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(54) Title: REFORMING PROCESS

(57) Abstract: A reforming process is described comprising the steps of (a) partially oxidising a feed-gas comprising a hydrocarbon feedstock with an oxygen containing gas, (b) bringing the composition of the resulting partially oxidised gas stream towards equilibrium by passing said partially oxidised gas stream over a reforming catalyst to provide a raw synthesis gas mixture, (c) cooling said raw synthesis gas mixture and (d) separating condensed water from the raw synthesis gas mixture, characterised in that prior to the step of separating the condensed water from the raw synthesis gas mixture, part of said raw synthesis gas mixture is recycled to the partial oxidation step. The recycle of raw synthesis gas mixture to the partial oxidation step provides an energy-efficient source of hydrogen and steam that may e.g. inhibit carbon formation.

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Reforming process

This invention relates to reforming processes in particular to autothermal reforming processes.

Autothermal reforming processes are widely employed in the generation of synthesis gas (syngas) mixtures comprising hydrogen and carbon oxides (carbon monoxide and/or carbon dioxide) suitable for the production of e.g. methanol, ammonia and liquid hydrocarbons using e.g. the Fischer-Tropsch process. In autothermal reforming processes a feed-gas comprising a hydrocarbon feedstock and optionally steam, carbon dioxide and other gasses is non-catalytically combusted at elevated pressure with an oxygen-containing gas and the resulting partially oxidised gas mixture brought to equilibrium by passing it over a reforming catalyst, to provide a raw synthesis gas mixture. The partial oxidation process is exothermic and the raw synthesis gas mixture is necessarily cooled, with separation of condensed water, to provide a synthesis gas suitable for use in methanol, ammonia or liquid hydrocarbon synthesis processes.

In reforming processes producing synthesis gas for the production of liquid hydrocarbons, the ratio of hydrogen to carbon monoxide in the synthesis gas is desirably about 2:1. However operation of the process under conditions necessary to achieve a hydrogen to carbon monoxide ratio of about 2:1, e.g. a low steam ratio, exposes the operator to a risk of carbon formation in the partial oxidation step and possibly on the reforming catalyst. Such carbon formation is undesirable as, in addition to the reduced efficiency of the reforming process, the carbon can foul the reforming apparatus and catalyst, resulting in higher pressure drop across the catalyst and reduced effectiveness of the reforming catalyst by physical poisoning.

We have realised that providing a hydrogen-containing gas to the partial oxidation step of an autothermal reforming process may inhibit carbon formation in the autothermal reformer.

Hydrogen may be provided by a step of steam reforming the hydrocarbon feedstock. However, this requires considerable investment in steam reforming equipment. Alternatively, hydrogen may be provided by recycling a hydrogen-containing gas to the partial oxidation step.

US 4938685 describes a process and equipment for producing a hot gas stream wherein a hydrocarbon-containing feed-gas is subjected to catalytic combustion with air in a bed of precious metal catalyst and ejector means are incorporated within the combustion apparatus to recycle the hot combusted gas, that contains hydrogen, to the feed-gas. Because the purpose of the apparatus is to provide a hot gas stream, e.g. for start-up of a partial oxidation process, no heat recovery is employed and the process is based upon catalytic combustion rather than autothermal reforming.

More typically, hydrogen is provided upstream of steam reforming processes, to perform hydrodesulphurisation on the hydrocarbon feedstock, by feeding a portion of a cooled, de-watered synthesis gas mixture, or by feeding a hydrogen-rich gas separated from said cooled, de-watered synthesis gas mixture, to the hydrodesulphurisation step. For example, EP-A-1002779 describes a process for providing hydrogen for hydrodesulphurisation wherein a hydrocarbon feedstock is subjected to steam reforming and a portion of the reformed gas, which is preferably de-watered, is recycled by means of an ejector driven by the hydrocarbon to the hydrodesulphurisation stage. It does not however describe an autothermal reforming process having a recycle of part of the raw synthesis gas mixture to a partial oxidation step. Furthermore utilising a cooled, de-watered synthesis gas as a source of hydrogen fed to an autothermal reformer, either by recycle or as a source of a hydrogen-rich gas, will generally require that the hydrogen-containing gas be re-heated and re-compressed prior to passing it to the reformer. Such re-heating and recompression requires additional heat-exchange and compression equipment. In particular, separation of water from the raw synthesis gas mixture changes its composition requiring that, where such de-watered synthesis gas is used as the source of hydrogen, higher levels of oxygen-containing gas be used in any partial oxidation process.

