the change in concentration of oxygen across the reactor. Passivation can be provided within the refurbishment facility so that oxidants are not introduced into the hydrocarbon production facility as these are hazardous substances that would require considerable safeguarding procedures to mitigate the risk of introducing them into the hydrocarbon production facility.

Once the reactor has been purged and the catalyst passivated, the reactor is opened by removing the catalyst retainers. Some of the particulate catalyst will fall out under gravity. Alternatively, the catalyst can be removed from the top of the reactor with the use of a vacuum.

For the proportion of the catalyst that does not easily fall out of the reactor following the de-waxing a number of different procedures can be used to release the trapped catalyst. These options are jetting, ultrasonic bath, chemical clean, drilling, and thermal cycling; and will now be briefly discussed.

Jetting

The blocked channels can be subjected to jetting using a high pressure spray of hot water. The water will be introduced at a temperature in the region of 80°C to 200°C and a pressure of around 100 to 140 bar. The water is introduced into the reactor using a special nozzle which covers a small number of channels. The reactor angle also contributes to the effectiveness of the treatment. Although only some of the channels may contain trapped catalyst, the nozzle introduces the water into a number of surrounding channels in order to ensure that the pressure difference between adjacent channels is not so high as to cause damage to the reactor.

In reactors where the reaction channels are configured to allow flow through directly, i.e. without a turn in the channel or manifold, the jetting can be applied to either end of the reactor thus minimising the distance travelled by the water before coming into contact with the trapped catalyst.
Ultrasonic bath

The reactor, or the relevant part of the reactor, is placed in an ultrasonic bath. The bath can be filled with water; an alcohol based fluid; an acidic or alkaline fluid or a solvent. The fluid will be maintained at a temperature between 50°C and 100°C or higher, but below the boiling point of the fluid. A number of transducers are fixed integrally with the bath and are configured to produce intense cavitation of the fluid, generating a series of small shock waves that agitate the fluid and produce mechanical disruption of the blocked bed. Treatment in the ultrasonic bath may take between a couple of hours and in the region of 48 hours.

Chemical clean

Channels which remain blocked can be subjected to chemical cleaning using solvents to dissolve the wax holding the catalyst particles within the channel. The solvent must be chosen with care in order to avoid damage to the reactor channel walls.

Drilling

If the catalyst remains trapped then it can be drilled out one channel at a time. This is only time efficient in circumstances where there are a small number of channels blocked.

Thermal cycling using heat exchanger

The coolant side of the reactor can be used in order to provide thermal cycling. This may consist of providing hot water on the coolant side so that the metal expands and the warm metal melts the wax. The process may then be completed by the introduction of liquid nitrogen or liquid carbon dioxide b cause the metal from which the process channels are formed to contract and release the trapped catalyst.

The above mentioned procedures can be prioritised according to the proportion of channels that are blocked and the time constraints on the catalyst removal process. The spent catalyst can then be regenerated or the cobalt may be reclaimed if the catalyst has reached the end of its useful life. The regeneration of the catalyst may take place within the reactor refurbishment facility or the catalyst may be transported to a location remote from the production plant in order to undergo regeneration.
CLAIMS

1. A plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the plant comprises:
   at least one syngas generation module,
   at least one Fischer-Tropsch synthesis module, and
   an ammonia removal bed positioned between the syngas generation module and the Fischer Tropsch module and configured to reduce the level of ammonia in the syngas.

2. The plant according to claim 1, wherein the ammonia removal bed is configured to reduce the level of ammonia in the syngas to below 100 ppb.

3. The plant according to claim 1 or claim 2, further comprising a bed configured to reduce cyanide levels in the syngas.

4. The plant according to any one of claims 1 to 3, wherein the Fischer-Tropsch module comprises at least one Fischer-Tropsch reactor including flow channels or tubes that have one dimension that is less than 20 mm.

5. A plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the plant comprises:
   a syngas generation module and
   a Fischer-Tropsch synthesis module and
   wherein the syngas generation module is an autothermai reforming module provided with an associated air separation unit and
   wherein waste nitrogen from the air separation unit is used to purge or inert the Fischer-Tropsch synthesis reactor.

6. The plant according to claim 5, wherein the nitrogen is provided to the Fischer-Tropsch module directly from the air separation unit.

7. The plant according to claim 5 or claim 6, wherein the Fischer-Tropsch module comprises at least one Fischer-Tropsch reactor including flow channels or tubes that have one dimension that is less than 20 mm.

8. The plant according to any one of claims 5 to 7 also comprising an ammonia removal bed positioned between the syngas generation module and the Fischer Tropsch module and configured to reduce the level of ammonia in the syngas.

9. A plant for processing a methane-containing feed gas to form heavier hydrocarbons, wherein the plant comprises:
   at least one syngas generation module;
   at least one Fischer-Tropsch synthesis module; and
   a refurbishment facility configured to provide one or more of the following: catalyst activation, reactor refurbishment and catalyst regeneration;
   wherein the refurbishment facility is integrated within the plant; and
wherein the refurbishment facility can run at the same time as the syngas generation module and the Fischer-Tropsch module.

10. The plant according to claim 9, wherein hydrogen for catalyst activation within the refurbishment facility is obtained from tail gas from the Fischer-Tropsch synthesis module.

11. The plant according to claim 9, wherein hydrogen for catalyst activation with the refurbishment facility is obtained from syngas from the syngas generation module.

12. The plant according to any one of claims 9 to 11, wherein the refurbishment facility further comprises an ultrasonic bath configured to aid the removal of catalyst from at least a part of either a syngas generation module or a Fischer-Tropsch synthesis module.

13. A method of filling a reactor with catalyst comprising the steps of:
   pouring catalyst into more than one channel simultaneously;
   vibrating the reactor in order to compact the catalyst;
wherein vibration is commenced before the pouring is complete.

14. The method according to claim 13, wherein the vibration and pouring occur simultaneously.

15. The method according to claim 13, wherein the vibration and pouring occur sequentially.

16. A reactor comprising a plurality of coterminous, substantially parallel reaction channels;
a particulate catalyst provided in one or more of the reaction channels;
a retainer configured to retain the particulate catalyst within the reaction channels.

17. The reactor according to claim 16, wherein an end surface of the reaction channels is configured to provide a flat surface for engagement with the retainer.

18. The reactor according to claim 16, wherein the retainer is flexible to conform to an end surface of the reaction channels.
Fig. 2
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G2/00 C01B3/38 B01J8/06 B01J19/24

ADD.

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)

CIOG C01B B01J

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubt on priority claim(s) one or more of which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search: 20 June 2016

Date of mailing of the international search report: 26/08/2016

Name and mailing address of the ISA:

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Vaz, Miguel
INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-12

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.
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This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12

A plant for processing a methane-containing feed gas to form heavier hydrocarbons

2. claims: 13-18

A reactor and a method of filling a reactor comprising a catalyst provided inside reaction channels