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(54) Title: PROCESS FOR REFORMING HYDROCARBONS

(57) Abstract: The invention relates to the production of synthesis gas by means of particularly a series arrangement of heat exchange reforming and autothermal reforming stages, in which the heat required for the reforming reactions in the heat exchange reforming stage,is provided by hot effluent synthesis gas from the autothermal reforming stage. More particularly, the invention relates to optimisation of the operation and control of an arrangement of heat exchange reforming and autothermal reforming stages and introduction of an additional waste heat boiler.

Title: Process for Reforming Hydrocarbons

The present invention relates to a process and plant for production of gas rich in hydrogen and carbon monoxide, particularly synthesis gas for the production of ammonia, methanol, dimethyl ether (DME), hydrogen and hydrocarbons by Fischer-Tropsch (FT) synthesis. The invention relates further to the production of synthesis gas by means of particularly a series arrangement of heat exchange reforming and autothermal reforming stages, in which the heat required for the reforming reactions in the heat exchange reforming stage is provided by hot effluent synthesis gas from the autothermal reforming stage. More particularly, the invention relates to optimisation of the operation and control of an arrangement, particularly a series arrangement, of heat exchange reforming and autothermal reforming stages and introduction of an additional waste heat boiler.

The use of a product stream of reformed gas as a source of heat in heat exchange reforming is known in the art. Thus, EP-A-0033128 and EP-A-0334540 deal with parallel arrangements, in which a hydrocarbon feed is introduced in parallel to a tubular reformer and heat exchange reformer. The partially reformed gas from the tubular reformer is then used as heat source for the reforming reactions in the heat exchange reformer.

Other parallel arrangements combine heat exchange reforming and autothermal reforming. EP-A-0983963, EP-A-1106570 and EP-A-0504471 deal with processes in which a

hydrocarbon feed is introduced in parallel to a heat exchange reformer and autothermal reformer. The hot product synthesis gas from the autothermal reformer is used as heat exchanging medium for the reforming reactions occurring in the heat exchange reformer. In particular, Fig. 1 of EP-A-1106570 discloses an embodiment in which the hot product synthesis gas from the autothermal reformer is used as heat exchanging medium for the reforming reactions occurring in parallel arranged heat exchange reformers. There is no disclosure of a heat exchanger such as a waste heat boiler or steam superheater arranged in parallel with a heat exchange reformer.

EP-A-0440258 discloses a process in which the hydrocarbon feed is first passed through a first heat exchange reformer to provide a partially reformed stream. The partially reformed stream is then introduced in parallel to a tubular reformer and second heat exchange reformer. The product streams from both reformers are combined and introduced to an autothermal reformer. The product gas from the autothermal reformer is used as heat source in the second heat exchange reformer, while the product gas from said second heat exchange reformer is used as heat source in the first heat exchange reformer.

Series arrangements are also known in the art. US Patent No. 4,824,658 and US Patent No.6,296,679 (Fig. 2 in both references) disclose a process in which the entire hydrocarbon feed is first introduced to a heat exchange reformer, then passed to a tubular reformer and finally to an autothermal reformer. The product gas from the

autothermal reformer is used as heat source in the heat exchange reformer.

US 4,376,717 and our US 2009/0184293 disclose a process in which a hydrocarbon feed is first passed through a tubular reformer; the partially reformed gas is then subjected to heat exchange reforming and finally autothermal reforming. The product gas from the latter is used as heat source in the heat exchange reforming.

Our patent DK 148882 discloses a process for production of synthesis gas, in which the hydrocarbon feed is passed through a heat exchange reforming and autothermal reformer, and where the product gas from the latter is used as heat source in the heat exchange reformer.

WO-A-03/051771, US 6,296,679 and WO-A-00/09441 disclose also a series arrangement. In particular, WO-A-00/09441 discloses a heat exchange reformer arranged in series with an autothermal reformer where the hot effluent gas (synthesis gas) from the autothermal reformer is used as heat exchanging medium to drive the reforming reactions of the heat exchange reformer. The thus cooled synthesis gas is then passed through a heat exchanger such as steam raising boiler (waste heat boiler). There is no disclosure of a heat exchanger such as a waste heat boiler or steam superheater arranged in parallel with the heat exchange reformer.

The use of heat exchange reformers in the production of synthetic fuels by the Fischer-Tropsch synthesis has significant benefits. Potential benefits compared to other technologies include reduced oxygen consumption,

lower capital cost per unit of product, and a higher carbon and energy efficiency. In plants for production of chemicals such as methanol, the use of heat exchange reformers has similar advantages.

In our co-pending patent application PCT/EP2011/006179 (WO-A-2012/084135) we disclose a process in which a hydrocarbon feed is passed through a heat exchange reformer and an autothermal reformer and where the product flow from the latter is used as heat source in the heat exchange reformer. Tail gas from the FT-synthesis is added after the heat exchange reformer and before the autothermal reformer. The addition of tail gas is adjusted to give the desired stoichiometric ratio of H_2/CO equal to about 2 in the effluent stream from the autothermal reformer. Steam is added downstream the autothermal reformer to reduce the aggressiviness of the gas passed to the heat exchange reformer with respect to metal dusting.

A specific embodiment also disclosed in PCT/EP2011/006179 (WO-A-2012/084135) is where part of the hydrocarbon feedstock bypasses the heat exchange reformer and is directed directly to the autothermal reformer. This reduces the efficiency of the total plant and increases the oxygen consumption compared to the embodiment without bypass.

It is generally preferred to direct all the product flow from the autothermal reformer to the heat exchange reformer. If only part of the flow is used as heating medium, the size of the heat exchange reformer must be

increased to compensate for a lower driving force (lower temperature difference) for heat transfer.

Heat exchange reformers may also be coupled in a similar manner with other partial oxidation reactors. In addition to autothermal reforming (ATR), such reactors include non-catalytic partial oxidation (POX) such as gasifiers, and catalytic partial oxidation (CPO), although autothermal reforming (ATR) is preferred. ATR and CPO are provided with a fixed bed of catalyst. As used herein the term autothermal reforming (ATR) encompasses also secondary reforming.

However, for many processes such as those mentioned above, especially for large scale plants comprising a heat exchange reformer and an autothermal reformer, it may be preferred to operate with a low steam-to-carbon ratio. This is for example the case when the produced synthesis gas is to be used for subsequent hydrocarbon synthesis via the Fischer-Tropsch (FT) synthesis. Operation at high steam-to-carbon ratios means higher flow rates due to the increased amount of steam in the feed. In other words, operating at high steam-to-carbon ratios means that the capital cost due to the use of larger equipment may be prohibitively large, especially for large scale plants. Furthermore, high steam-to-carbon ratio means that a larger amount of carbon dioxide is formed in the process. This is in many cases a disadvantage such as for example in plants for the production of synthetic fuels by the low temperature Fischer-Tropsch synthesis. In the low temperature

Fischer-Tropsch synthesis carbon dioxide is considered an inert and not a reactant.

Yet, operating at low steam-to-carbon ratios in plants comprising a heat exchange reformer creates also a number of challenges. One such challenge is the risk of carbon formation on the catalyst in the heat exchange reformer:

$$CH_4 \rightarrow C + 2H_2 \qquad (1)$$

Carbon on the catalyst may also be formed from higher hydrocarbons (hydrocarbons with two or more carbon atoms in the molecule) or from carbon monoxide according to similar reactions as described in the literature.

The formed carbon may lead to catalyst deactivation and/or catalyst disintegration and build-up of pressure drop. This is undesired.

The risk of carbon formation is linked to the catalyst temperature and the steam-to-carbon ratio. For a given feed gas composition and pressure, the steam-to-carbon ratio in the feed gas must be raised if the catalyst temperature is increased. As a higher steam-to-carbon ratio may be uneconomical as described above, it is important to be able to control the temperature in the catalyst of the heat exchange reformer to avoid addition of excessive steam. The temperature control thereby enables operation closer to the carbon limit without exceeding it. In most cases the catalyst temperature reaches its maximum at the outlet of the heat exchange reformer.

Another challenge for the use of heat exchange reformers is metal dusting corrosion. In many cases especially at low steam-to-carbon ratios the prevention or minimisation of metal dusting requires the use of high alloy and/or special materials in the reactor itself. Such alloys are generally expensive and it is therefore generally desired to minimise the size and the heat transfer surface of the heat exchange reformer reactor itself.

In the aforementioned processes comprising a heat exchange reformer upstream and in series with an autothermal reformer, the simultaneous control of the catalyst exit temperature from the heat exchange reformer and the synthesis gas production and quality (e.g obtaining the desired H_2/CO-ratio of about 2 for production of synthesis gas for the FT-synthesis) is not straightforward. This is particularly the case when it is considered that the synthesis gas production unit is required to operate under different conditions such as part load and with different natural gas feed and tail gas compositions. Furthermore, the plant production should remain unaffected even in the case of progressive fouling of the heat exchange reformer itself. Fouling is known to the industry and in the art and has in this case the consequence that the heat transferred from the effluent of the autothermal reformer to the catalyst side of the heat exchange reformer is reduced.

In several of the processes described above, the hydrocarbon feed is passed through a heat exchange reformer and then an autothermal reformer and the product

flow from the latter is used as heat source in the heat exchange reformer.

Fouling is known to the person skilled in the art as unwanted material accumulating on the surface of the heat exchanging equipment. This material creates extra resistance to the heat exchange. In a heat exchange reformer the consequence will be that the heat transferred from the effluent of the autothermal reformer to the catalyst side of the heat exchange reformer is reduced.

In the initial period of operation, fouling is generally very low. However, over time, fouling of the heat exchange reformer surface may take place reducing the heat transferred from the autothermal reformer effluent stream to the catalyst side of the heat exchange reformer. This means that the exit temperature from the catalyst side of the heat exchange reformer will drop if no countermeasures are taken. The autothermal reformer exit temperature will as a consequence of the lower heat exchange reformer exit temperature also decrease, which again will lead to an additional drop in the heat exchange reformer outlet temperature and so forth. This feed and effluent relationship between the autothermal reformer and heat exchange reformer means that the effect of fouling is amplified, thus a small decrease in the heat exchange reformer ability to transfer heat may lead to a large decrease in heat exchange reformer exit temperature.

This will in turn lead to reduced plant efficiency and/or reduced production, and/or increased oxygen consumption per unit of synthesis gas produced.

In order to maintain conversion of the hydrocarbon feedstock and maintain production, various countermeasures may be considered. The first is to preheat the feedstock to the heat exchange reformer to a higher temperature. However, this requires import of additional fuel and reduces the overall plant energy efficiency. Another alternative is to accept the lower exit temperature (and thereby the lower conversion of the hydrocarbon feedstock) from the heat exchange reformer and increase the conversion in the autothermal reformer. However, this requires additional oxygen and thereby increases the capital cost associated with the expensive air separation unit (ASU) used to produce the oxygen. In addition, the plant efficiency will normally drop.

An alternative would be to design the size of the heat exchange reformer to take into account the reduction of the heat transfer due to fouling. However, in this case the temperature at the outlet of the heat exchange reformer on the catalyst side during the initial period of operation (before any significant fouling has occurred) could become too high thus increasing the risk of carbon formation on the catalyst.

As described above in one embodiment of the aforementioned patent application PCT/EP2011/006179 (WO-A-2012/084135), part of the hydrocarbon feedstock bypasses the heat exchange reformer and is directed to

the autothermal reformer. In such an embodiment, the fraction of the hydrocarbon feedstock bypassing the heat exchange reformer can be used to control the temperature out of the heat exchange reformer. The heat exchange reformer may for example be designed for a specific bypass during start of operation (before fouling has taken place). As fouling occurs the fraction of the flow bypassing the heat exchange reformer can be increased to maintain the catalyst outlet temperature from the heat exchange reformer. Production can be maintained by increasing the hydrocarbon feedstock flow. However, the plant efficiency will also drop in this case.

It is thus the objective of the present invention to provide a process for production of synthesis gas comprising a heat exchange reformer and an autothermal reformer where the exit temperature from the heat exchange reformer and the synthesis gas production can be maintained during operation with no or very limited loss of efficiency and with no or a very limited increase in the oxygen consumption.

This and other objectives are solved by the present invention.

The preferred layout of a plant for production of synthesis gas is a heat exchange reformer upstream and in series with an autothermal reformer, as per Figures 1-5.

According to the present invention, a process for the production of synthesis gas from a hydrocarbon feedstock is provided. The method comprises the first step of:

a. reforming at least a portion of said hydrocarbon feedstock in an endothermic reforming stage in a heat exchange reformer and withdrawing from the heat exchange reformer an effluent stream of primary reformed gas.

By the term "hydrocarbon feedstock" is meant a stream fed to the process which comprises hydrocarbons. In the broadest sense, hydrocarbons are organic compounds comprising hydrogen and carbon. The hydrocarbons may be as simple as e.g. methane CH_4, and may comprise more complex molecules. In addition to the hydrocarbons, the hydrocarbon feedstock may comprise water and/or CO_2. The process according to the invention may optionally comprise an additional step of adding water and/or CO_2 to a hydrocarbons to provide the hydrocarbon feedstock, prior to the reforming step (step a.).

The term "at least a portion" may comprise the entire hydrocarbon feedstock, or simply a portion thereof.

By "indirect heat exchange" is meant that there is no direct contact between the catalyst and the heating medium, and thereby between the flow passing through the catalyst and the heating medium, because these are separated by a metal wall, i.e. the wall of the tube containing the catalyst.

The hydrocarbons (for example desulphurised natural gas) are mixed with steam and/or carbon dioxide and the resultant hydrocarbon feedstock is directed to the catalyst side of the heat exchange reformer. In the heat

exchange reformer, the gas is then steam reformed according to the following reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

Reactions similar to reaction (2) may take place for any higher hydrocarbon present in the feedstock. "Higher hydrocarbons" are hydrocarbons with 2 or more carbon atoms in the molecule (e.g. ethane, propane etc). The gas leaving the heat exchange reformer is close to chemical equilibrium for reactions (2) and (3) above. Typically, the exit temperature is 600-850°C, preferably 675-775°C and more preferably 700-750°C.

Step (b) of the process of the invention involves

b. passing the primary reformed gas from the heat exchange reformer through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and withdrawing a stream of hot effluent synthesis gas

Autothermal reforming is described widely in the art and open literature. Typically, the autothermal reforming reactor comprises a burner, a combustion chamber, and catalyst arranged in a fixed bed all of which are contained in a refractory lined pressure shell. Autothermal reforming is for example described in Chapter 4 in "Studies in Surface Science and Catalysis", Vol. 152 (2004) edited by Andre Steynberg and Mark Dry.As used herein the term autothermal reforming (ATR) encompasses

also secondary reforming. Secondary reforming is reforming conducted in a reformer under the addition of air or oxygen and in which the reformer is fed by primary reformed gas, i.e. reactors using as hydrocarbon feed reformed gas from a primary reformer such as a steam methane reformer (SMR) or heat exchange reformer.

It would be understood by the skilled person that ATR and POx imply the use of a burner at the top of the reactor. ATR and CPO use a catalyst bed below the combustion zone. CPO means a catalytic reactor or catalytic gasifier which does not always require the use of a burner, but a mixer instead. Further, in a POx (gasifier) there is no use of catalyst.

The partially reformed gas leaving the heat exchange reformer is thus passed to the autothermal reformer. In the autothermal reformer, oxidant gas such as a gas containing at least 90 vol% oxygen and in some cases steam is added. Synthesis gas ("syngas") is formed by a combination of steam reforming and partial oxidation in the autothermal reformer.

By the term "oxidant gas" is meant a stream comprising oxygen, preferably more than 75 vol%, and more preferably more than 85 vol% oxygen. Examples of oxidant gas are air, oxygen, mixture of oxygen and steam, and oxygen enriched air.

The gas leaving the ATR is free of oxygen and generally reactions (2) and (3) above are close to chemical equilibrium. The temperature of this hot effluent

synthesis gas from the ATR is between 950 and 1100°C, typically between 1000 and 1075°C.

The hot effluent synthesis gas leaving the autothermal reformer, or CPO, or POx, comprises carbon monoxide, hydrogen, carbon dioxide, steam, residual methane, and various other components including nitrogen and argon.

The hot effluent synthesis gas from step (b) is then split into at least a first and a second synthesis gas stream, wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (a). Accordingly, the first synthesis gas stream is passed to the non-catalytic side (hereinafter also called "shell side") of the heat exchange reformer. This first synthesis gas stream is cooled by supplying heat to the catalytic side of the heat exchange reformer by indirect heat exchange to produce a cooled first synthesis gas stream. The exit temperature from the shell side of the heat exchange reformer would typically be in the range from 450-800°C.

The second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream. Preferably, said second heat exchanger is a Waste Heat Boiler (WHB) for the production of steam. Accordingly, the second heat exchanger is a heat exchanger in which at least a portion, preferably a major portion, particularly 50% or more such as 90% or most preferably 100% of this second synthesis gas stream is used to heat a stream for which no reforming reactions take place. Preferably the

second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange with a stream for which no reforming reactions take place. Preferably said stream is a stream different from said hydrocarbon feedstock, such as a boiling feed water stream to raise steam. Preferably said second heat exchanger is a waste heat boiler or steam superheater. Additional such heat exchangers may be arranged in parallel or in series with said second heat exchanger.

Preferably, after leaving the heat exchange reformer, the first cooled synthesis gas stream is further cooled in a third heat exchanger to produce a further cooled first synthesis gas stream. Preferably, the third heat exchanger is a Waste Heat Boiler (WHB) for production of steam.

The further cooled first synthesis gas stream may be mixed together with the cooled second synthesis gas stream from the second heat exchanger to provide a raw synthesis gas product stream, as shown in Figures 2-5.

This raw synthesis gas product stream obtained from combining the cooled second synthesis gas stream and the further cooled first synthesis gas stream may be further cooled in one or several additional heat exchangers. This cooling may bring the synthesis gas stream below the dew point temperature. Some or all of the water may thus be removed by condensation to produce a final synthesis gas stream which is directed to the synthesis section of the plant, e.g. Fischer-Tropsch synthesis section.

Alternatively, the first and second synthesis gas streams may be used separately.

In cases where the synthesis gas is required for a Fischer-Tropsch synthesis unit, a tail gas from the Fischer-Tropsch synthesis unit may be added either upstream or downstream the catalytic side of the heat exchange reformer. Preferably, the tail gas is added upstream the autothermal reforming reactor and downstream the catalytic side of the heat exchange reforming reactor, i.e. the tail gas is added to the primary reformed gas (see Figure 4). The tail gas contains carbon monoxide, carbon dioxide, hydrogen, various hydrocarbons including olefins and paraffins and a range of other components.

The bypass ratio (defined as the ratio of the flow of second synthesis gas stream to the total flow of the hot effluent synthesis gas from the autothermal reformer) is typically between 1% and 30%, or between 1 and 35%, preferably between 1% and 20%, such as 4 or 16%, most preferably between 1% and 12%.

A plant would typically be designed for a given bypass ratio at the start of operation, for instance 12%. As operation proceeds, the exterior surface of the heat exchange reformer tubes may become fouled leading to a lower amount of heat transferred. The actual bypass ratio when the plant is in operation will then be adjusted to reach certain objectives such as a target catalyst exit temperature from the heat exchange reformer. The reduction of the bypass ratio from for instance 12% to

for instance 1% will increase the difference between the temperature of the stream on the shell side and the temperature on the catalyst side of the heat exchange reformer. The higher temperature difference will increase the heat transferred thus compensating for the effect of fouling. Accordingly in one embodiment of the invention, - as the process proceeds - the bypass ratio is reduced with time.

Should the input of hydrocarbon feedstock be reduced, the flow through the heat exchange reformer and autothermal reformer are also reduced. In such a part load situation the heat exchanger reformer may be too big, which in turn can lead to an undesirable increase in the temperature at the catalyst outlet of the heat exchange reformer. In this case, the bypass ratio may be increased during this "low load" operation period to reduce the heat transferred and thereby decreasing the catalyst exit temperature. Such a case is for example a start-up situation of a downstream synthesis section such as a Fischer-Tropsch synthesis unit as it is described further below in which operation for example takes place with a reduced amount of hydrocarbon feedstock, i.e. reduced load, for instance about 50% of the natural gas feed rate.

The adjustment of the bypass ratio can conveniently be done by appropriate valves located downstream the shell side of the heat exchange reformer (preferably downstream the third heat exchanger) and also downstream the second heat exchanger used to cool the second synthesis gas stream.

An optional third step of the process involves:

c. adding a stream comprising steam to either said hot effluent synthesis gas from step (b) or to said first synthesis gas stream.

The addition of steam reduces the thermodynamic potential for metal dusting corrosion. Preferably, the stream comprising steam consists of more than 99% of steam. For reasons of economy, the steam is preferably added to the first synthesis gas stream. Further details can be gained from co-pending application PCT/EP2011/006179 (WO-A-2012/084135).

In one aspect of the invention a small amount of the hydrocarbon feedstock bypasses the heat exchange reformer and is directed to the autothermal reformer. This small amount is in this embodiment less than 25%, preferably less than 10% and most preferably less than 5%.

In another preferred aspect of the invention, the hydrocarbon feedstock is subjected to a step of pre-reforming, preferably adiabatic prereforming before being directed to the heat exchange reformer. In the adiabatic prereformer most or all of the higher hydrocarbons (hydrocarbon compounds with 2 or more carbon atoms) are converted according to the following reactions:

$$C_nH_m + nH_2O \rightarrow (½m+n)H_2 + nCO \qquad (4)$$

$$3H_2 + CO \leftrightarrow CH_4 + H_2O \qquad (5)$$

$CO + H_2O \leftrightarrow H_2 + CO_2$ (6)

Reactions (5) and (6) are normally close to equilibrium at the outlet of the prereformer.

In another aspect, the process and plant of the invention are also particularly useful during operation of the plant without recycle of tail gas from the Fischer-Tropsch synthesis section or during start-up of the Fischer-Tropsch synthesis section in a plant for producing hydrocarbons. In this situation no tail gas is available for recycling from the Fischer-Tropsch section as this section is not yet in operation. In a plant based on heat exchange reforming followed by autothermal reforming in series the H_2/CO-ratio which can be generated without recycle of tail gas may not be low enough to allow the start-up or operation of the Fischer-Tropsch section.

In order to obtain an H_2/CO-ratio as low as possible, preferably H_2/CO molar ratio of 2.5 or below, such as 2.4 or 2.3 or 2.2 or 2.1 or 2.0, and as required by the Fischer-Tropsch synthesis section, recycle of part or all of the synthesis gas produced by cooling of the hot effluent gas from the autothermal reforming may be carried out. Typically, this recycle is done after most of the water has been removed by condensation as described earlier.

Recycle of the synthesis gas from the ATR during start-up of a downstream synthesis section such as a Fischer-Tropsch unit will often be done to a point downstream the

catalytic side of the heat exchange reformer and upstream the ATR. This means that as the recycle increases (to bring down the H_2/CO-ratio), the flow to the shell side of the heat exchange reformer also increases. This occurs without a similar increase in the flow to the catalytic side of the heat exchange reformer. In such a situation, the heat exchanger reformer catalyst outlet temperature may become undesirably high, as more flow is added to the shell side, but not to the tube side of the heat exchange reformer, thereby increasing the heat input to the tube side (catalytic side). This may result in carbon formation on the catalyst in the heat exchange reformer as described above. By splitting the hot effluent synthesis gas from the ATR into first and second synthesis gas streams, as per the present invention, gas flow can be diverted from the shell-side of the heat exchange reformer (first synthesis gas stream) to the second synthesis gas stream. This allows a corresponding reduction in the heat input at the shell-side of the heat exchange reformer and will also reduce the H_2/CO-ratio (H_2/CO molar ratio) of the gas leaving the autothermal reformer. This is an advantage for start-up of the Fischer-Tropsch section.

Accordingly, the invention encompasses also a process for starting up the hydrocarbon synthesis section of a gas-to-liquid process comprising:

a. reforming at least a portion of a hydrocarbon feedstock in an endothermic reforming stage in a heat exchange reformer and withdrawing from the heat exchange reformer an effluent stream of primary reformed gas;

b. passing the primary reformed gas from the heat exchange reformer through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and withdrawing a stream of hot effluent synthesis gas;

characterised in that the process further comprises the step of splitting the hot effluent synthesis gas into at least a first synthesis gas stream and a second synthesis gas stream,

wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (a);

wherein said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream;

and wherein the process comprises a further step after the first synthesis gas stream has passed through the heat exchange reformer of: cooling the first synthesis gas stream to a temperature sufficiently low for steam to condense, separating the synthesis gas from said condensate, and recycling part or all of this synthesis gas to the ATR, CPO or POx.

As described before, the second heat exchanger is a heat exchanger in which at least a portion, preferably a major portion, particularly 50% or more such as 90% or most preferably 100% of this second synthesis gas stream is used to heat a stream for which no reforming reactions take place. Preferably the second synthesis gas stream is directed to a second heat exchanger in which it is cooled

by indirect heat exchange with a stream for which no reforming reactions take place. Preferably said stream is a stream different from said hydrocarbon feedstock, such as a boiling feed water stream to raise steam. Preferably said second heat exchanger is a waste heat boiler or steam superheater. Additional such heat exchangers may be arranged in parallel or in series with said second heat exchanger.

Preferably, this process further comprises adding the second synthesis gas stream to the first synthesis gas stream after it has passed through the heat exchange reformer. Thus, the combined stream is subsequently further cooled to a temperature sufficiently low to allow steam to condense, separating the synthesis gas from the water and recycling preferably part of the synthesis gas to the ATR, CPO, or POX. The portion of the synthesis gas which is not recycled is preferably directed to the hydrocarbon synthesis section, e.g. Fischer-Tropsch synthesis.

In one embodiment of this process the bypass ratio, being the ratio of the flow of second synthesis gas stream to the flow of the effluent stream from the ATR or CPO or POx, is between 10% and 40%, preferably between 20% and 35%, more preferably 30% or 35%

In another embodiment of this process for starting up, as the process proceeds, the bypass ratio is constant with time.

In one embodiment, the hydrocarbon synthesis section is a Fischer-Tropsch synthesis section.

As the process proceeds and the amount of synthesis gas recycled to the ATR, CPO, or POX is increased, the H_2/CO molar ratio of the synthesis gas is reduced with time to a value below 2.5 or 2.4, preferably below 2.3 or 2.2, more preferably below 2.1.

The starting up process enables a significant reduction in the required synthesis gas recycle flow for obtaining the desired H_2/CO molar ratio for downstream process, such as 2.3 or below for a gas-to-liquid process such as Fischer-Tropsch synthesis. The reduced recycle translates into smaller and cheaper recycle equipment requiring less compression power. Further, despite the lower load used during start-up the invention enables obtaining a lower catalyst outlet temperature of the heat exchange reformer; hence, the starting up operation can be conducted with a larger margin to the carbon formation limit, i.e. with less risk of carbon formation.

In yet another aspect, and in the case where the synthesis gas produced is for a Fischer-Tropsch process or other downstream process in which the tail gas produced contains olefins, the tail gas is subjected to a step of hydrogenation before being directed to the autothermal reformer. In the hydrogenation step, part or all of the unsaturated hydrocarbons such as olefins are converted into paraffins according to the following reaction (given for olefins);

$C_nH_{2n} + H_2 \leftrightarrow C_nH_{2n+2}$ (for $n \geq 2$) (7)

The hydrogenation of olefins reduces the potential for i.a. carbon laydown.

The division of the hot effluent gas stream leaving the autothermal reformer appears contradictory to optimising the process from a capital cost point of view. The heat exchange reformer itself becomes larger because the flow of the stream on the shell side is reduced. This reduces the difference between the temperature on the shell side and the catalyst side of the heat exchange reformer. This means that to transfer a specified amount of heat, the heat transfer area of the heat exchange reformer must be increased. Furthermore, an additional heat exchanger (preferably a Waste Heat Boiler) is introduced, which adds further cost.

However, we have found that the disadvantages mentioned above are outweighed by the possibility to ensure that the maximum catalyst temperature out of the heat exchange reformer is not exceeded and especially by the improved possibility of maintaining the production and plant efficiency over time independently of fouling, load and different compositions of natural gas and/or tail gas.

The primary reformed gas may be mixed with tail gas from a Fischer-Tropsch synthesis stage or other downstream process for the production of hydrocarbons, such as tail gas (off-gas) from a process for the production of gasoline from methanol and dimethyl ether, as for instance disclosed in our US 4,520,216 and US 4,481,305.

The addition of such tail gas to the synthesis gas production section enables that there is sufficient carbon dioxide during the reforming to achieve the desired H_2/CO molar ratio, typically about 2.0 particularly for Fischer-Tropsch synthesis.

As used herein "tail gas" means off-gas from the Fischer-Tropsch synthesis stage for the production of diesel or downstream process for the production of gasoline which is not re-used in said stage.

A separate stream rich in CO_2, i.e. with at least 90 vol% CO_2 may be added to the primary reformed gas, or upstream the heat exchange reformer. In one aspect, therefore, the process according to the invention comprises mixing the primary reformed gas or the hydrocarbon feedstock with a gas stream comprising at least 90 vol% CO_2.

The heat exchange reformer design may be selected from any heat exchanger layout which can transfer heat from the effluent of the autothermal reformer to the process gas. This includes: shell and tube heat exchanger with segmental baffles, double segmental baffles, disc & doughnut baffles, rod baffles, single helix, double helix, expanded metal baffle or any other suitable baffle configuration including no baffles; double-tube reactor with catalyst disposed inside the double tubes, catalyst disposed outside the double tubes, and/or catalyst disposed outside and inside the double tubes.

Suitably, the process of the invention further comprises the step of converting the separated synthesis gas into

ammonia synthesis gas, methanol synthesis gas, dimethyl ether (DME) synthesis gas, synthesis gas for production of hydrocarbons by Fischer-Tropsch synthesis, or synthesis gas for the production of hydrogen, and further converting said synthesis gas into the respective product in the form of ammonia, methanol, DME, liquid hydrocarbons, or hydrogen.

In a particular embodiment of the invention, a portion of the hydrocarbon feedstock bypasses the heat exchange reformer to form a by-pass stream. Tail gas is added to this by-pass stream in case the resultant synthesis gas is to be used for the Fischer-Tropsch synthesis or downstream process for the production of gasoline as described above.

A portion of the hydrocarbon feedstock may be added as a by-pass stream to the primary reformed gas to form a combined stream before entering the ATR, CPO or POX. In a particular embodiment, tail gas is added to this by-pass stream and the thereby formed stream is combined with the primary reformed gas in case the resultant synthesis gas is to be used for the Fischer-Tropsch synthesis or downstream process for the production of gasoline as described above.

During the process, the pressure measured at the outlet of the ATR is suitably between 15-80 bar, preferably between 20-50 bar.

In the process according to the invention, the process steam-to-carbon ratio ($S/C_{process}$) is suitably in the range

0.4-3.0, preferably 0.5-1.2, more preferably 0.50-1.00. In particular, when the synthesis gas is to be used for the Fischer-Tropsch synthesis, the process steam-to-carbon ratio ($S/C_{process}$) is between 0.4 and 1.3, preferably between 0.6 and 1.1.

The process steam-to-carbon ratio, $S/C_{process}$, means the number of moles steam divided by the number of moles of hydrocarbon carbon. The number of moles of steam includes all the steam added to the hydrocarbon feedstock, e.g. natural gas, upstream the heat exchange reformer. The hydrocarbon carbon includes the hydrocarbons present in the feedstock. The $S/C_{process}$ ratio is measured upstream the heat exchange reformer, or upstream the pre-reformer (if present).

Suitably, for a Fischer-Tropsch process, the H_2/CO-molar ratio in the stream of cooled synthesis gas in the first synthesis gas stream is in the range of 1.7 to 2.3, preferably in the range 1.9 to 2.1.

In the case of methanol synthesis, the following molar ratio of components of the synthesis gas lies between 1.7 and 2.3, preferably between 1.9 and 2.1:

$$\frac{H_2 - CO_2}{CO + CO_2}$$

In a specific embodiment the process comprising using valves installed immediately downstream said heat exchangers, preferably waste boilers, for the cooling of

the first and second synthesis gas stream for control of the bypass ratio.

In a particular embodiment of the invention, two or more heat exchange reformers are operated in parallel. This may provide advantages with respect to the ease of fabrication of vessels with large diameters containing hundreds of reformer tubes and may allow fine control of the process as well as easier maintenance.

In this embodiment,

- at least a second portion of said hydrocarbon feedstock is reformed in an endothermic reforming stage in a second heat exchange reformer and second effluent stream of primary reformed gas is withdrawn from said second heat exchange reformer;
- said second effluent stream of primary reformed gas is combined with the effluent stream of primary reformed gas obtained from the reforming the first portion of said hydrocarbon feedstock;
- the combined primary reformed gases from the heat exchange reformers are passed through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and a stream of hot effluent synthesis gas is withdrawn;
- the hot effluent synthesis gas from the autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), is split into at least a first synthesis gas stream, a second synthesis gas stream and a third synthesis gas stream,

As before, the first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (a); and said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream. In addition, the third synthesis gas stream is used as heating medium in indirect heat exchange in the second heat exchange reformer.

Also as described before, the second heat exchanger is a heat exchanger in which at least a portion, preferably a major portion, particularly 50% or more such as 90% or most preferably 100% of this second synthesis gas stream is used to heat a stream for which no reforming reactions take place. Preferably the second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange with a stream for which no reforming reactions take place. Preferably said stream is a stream different from said hydrocarbon feedstock, such as a boiling feed water stream to raise steam. Preferably said second heat exchanger is a waste heat boiler or steam superheater. Additional such heat exchangers may be arranged in parallel or in series with said second heat exchanger. The invention also provides a plant for the production of synthesis gas from a hydrocarbon feedstock, as illustrated schematically in Figures 1-5.

The plant comprises an arrangement of:

- at least one heat exchange reformer for producing a primary reformed gas by reforming at least a portion of said hydrocarbon feedstock,

- an autothermal reformer (ATR), or catalytic partial oxidation apparatus (CPO) or a partial oxidation apparatus (POX) for producing said hot effluent synthesis gas from at least a portion of the primary reformed gas from said heat exchange reformer,
- optionally, means for adding steam to said hot effluent synthesis gas thereby forming said mixture stream,
- means for splitting the mixture stream/hot effluent synthesis gas into at least a first synthesis gas stream and a second synthesis gas streams,
- means for supplying the first synthesis gas stream into the shell-side of the heat exchange reformer, and
- a second heat exchanger through which the second synthesis gas stream is fed.

Preferably, said second heat exchanger is a waste heat boiler or steam superheater.

In a specific embodiment the plant comprises also a first heat exchanger, preferably a waste heat boiler, for further cooling of the first synthesis gas after passing through the heat exchange reformer.

In another specific embodiment the plant comprises also valves installed immediately downstream said first and second heat exchanger. Such valves are advantageously used for control of the bypass ratio.

As mentioned above, preferably said first and second heat exchanger is a waste heat boiler.

Suitably, the plant further comprises an adiabatic pre-reformer upstream the heat exchange reformer.

In Fig. 1, a hydrocarbon feedstock 10 is formed in a pre-reformer 15 from a hydrocarbon stream 11 and steam 12. The hydrocarbon feedstock 10 is passed to the heat-exchange reformer 25 where it is catalytically steam reformed and thereafter leaves the heat-exchange reformer as stream 30. The primary reformed gas 30 is fed to an autothermal reformer 75 to which oxidant 80 is also supplied. The primary reformed gas is partially combusted and brought towards equilibrium over reforming catalyst in the autothermal reformer 75. The hot effluent synthesis gas 90 from the autothermal reformer 75 is split into first 111 and second 112 synthesis gas streams. Heat is recovered from the first synthesis gas stream 111 by passing it to the heat exchange reformer 25. This first synthesis gas stream 111 is cooled by heat exchange with the gas undergoing reforming over the catalyst in the heat-exchange reformer 25. The thus cooled first synthesis gas stream 111 leaves the heat exchange reformer as stream 121. The second synthesis gas stream 112 is passed through a waste heat boiler 115 to produce a cooled second synthesis gas stream 122 via heat exchange. In the embodiment shown in Figure 1, the cooled second synthesis gas stream 122 and the cooled first synthesis gas stream 121 are not combined.

In Fig. 2, a hydrocarbon feedstock 10 is formed in a pre-reformer 15 from a hydrocarbon stream 11 and steam 12. The hydrocarbon feedstock 10 is passed to the heat-exchange reformer 25 where it is catalytically steam reformed and thereafter leaves the heat-exchange reformer as stream 30. The primary reformed gas stream 30 is fed to an autothermal reformer 75 to which oxidant 80 is also supplied. The primary reformed gas stream 30 is partially combusted and brought towards equilibrium over reforming catalyst in the autothermal reformer 75. The hot effluent synthesis gas 90 from the autothermal reformer 75 is split into first 111 and second 112 synthesis gas streams. Heat is recovered from the first synthesis gas stream 111 by passing it to the heat exchange reformer 25. This first synthesis gas stream 111 is cooled by heat exchange with the gas undergoing reforming over the catalyst in the heat-exchange reformer 25. The thus cooled first synthesis gas stream leaves the heat exchange reformer as stream 121. The cooled first synthesis gas stream 121 is then further cooled in a third heat exchanger 116 (e.g. a waste heat boiler) to provide a further cooled first synthesis gas stream 131. The second synthesis gas stream 112 is passed through a waste heat boiler 115 to produce steam via heat exchange. As shown in Figure 2, the cooled second synthesis gas stream 122 then rejoins the further cooled first synthesis gas stream 131 downstream of the heat exchange reformer 25 and the third heat exchanger 131 to form a combined synthesis gas stream 120.

Fig. 3 illustrates a development of the embodiment of Fig. 2. Figure 3 also shows the step in which the hot

effluent synthesis gas 90 from the autothermal reformer 75 is mixed with a H_2O stream 100 to form combined stream 105 prior to being split into first 111 and second 112 synthesis gas streams. In addition, Figure 3 shows the step in which the combined synthesis gas stream 120 is further cooled in the cooling train and separation units 125 and separated into the product synthesis gas 130 and process condensate 140.

Fig. 4 illustrates a development of the embodiment of Figure 3, in that the primary reformed gas 30 is mixed with Fischer-Tropsch tail gas 60 forming the ATR feed stream 70. The primary reformed gas 30 is mixed with tail gas 60 (containing CH_4, higher hydrocarbons, olefins etc.) and other gases (H_2, CO, CO_2, N_2 etc.). This feed stream 70 is fed to the ATR 75 where it is partly combusted and further catalytically reformed to equilibrium. Figure 4 also shows the optional step in which the hot effluent synthesis gas 90 from the autothermal reformer 75 is mixed with a H_2O stream 100 to form combined stream 105 prior to being split into first 111 and second 112 synthesis gas streams. Finally in Figure 4, the cooled synthesis gas 120 leaving the heat exchange reformer 25 is further cooled in cooling train and separation units 125 to a low temperature, e.g. 40-80°C, and separated as synthesis gas 130 from the condensate, i.e. water and dissolved gases. The heat may be used for steam and preheating purposes.

The embodiment of Figure 5 is based on that of Figure 4. The hydrocarbon feedstock 10 is divided into two streams 20 and 40. The first stream 20 is fed to the heat-

exchange reformer 25 where it is catalytically steam reformed and thereafter leaves the heat-exchange reformer as primary reformed gas 30. The second stream 40 is preheated in a heat exchanger 45 to provide preheated stream 50. Preheated stream 50 and primary reformed gas 30 are mixed together with Fischer-Tropsch tail gas 60 forming the ATR feed stream 70. The ATR feed stream is fed to the autothermal reformer 75 to which oxidant 80 is also supplied. The ATR feed stream is partially combusted and brought towards equilibrium over reforming catalyst in the autothermal reformer 75. The hot effluent synthesis gas 90 from the autothermal reformer 75 is split into first 111 and second 112 synthesis gas streams. Heat is recovered from the first synthesis gas stream 111 by passing it to the heat exchange reformer 25. This first synthesis gas stream 111 is cooled by heat exchange with the gas undergoing reforming over the catalyst in the heat-exchange reformer 25. The thus cooled first synthesis gas stream leaves the heat exchange reformer as stream 121. The cooled first synthesis gas stream 121 is then further cooled in a third heat exchanger 116 (e.g. a waste heat boiler) to provide a further cooled first synthesis gas stream 131. The second synthesis gas stream 112 is passed through a waste heat boiler 115 to produce steam via heat exchange. As shown in Figure 2, the cooled second synthesis gas stream 122 then rejoins the further cooled first synthesis gas stream 131 downstream of the heat exchange reformer 25 and the third heat exchanger 131 to form a combined synthesis gas stream 120. In addition, Figure 5 shows the step in which the combined synthesis gas stream 120 is further cooled in the cooling train and separation

units 125 and separated into the product synthesis gas 130 and process condensate 140.

In Figures 2-5 valves are indicated downstream heat exchangers 115 and 116. It is preferred that one or both of these valves are installed and used for control of the bypass ratio.

In a further aspect, the invention provides a parallel arrangement of heat exchange reformer and autothermal reformer (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX). As such, a process for the production of synthesis gas from a hydrocarbon feedstock is provided, comprising the steps of:

a. dividing the hydrocarbon feedstock into at least a first and a second hydrocarbon feedstock stream;
b. reforming said first hydrocarbon feedstock stream in an endothermic reforming stage in one or more heat exchange reformers and withdrawing from the heat exchange reformer an effluent stream of reformed gas;
c. passing the second hydrocarbon feedstock stream through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and withdrawing a stream of hot effluent synthesis gas;

characterised in that the process comprises the step of splitting said hot effluent synthesis gas into at least a first synthesis gas stream and a second synthesis gas stream,

wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (b);
and wherein said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream.

Also as before, the second heat exchanger is a heat exchanger in which at least a portion, preferably a major portion, particularly 50% or more such as 90% or most preferably 100% of this second synthesis gas stream is used to heat a stream for which no reforming reactions take place. Preferably the second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange with a stream for which no reforming reactions take place. Preferably said stream is a stream different from said hydrocarbon feedstock, such as a boiling feed water stream to raise steam. Preferably said second heat exchanger is a waste heat boiler or steam superheater. Additional such heat exchangers may be arranged in parallel or in series with said second heat exchanger. In a particular embodiment according to this further aspect of the invention, the first synthesis gas stream may be combined with reformed gas from the heat exchange reformer prior to delivering heat to said heat exchange reformer.

The plant for the production of synthesis gas from a hydrocarbon feedstock in a parallel arrangement comprises an arrangement of:

- means for dividing the hydrocarbon feedstock into at least a first and a second hydrocarbon feedstock stream;
- at least one heat exchange reformer arranged for reforming said first hydrocarbon feedstock stream in an endothermic reforming stage so as to provide an effluent stream of reformed gas;
- an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), arranged for passing the second hydrocarbon feedstock stream through so as to provide a stream of hot effluent synthesis gas;
- optionally, means for adding steam to said hot effluent synthesis gas thereby forming a mixture stream,
- means for splitting the mixture stream/hot effluent synthesis gas into at least a first synthesis gas stream and at least a second synthesis gas stream;
- means for supplying the first synthesis gas stream into the shell-side of the heat exchange reformer, and
- a second heat exchanger through which the second synthesis gas stream is fed.

In a specific embodiment the plant comprises also a third heat exchanger, arranged downstream the shell-side of the heat exchange reformer, for further cooling of the first synthesis gas after passing through the heat exchange reformer. It would be understood that such third heat exchanger is arranged in series with the heat exchange reformer.

In another specific embodiment the plant comprises means for combining the cooled second synthesis gas from the second heat exchanger with the further cooled first synthesis gas from the third heat exchanger.

In yet another specific embodiment the plant comprises also means for adjusting the bypass ratio, preferably valves installed or arranged downstream, more preferably immediately downstream said second and third heat exchangers.
Preferably said second and third heat exchanger is a waste heat boiler.

Suitably, the plant further comprises an adiabatic pre-reformer upstream the heat exchange reformer.

In yet another aspect the invention as recited in claim 22 encompasses also the use of the process according to any one of claims 1-16, or the plant according to any one of claims 17-21, during start-up of the Fischer-Tropsch synthesis section in a plant for producing hydrocarbons or downstream process for production of gasoline.
The present invention should not be limited by the above description and enclosed figures. Instead, the skilled person will be able to combine features from various embodiments, while remaining within the scope of the claims. In particular, some embodiments show that steam is added to the hot effluent synthesis gas 90 from the ATR, and that the cooled first 121 and second 122 synthesis gas streams are combined - these steps are optional.

Example 1

A process utilizing the bypass stream of the present invention as shown in Fig 4 is presented in this example (as New layout). This is compared a process where the bypass stream of the present invention is not used (Reference layout).

It is shown that it is possible, by implementing the present invention, to counteract the influence of fouling of the heat exchanger surface in a heat exchange reformer, by controlling the amount of hot effluent synthesis gas from an autothermal reformer sent to the shell side of the heat exchange reformer, thereby obtaining constant performance of the plant.

The feed gas (not shown in fig.4) is mixed with hydrogen and desulphurized to form stream 11. It is mixed with steam (stream 12 in Fig. 4) and is sent to an adiabatic prereformer (15). The effluent from the prereformer (stream 10) is sent to the process side of a heat exchange reformer (25). The effluent from the heat exchange reformer (stream 30) is mixed with tail gas (stream 60) and sent to an autothermal reformer (75), where it is partly combusted and reformed to equilibrium producing a hot effluent stream (stream 90). No steam (stream 100) is mixed into the hot effluent stream.

Four cases are shown:

Case 1.1. Reference layout Start-Of-Run (Ref SOR). The heat exchange reformer is unfouled, and all gas from the

autothermal reformer is sent to the heat exchange reformer, i.e. bypass ratio = 0.

Case 1.2. Reference layout End-Of-Run (Ref EOR). The heat exchange reformer is fouled, and all gas from the autothermal reformer is sent to the heat exchange reformer, i.e. bypass ratio = 0.

Case 1.3. New layout Start-Of-Run (New SOR). The heat exchange reformer is unfouled, and 88 % of the gas from the autothermal reformer is sent to the heat exchange reformer. 12 % is bypassed (bypass ratio) via stream 112.

Case 1.4. New layout End-Of-Run (New EOR). The heat exchange reformer is fouled, and 99 % of the gas from the autothermal reformer is sent to the heat exchange reformer. 1 % is bypassed (bypass ratio) via stream 112.

The performance of the heat exchange reformer in the 4 cases is summarized in Table 1.1

It is seen that it is possible to have the same performance of the heat exchange reformer at Start-Of-Run and End-Of-Run using the new layout as per the present invention. The outlet temperature and the transferred duty are the same at SOR and EOR conditions. Transferred duty is the amount of energy that is transferred per unit time from the shell side gas stream to the tube side gas stream in the heat exchange reformer. By gradually adjusting the amount of gas from the autothermal reformer throughout the operating period from unfouled to fouled

conditions, it is possible to maintain the same performance at any time.

This is not the case in the Reference layout (without bypass stream). The performance is inferior at EOR conditions compared to the SOR. The outlet temperature at EOR conditions is 15°C less and the transferred duty is 8.1 Gcal/h less corresponding to 7%.

Table 1.1 Performance of heat exchange reformer.

Case		1.1. Ref SOR	1.2. Ref EOR	1.3. New SOR	1.4. New EOR
Bypass	%	0	0	12	1
Fouling		No	Yes	No	Yes
Tout (STM 10)	°C	730	715	730	730
Tout (STM 121)	°C	649	678	591	639
Transferred duty	Gcal/h	115.6	107.5	116.2	116.3

Table 1.2 show the overall performance of the syngas plant for the 4 cases. It is seen that in the new layout, utilizing the present invention, the same amount of syngas and CO is produced at EOR conditions compared to SOR. The amount of CO produced per unit natural gas and per unit oxygen is also constant throughout the operating period from unfouled to fouled conditions.

In the Reference layout, the amount of syngas and CO produced at EOR condition is less at EOR conditions compared to SOR. The amount of CO produced is 1213 Nm3/h less corresponding to 0.7%. The amount of CO produced per unit natural gas and per unit oxygen is also less, per unit oxygen the amount is 2.3% less.

Table 1.2. Overall process performance

Case		1.1. Ref SOR	1.2. Ref EOR	1.3. New SOR	1.4. New EOR
Bypass ratio	%	0	0	12	2
Fouling		No	Yes	No	Yes
NG feed	Nm3/h	150000	150000	150000	150000
Ox flow	Nm3/h	88614	90031	88556	88512
Syngas flow (Dry)	Nm3/h	611403	607726	611438	611579
CO prod	Nm3/h	175258	174045	175280	175324
CO prod/NG feed flow		1.168	1.160	1.169	1.169
CO prod/Oxygen flow		1.978	1.933	1.979	1.981

In summary, this example shows that the performance of the heat exchange reformer and a syngas plant can sustain constant performance by using a layout including a bypass stream according to the present invention. If the bypass stream of the invention is not used, and all the gas from the autothermal reformer is sent to the heat exchange reformer, the result will be a gradual decrease in performance.

Example 2

A process utilizing the present invention as shown in Fig 3 (no tail gas addition) is presented in this example (as

new layout). This is compared to the Reference layout which is a process where the present invention is not used, i.e. all gas (stream 111 in Fig. 3) is send through the shell side of the heat exchange reformer.

It is shown that it is possible, by implementing the present invention, to counteract the influence of fouling of the heat exchanger surface in a heat exchange reformer, by controlling the amount of hot effluent synthesis gas from an autothermal reformer sent to the shell side of the heat exchange reformer.

Referring to Fig. 3. The feed gas (not shown in Fig. 3) is mixed with hydrogen and desulphurized to form stream 11. It is mixed with steam (stream 12) and is sent to an adiabatic prereformer (15). The effluent from the prereformer (stream 10) is sent to the process side of a heat exchange reformer (25). The effluent from the heat exchange reformer (stream 30) is sent to an autothermal reformer (75), where it is partly combusted and reformed to equilibrium producing a hot effluent stream (stream 90). No steam (stream 100) is mixed into the hot effluent stream. No tail gas is mixed into the heat exchange reformer effluent (stream 30).

Four cases are shown:

2.1. Reference layout Start-Of-Run (Ref SOR). The heat exchange reformer is unfouled, and all gas from the autothermal reformer is sent to the heat exchange reformer via stream 111, i.e. bypass ratio = 0.

2.2. Reference layout End-Of-Run (Ref EOR). The heat exchange reformer is fouled and all gas from the autothermal reformer is sent to the heat exchange reformer via stream 111, i.e. bypass ratio = 0.

2.3. New layout Start-Of-Run (New SOR). The heat exchange reformer is unfouled, and 84 % of the gas from the autothermal reformer is sent to the heat exchange reformer (stream 111). 16 % is bypassed via stream 112, i.e. bypass ratio = 16%.

2.4. New layout End-Of-Run (New EOR). The heat exchange reformer is fouled and 96 % of the gas from the autothermal reformer is sent to the heat exchange reformer (stream 111). 4 % is bypassed via stream 112, ie. bypass ratio = 4%.

The performance of the heat exchange reformer in the 4 cases is summarized in Table 2.1.
It is seen that it is possible to have the same performance of the heat exchange reformer at Start-Of-Run and End-Of-Run using the new layout with the present invention. The outlet temperature and the transferred duty are the same at SOR and EOR conditions. Transferred duty is the amount of energy that is transferred per unit time from the shell side gas stream to the tube side gas stream in the heat exchange reformer. By gradually adjusting the amount of gas from the autothermal reformer throughout the operating period from unfouled to fouled conditions, it is possible to maintain the same performance at any time.

This is not the case in the Reference layout. The performance is inferior at EOR conditions compared to the SOR. The outlet temperature at EOR conditions is 19°C less and the transferred duty is 8.5 Gcal/h less corresponding to 10 %.

Table 2.1. Performance of heat exchange reformer

Case		2.1 Ref SOR	2.2 Ref EOR	2.3 New SOR	2.4 New EOR
Shell bypass	%	0	0	16	4
Fouling		No	Yes	No	Yes
Tout (STM 30)	°C	685	666	685	685
Tout (STM 121)	°C	646	687	566	627
Transferred duty	Gcal/h	85.88	77.30	85.78	86.15

Table 2.2 shows the overall performance of the syngas unit for the 4 cases. It is seen that in the new layout, utilizing the present invention, the synthesis gas module from SOR is maintained at EOR operation. Also, the same amount of syngas and CO is produced at EOR conditions compared to SOR.

The amount of CO produced per unit natural gas and per unit oxygen is also constant throughout the operating period from unfouled to fouled conditions.

In the Reference layout, the synthesis gas module has decreased by 1.5% at EOR compared to SOR. The amount of

syngas and CO produced at EOR condition is less than at SOR conditions. The amount of produced CO is 342 Nm3/h less corresponding to 0.3 %. The amount of CO produced per unit natural gas and per unit oxygen is also less; the latter by 2.7%.

Table 2.2. Overall process performance

Case		2.1 Ref SOR	2.2 Ref EOR	2.3 New SOR	2.4 New EOR
Shell bypass	%	0	0	16	4
Fouling		No	Yes	No	Yes
NG feed	Nm3/h	150000	150000	150000	150000
Ox flow	Nm3/h	71477	73264	71470	71466
Syngas flow (STM 90)	Nm3/h	566063	566632	566061	566060
Module (H_2-CO_2)/(CO+CO_2)	Nm3/Nm3	2.00	1.97	2.00	2.00
CO prod	Nm3/h	117771	117429	117772	117773
CO prod/NG feed flow		0.785	0.783	0.785	0.785
CO prod/O_2 flow		1.648	1.603	1.648	1.648

In summary, this example shows that the performance of the heat exchange reformer in a syngas plant can sustain constant performance by using a layout of the present invention. If this invention is not used, and all the gas from the autothermal reformer is sent to the heat

exchange reformer a gradual decrease in performance will be the consequence.

Example 3. Start-up

A process utilizing the present invention as shown in Fig 3 is presented in this example (as new layout). This is compared to the Reference layout which is a process where the present invention is not used, i.e. all gas leaving the autothermal reformer is sent through the shell side of the heat exchange reformer (bypass ratio = 0).

In this example it is shown that it is possible, by implementing the present invention, to counteract an excessive temperature increase in the stream leaving the process side of the heat exchange reformer (stream 30) during an operating configuration, in which part of the synthesis gas (stm 130) is recycled to the Autothermal Reformer (75) in order to reach an H_2/CO-ratio low enough for starting (or operating) an FT-synthesis unit in case no tail gas is available. In the present example the target H_2/CO-ratio has been set to 2.3 but various FT synthesis will have various requirements in many cases different from H_2/CO=2.3. Note that the recycle of part of the synthesis gas (stm 130) to the Autothermal Reformer (75) is not shown in Fig. 3.

In this case the heat exchange reformers have been designed for normal operation with a feed flow of 150,000 Nm3/hr. of natural gas (see Example 1). The heat exchange reformers have been designed to have an exit temperature from the catalyst side of 730°C during normal operation

at unfouled conditions. The unit in this example 3 operates with a natural gas feed rate of 75,000 Nm3/hr. corresponding to 50% of the design flow rate.

Referring to Fig. 3; the feed gas (not shown in Fig.3) is mixed with hydrogen and desulphurized to form stream 11. It is mixed with steam (stream 12) and is sent to an adiabatic prereformer (15). The effluent from the prereformer (stream 10) is sent to the process side of a heat exchange reformer (25). The effluent from the heat exchange reformer (stream 30) and a portion of the synthesis gas (stream 130) are combined and sent to the autothermal reformer (75), in which it is partially combusted using oxygen (stream 80) and reformed to equilibrium producing a hot effluent stream (stream 90). No steam (stream 100) is mixed into the hot effluent stream. No tail gas is mixed into the heat exchange reformer effluent (stream 30) at this operating point.

In all three cases the flow, feed gas composition, temperature, pressure, and steam-to-carbon ratio have the same values in the stream just upstream the heat exchange reformer (stream 10 in Fig. 3).
Three cases are shown:

3.1. Reference layout (unfouled). All gas from the autothermal reformer is sent to the heat exchange reformer via stream 111. No flow in the bypass steam 112, i.e. bypass ratio = 0.

3.2. New layout (unfouled). 70.1 % of the gas from the autothermal reformer is sent to the heat exchange

reformer (stream 111). 29.9 % is bypassed via stream 112, i.e. bypass ratio = 30%.

3.3. New layout (unfouled). 64.6% of the gas from the autothermal reformer is sent to the heat exchange reformer (stream 111). 35.4 % is bypassed via stream 112, i.e. bypass ratio = 35%.

The performances of the heat exchange reformers in the 3 cases are summarized in Table 3.1.

It is seen that it is possible to considerably reduce the transferred duty and process side outlet temperature of the heat exchange reformer using the new layout with the present invention. Transferred duty is the amount of energy which is transferred per unit time from the shell side gas stream to the tube side gas stream in the heat exchange reformer. By adjusting the amount of gas from the autothermal reformer to the heat exchange reformer shell side, it is possible to maintain conditions without excessive temperatures at the catalyst outlet of the heat exchange reformer also at reduced load and with recycle of part of the synthesis gas for example for start-up of the downstream Fischer-Tropsch synthesis unit.

This is not the case in the Reference layout. The large transferred duty in case 3.1 results in a large temperature increase of the process side gas (stream 30) from 730°C at normal operation to 781°C, both at un-fouled condition.

Table 3.1. Performance of heat exchange reformer

Case		3.1 Reference un-fouled	3.2 New layout un-fouled	3.3 New layout un-fouled
Shell bypass	%	0	29.9	35.4
Fouling		No	No	No
Tout (STM 30)	°C	781	743	730
Tout (STM 121)	°C	632	529	513
Transferred duty*	Gcal/h	68.39	57.03	53.28

Table 3.2 shows the overall performance of the syngas unit for the 3 cases. It is seen that in the New layout, utilizing the present invention, the required synthesis gas recycle flow for obtaining H_2/CO =2.3 in the synthesis gas decreases considerably (by 11.3% with a shell bypass of 29.9%) compared to the reference layout. This has a positive impact on the recycle equipment which becomes smaller and cheaper and requiring less power. Also, due to the lower temperature the new layout utilizing the present invention, results in operation with a larger margin to the carbon formation limit (reaction according to eq. 1) compared to the reference layout. As indicated previously, for otherwise identical conditions, the margin to carbon formation increases with decreasing temperature. The catalyst temperature is substantially lower in the new layout compared to the reference layout.

Table 3.2. Overall process performance

Case		3.1 Reference	3.2 New layout	3.3 New layout
Shell bypass	%	0	29.9	35.4
Fouling		No	No	No
NG feed	Nm3/h	75000	75000	75000
Ox flow	Nm3/h	39244	40633	41093
Syngas flow (STM 90)	Nm3/h	439698	422686	416030
H_2/CO ratio	Nm3/Nm3	2.30	2.30	2.30
Syngas recycle flow	Nm3/h	160,000	142,000	135,000
CO prod (STM 130)	Nm3/h	60167	59938	59835

In summary, this example shows that by using a layout with the present invention excessive temperatures outlet the process side of the heat exchange reformer during low load and process configurations for start-up of a downstream Fischer-Tropsch unit can be avoided. Further, the required synthesis gas recycle flow for reaching the desired H_2/CO ratio is smaller, and the distance to the carbon limit for CH_4 decomposition is larger than in the reference case.

CLAIMS

1. Process for the production of synthesis gas from a hydrocarbon feedstock, comprising the steps of:
   a. reforming at least a portion of said hydrocarbon feedstock in an endothermic reforming stage in a heat exchange reformer and withdrawing from the heat exchange reformer an effluent stream of primary reformed gas;
   b. passing the primary reformed gas from the heat exchange reformer through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and withdrawing a stream of hot effluent synthesis gas;

   characterised in that the process further comprises the step of splitting the hot effluent synthesis gas into at least a first synthesis gas stream and a second synthesis gas stream,
   wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (a);
   and wherein said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream.

2. Process according to claim 1, further comprising the step of:

c. adding a stream comprising steam to either said hot effluent synthesis gas from step (b) or to said first synthesis gas stream.

3. Process according to claims 1 or 2 wherein the hydrocarbon feedstock is subjected to a step of pre-reforming, preferably adiabatic pre-reforming before being directed to the heat exchange reformer.

4. Process according to any one of claims 1 - 3, wherein the process comprises a further step after the first synthesis gas stream has passed through the heat exchange reformer of: cooling the first synthesis gas stream to a temperature sufficiently low for the steam to condense, and separating the synthesis gas from said condensate.

5. Process according to any one of claims 1 – 4 further comprising mixing the primary reformed gas with tail gas from a Fischer-Tropsch synthesis stage or downstream process for the production of gasoline.

6. Process according to any one of claims 1-5, wherein the bypass ratio, being the ratio of the flow of second synthesis gas stream to the flow of the effluent stream from the autothermal reformer, is between 1% and 30%, preferably between 1% and 20%, most preferably between 1% and 12%.

7. Process according to claim 6, wherein – as the process proceeds - the bypass ratio is reduced with time.

8. Process according to any one of claims 1 - 4 comprising mixing the primary reformed gas or the hydrocarbon feedstock with a gas stream comprising at least 90 vol% CO_2.

9. Process according to any of claims 1 to 8, wherein the heat exchange reformer is selected from a tube and shell heat exchanger, and double-tube reactor with catalyst disposed inside the double tubes, catalyst disposed outside the double tubes, and/or catalyst disposed outside and inside the double tubes.

10. Process according to any of claims 1 to 9, wherein the primary reformed gas from the heat exchange reformer is passed through an autothermal reforming stage (ATR).

11. Process according to any one of the preceding claims, further comprising the step of converting the separated synthesis gas into ammonia synthesis gas, methanol synthesis gas, dimethyl ether (DME) synthesis gas, synthesis gas for production of hydrocarbons by Fischer-Tropsch synthesis, or synthesis gas for the production of hydrogen, and further converting said synthesis gas into the respective product in the form of ammonia, methanol, DME, liquid hydrocarbons in a downstream process for production of gasoline, or hydrogen.

12. Process according to any of claims 1 – 11 wherein a portion of the hydrocarbon feedstock is led directly as a by-pass stream to the primary reformed gas to form a combined stream before entering the ATR, CPO or POX.

13. Process according to any of claims 1 to 12, wherein the process steam-to-carbon ratio ($S/C_{process}$) is in the range 0.4-3.0, preferably 0.5-1.2, more preferably 0.5-1.0.

14. Process according to any of the claims 1 to 13, wherein the H_2/CO-molar ratio in said stream of cooled synthesis gas in the first synthesis gas stream is in the range of 1.7 to 2.3.

15. Process according to any claims 1-3 and 5-14, wherein, after the heat exchange reformer, the cooled, or further cooled, first synthesis gas stream and the cooled second synthesis gas stream are mixed together to provide a raw synthesis gas product stream.

16. Process according to any one of the preceding claims, wherein:
- at least a second portion of said hydrocarbon feedstock is reformed in an endothermic reforming stage in at least a second heat exchange reformer and an second effluent stream of primary reformed gas is withdrawn from said second heat exchange reformer;

- said second effluent stream of primary reformed gas is combined with the effluent stream of primary reformed gas obtained from the reforming the first portion of said hydrocarbon feedstock;
- the combined primary reformed gases from the heat exchange reformers are passed through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and a stream of hot effluent synthesis gas is withdrawn;
- the hot effluent synthesis gas from the autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), is split into at least a first synthesis gas stream, a second synthesis gas stream and a third synthesis gas stream,

and wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (a);
and wherein said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream;
and wherein said third synthesis gas stream is used as heating medium in indirect heat exchange in the second heat exchange reformer.

17. Plant for the production of synthesis gas from a hydrocarbon feedstock, comprising an arrangement of:
- at least one heat exchange reformer for producing a primary reformed gas by reforming of at least a portion of said hydrocarbon feedstock,

- an autothermal reformer (ATR), or catalytic partial oxidation apparatus (CPO) or a partial oxidation apparatus (POX) for producing said hot effluent synthesis gas from at least a portion of the primary reformed gas from said heat exchange reformer,
- optionally, means for adding steam to said hot effluent synthesis gas thereby forming a mixture stream,
- means for splitting the mixture stream or hot effluent synthesis gas into at least a first synthesis gas stream and at least a second synthesis gas stream,
- means for supplying the first synthesis gas stream into the shell-side of the heat exchange reformer, and
- a second heat exchanger through which the second synthesis gas stream is fed.

18. Plant according to claim 17 further comprising an adiabatic pre-reformer upstream the heat exchange reformer.

19. Plant according to any one of claims 17-18, further comprising a third heat exchanger arranged downstream the shell-side of the heat exchange reformer so as to further cool the first synthesis gas stream.

20. Plant according to claim 19, comprising means for combining the cooled second synthesis gas from the

second heat exchanger with the further cooled first synthesis gas from the third heat exchanger.

21. Plant according to claim 19, comprising means for adjusting the bypass ratio, said means for adjusting the bypass ratio being arranged downstream said second and third heat exchangers.

22. Use of the process according to any one of claims 1-16, or the plant according to any one of claims 17-21, during start-up of the Fischer-Tropsch synthesis section in a plant for producing hydrocarbons or downstream process for production of gasoline.

23. Process for the production of synthesis gas from a hydrocarbon feedstock, comprising the steps of:

a. dividing the hydrocarbon feedstock into at least a first and a second hydrocarbon feedstock stream;
b. reforming said first hydrocarbon feedstock stream in an endothermic reforming stage in one or more heat exchange reformers and withdrawing from the heat exchange reformer an effluent stream of reformed gas;
c. passing the second hydrocarbon feedstock stream through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and withdrawing a stream of hot effluent synthesis gas;

characterised in that the process comprises the step of splitting said hot effluent synthesis gas into at

least a first synthesis gas stream and a second synthesis gas stream,
wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (b);
and wherein said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by indirect heat exchange to produce a cooled second synthesis gas stream.

24. Process according to claim 23, wherein the first synthesis gas stream is combined with reformed gas from the heat exchange reformer prior to delivering heat to said heat exchange reformer.

25. Plant for the production of synthesis gas from a hydrocarbon feedstock, comprising an arrangement of:
- means for dividing the hydrocarbon feedstock into at least a first and a second hydrocarbon feedstock stream;
- at least one heat exchange reformer arranged for reforming said first hydrocarbon feedstock stream in an endothermic reforming stage so as to provide an effluent stream of reformed gas;
- an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), arranged for passing the second hydrocarbon feedstock stream through so as to provide a stream of hot effluent synthesis gas;
- optionally, means for adding steam to said hot effluent synthesis gas thereby forming a mixture stream,

- means for splitting the mixture stream or hot effluent synthesis gas into at least a first synthesis gas stream and at least a second synthesis gas stream;
- means for supplying the first synthesis gas stream into the shell-side of the heat exchange reformer, and
- a second heat exchanger through which the second synthesis gas stream is fed.

26. Process for starting up the hydrocarbon synthesis section of a gas-to-liquid process comprising:

c. reforming at least a portion of a hydrocarbon feedstock in an endothermic reforming stage in a heat exchange reformer and withdrawing from the heat exchange reformer an effluent stream of primary reformed gas;

d. passing the primary reformed gas from the heat exchange reformer through an autothermal reforming stage (ATR), catalytic partial oxidation stage (CPO) or partial oxidation stage (POX), and withdrawing a stream of hot effluent synthesis gas;

characterised in that the process further comprises the step of splitting the hot effluent synthesis gas into at least a first synthesis gas stream and a second synthesis gas stream,
wherein said first synthesis gas stream is used as heating medium in indirect heat exchange in the heat exchange reformer of step (a);
wherein said second synthesis gas stream is directed to a second heat exchanger in which it is cooled by

indirect heat exchange to produce a cooled second synthesis gas stream;
and wherein the process comprises a further step after the first synthesis gas stream has passed through the heat exchange reformer of: cooling the first synthesis gas stream to a temperature sufficiently low for steam to condense, separating the synthesis gas from said condensate, and recycling part or all of this synthesis gas to the ATR, CPO or POx.

27. Process according to claim 26 further comprising adding the second synthesis gas stream to the first synthesis gas stream after it has passed through the heat exchange reformer.

28. Process according to claim 27-28 wherein the bypass ratio, being the ratio of the flow of second synthesis gas stream to the flow of the effluent stream from the ATR or CPO or POx, is between 10% and 40%, preferably between 20% and 35%, more preferably 30% or 35%.

29. Process according to claim 28 wherein as the process proceeds, the bypass ratio is constant with time.

30. Process according to any of claims 26-29 wherein as the process proceeds the H_2/CO molar ratio of the synthesis gas is reduced with time to a value below 2.5 or 2.4, preferably below 2.3 or 2.2, more preferably below 2.1.

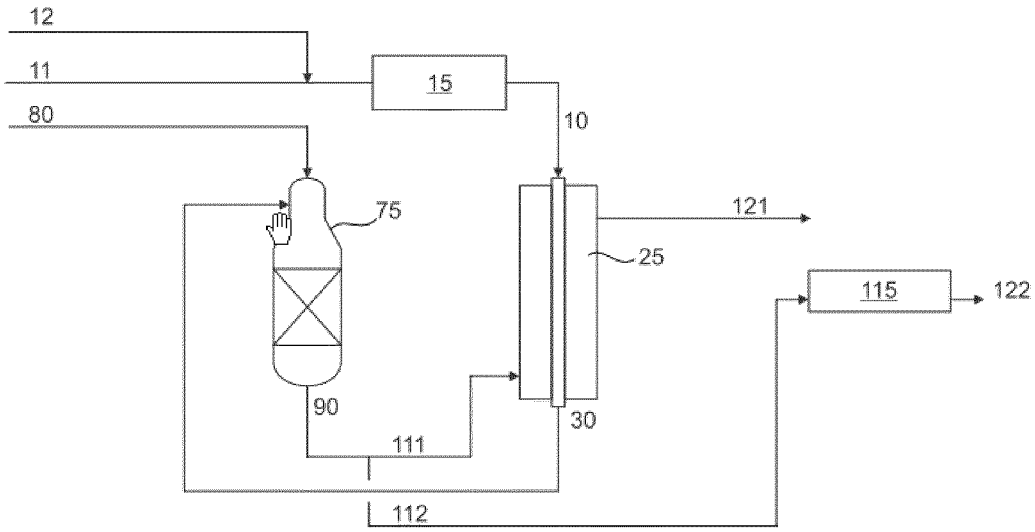


Fig. 1

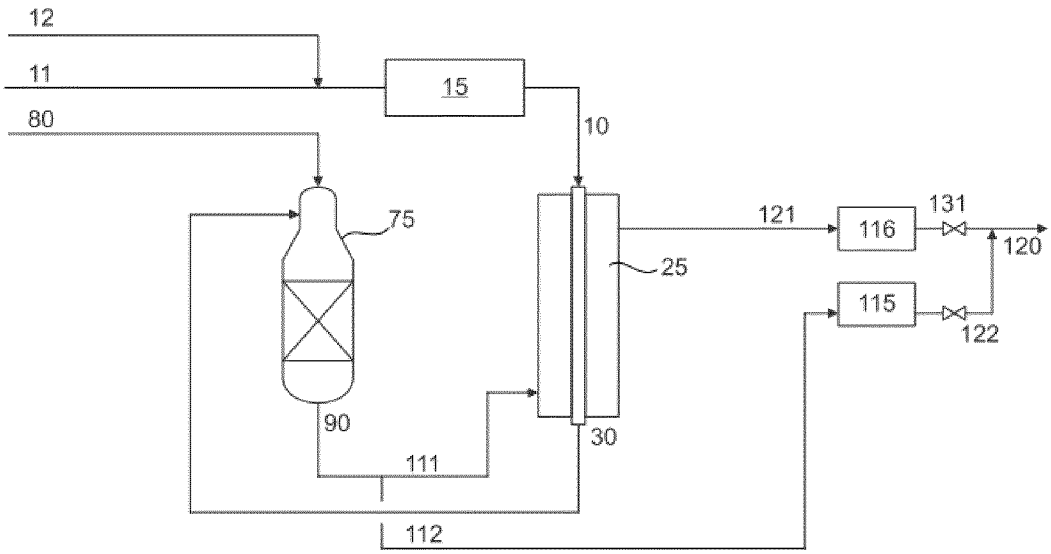


Fig. 2

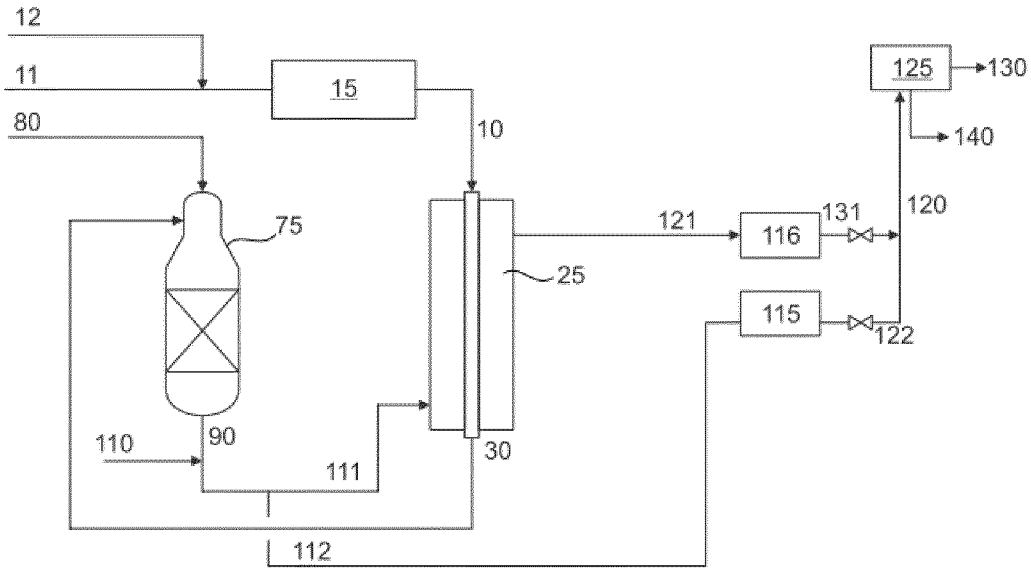

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Fig. 3

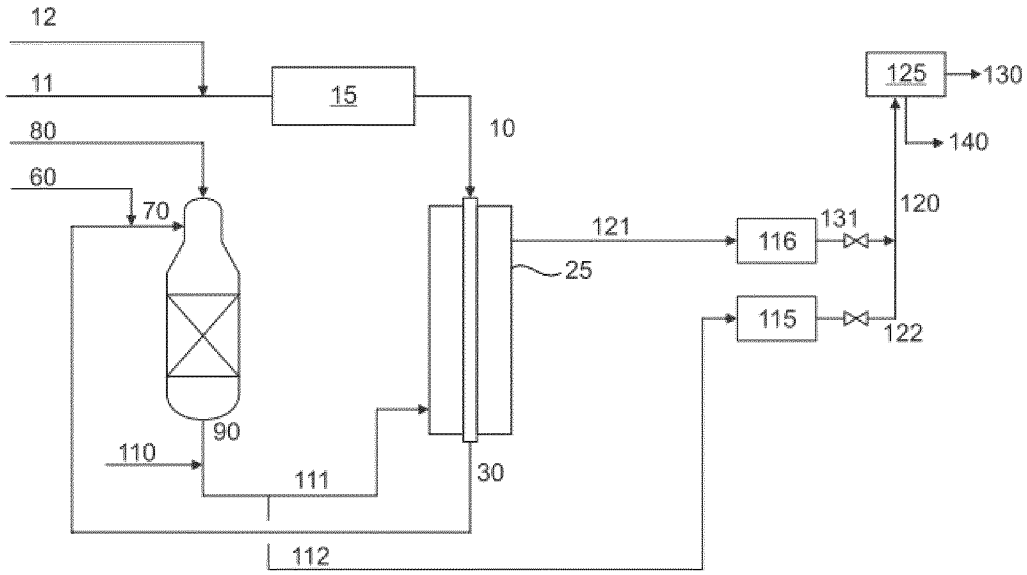

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Fig. 4

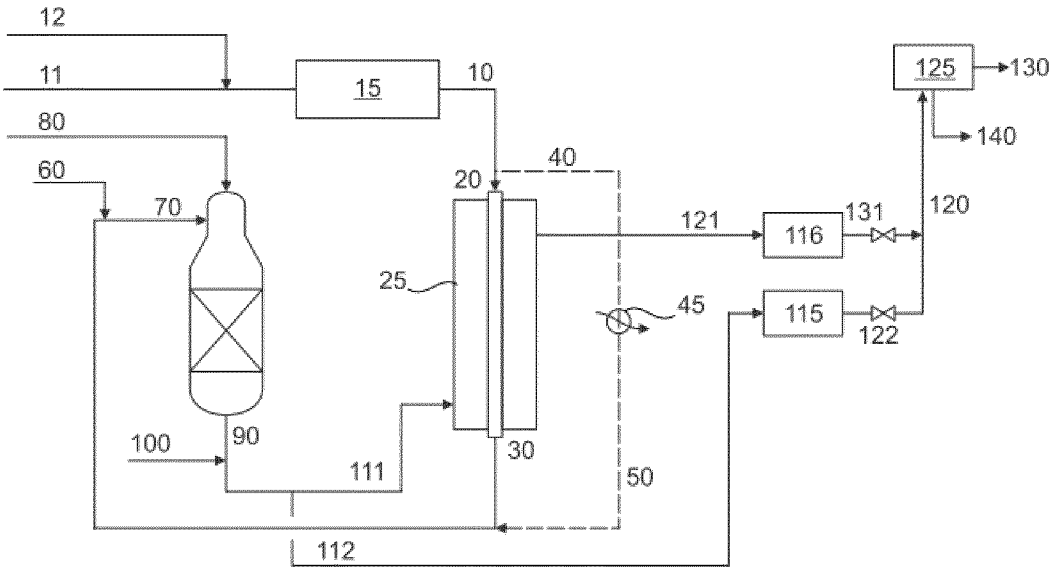

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Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062096

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38
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)
C01B

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 106 570 A2 (TOPSOE HALDOR AS [DK]) 13 June 2001 (2001-06-13) cited in the application the whole document	1-30
X	WO 00/09441 A2 (ICI PLC [GB]; ABBOTT PETER EDWARD JAMES [GB]) 24 February 2000 (2000-02-24) cited in the application figure 1	1-30
X	WO 03/051771 A1 (JOHNSON MATTHEY PLC [GB]; ABBOTT PETER EDWARD JAMES [GB]; CREWDSON BER) 26 June 2003 (2003-06-26) cited in the application figure 1	1-30

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

[X] 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 doubts on priority claim(s) or 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

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

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

"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	Date of mailing of the international search report
16 October 2013	28/10/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Engelen, Karen

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062096

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/184293 A1 (HAN PAT A [DK]) 23 July 2009 (2009-07-23) cited in the application the whole document	1-30
X	US 6 296 679 B1 (KATO HAJIME [JP]) 2 October 2001 (2001-10-02) cited in the application figure 1	1-30
X	EP 0 440 258 A2 (TOPSOE HALDOR AS [DK]) 7 August 1991 (1991-08-07) cited in the application the whole document	1-30

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/062096

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.:

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-22

   Process and plant for the production of synthesis gas in which a hydrocarbon feedstock is reformed in a heat exchange reformer, the primary reformed gas from the heat exchange reformer being fed to an ATR, CPO, or POX, the effluent from this reactor being split into a first and second stream, the first stream is used as heating medium in the heat exchange reformer, the second stream in a heat exchanger. Use of the process or the plant during start-up of the Fischer-Tropsch synthesis section in a plant for producing hydrocarbons or downstream process for production of gasoline.

   ---

2. claims: 23-25

   Process and plant for the production of synthesis gas in which a hydrocarbon feedstock is reformed in a heat exchange reformer and in parallel a hydrocarbon feedstock is fed to an ATR, CPO, or POX, the effluent from this reactor being split into a first and second stream, the first stream is used as heating medium in the heat exchange reformer, the second stream in a heat exchanger.

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3. claims: 26-30

   Process for starting up the hydrocarbon synthesis section of a gas-to-liquid process in which a hydrocarbon feedstock is reformed in a heat exchange reformer, the primary reformed gas from the heat exchange reformer is passed through an ATR, CPO or POX, and the effluent from this reactor is split into a first stream and a second stream, the first stream is used as heating medium in the heat exchange reformer, the second stream in a second heat exchanger; after the first stream has passed through the heat exchange reformer the first stream is cooled to a temperature sufficiently low for steam to condense, the synthesis gas is separated from the condensate, and is recycled to the ATR, CPO or POX.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/062096

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1106570 A2	13-06-2001	CA 2326950 A1	02-06-2001
		CN 1314203 A	26-09-2001
		CN 101015784 A	15-08-2007
		EP 1106570 A2	13-06-2001
		JP 5190162 B2	24-04-2013
		JP 2001190946 A	17-07-2001
		NO 20006105 A	05-06-2001
WO 0009441 A2	24-02-2000	AU 742314 B2	20-12-2001
		AU 4923299 A	06-03-2000
		ID 27781 A	26-04-2001
		MY 122316 A	29-04-2006
		US 2002006968 A1	17-01-2002
		WO 0009441 A2	24-02-2000
WO 03051771 A1	26-06-2003	AT 473943 T	15-07-2010
		AU 2002352397 A1	30-06-2003
		CA 2469079 A1	26-06-2003
		EP 1456121 A1	15-09-2004
		MY 134800 A	31-12-2007
		UA 80269 C2	10-09-2007
		US 2005118089 A1	02-06-2005
		WO 03051771 A1	26-06-2003
		ZA 200404349 A	29-08-2005
US 2009184293 A1	23-07-2009	NONE	
US 6296679 B1	02-10-2001	AU 4470697 A	24-04-1998
		CA 2267780 A1	09-04-1998
		DE 69736438 T2	02-08-2007
		EP 0959120 A1	24-11-1999
		JP 4073960 B2	09-04-2008
		US 6296679 B1	02-10-2001
		WO 9814536 A1	09-04-1998
EP 0440258 A2	07-08-1991	AT 113260 T	15-11-1994
		AU 624759 B2	18-06-1992
		AU 7017391 A	08-08-1991
		CA 2035331 A1	03-08-1991
		CN 1056850 A	11-12-1991
		CS 9100248 A2	13-08-1991
		DE 69104735 D1	01-12-1994
		DK 28390 A	03-08-1991
		EP 0440258 A2	07-08-1991
		ES 2065556 T3	16-02-1995
		JP H0675670 B2	28-09-1994
		JP H04215837 A	06-08-1992
		RU 2053957 C1	10-02-1996
		SK 279079 B6	03-06-1998
		US 5167933 A	01-12-1992
		ZA 9101771 A	27-11-1991