We have found that direct recycle of a portion of the raw synthesis gas mixture to the partial oxidation step in an autothermal reforming process provides an energy- and oxidant-efficient source of hydrogen.

Accordingly the invention provides a reforming process comprising the steps of;

(a) partially oxidising a feed-gas comprising a hydrocarbon feedstock with an oxygen-containing gas,
(b) bringing the composition of the resulting partially oxidised gas stream towards equilibrium by passing said partially oxidised gas stream over a reforming catalyst to provide a raw synthesis gas mixture,
(c) cooling said raw synthesis gas mixture and
(d) separating condensed water from the raw synthesis gas mixture,

characterised in that prior to the step of separating the condensed water from the raw synthesis gas mixture, part of said raw synthesis gas mixture is recycled to the partial oxidation step.

The hydrocarbon feedstock may be methane, natural gas, ethane, LPG, naptha or other stream containing hydrocarbons. The hydrocarbon feedstock is preferably methane, accordingly, where natural gas is used it preferably contains a high proportion (i.e. >90% by volume) of methane. Preferably, the hydrocarbon feedstock has been subjected to a step of desulphurisation. Desulphurisation of the hydrocarbon feedstock prevents poisoning of the reforming and synthesis catalysts downstream of the reforming process. Desulphurisation may

be achieved by passing the hydrocarbon through a bed of a hydrodesulphurisation catalyst such as a cobalt-molybdenum catalyst and then through a bed of hydrogen sulphide absorbent such as zinc-oxide.

In one embodiment, in particular where hydrocarbons other than methane are present in the feedstock, it may be desirable to subject the hydrocarbon feedstock to a step of pre-reforming whereby a hydrocarbon feedstock is mixed with steam and the mixture subjected to adiabatic low temperature steam reforming. In such a step, the hydrocarbon/steam mixture is heated, typically to a temperature in the range 400-700°C, and then passed adiabatically through a bed of a suitable reforming catalyst, usually a catalyst having a high nickel content, for example above 40% by weight. During such a pre- reforming step, some methane is reformed and any hydrocarbons higher than methane react with steam to give a mixture of methane, steam, carbon oxides and hydrogen. Thus by including a pre-reforming step, the higher hydrocarbons which can crack to form carbon more readily than methane are eliminated. Thus the feed-gas to the partial oxidation step may preferably comprise a pre-reformed gas mixture. The pre-reformed gas mixture will comprise methane, hydrogen, steam, some carbon oxides and any unreacted higher hydrocarbon.

Steam may be added to the autothermal reforming process to augment the steam formed by the partial oxidation of the hydrocarbon feedstock. The steam may be added as part of the feed gas, e.g. by adding steam to the hydrocarbon feedstock, and/or may be added to the oxygen-containing gas. If the feed-gas to the partial oxidation step is a pre-reformed gas mixture, this will contain steam but if required, steam may be added to the pre-reformed gas mixture. Alternatively steam may be added separately to the reformer apparatus. Hence, steam introduction may be effected by direct injection to the reformer of steam at a suitable pressure and/or by saturation of the feedstock or pre-reformed gas mixture by contact of the latter with a stream of heated water, or by mixing with the oxygen-containing gas. Where steam is added, the amount of steam introduced is such as to give a steam ratio of 0.2 to 2, i.e. 0.2 to 2 moles of steam per gram atom of hydrocarbon carbon in the feedstock. The amount of steam is preferably minimised as this leads to a lower cost, more efficient process. It is preferred that the steam ratio is 0.2 to1.5 and more preferably 0.2 to 1.0.

The oxygen-containing gas is a gas containing free oxygen (O_2). The oxygen-containing gas may be air, oxygen-enriched air (i.e. air having >21% by volume oxygen) or substantially pure oxygen (i.e. oxygen >95% purity). Substantially pure oxygen may be provided by means of an air-separation unit (ASU) which may be powered for example by turbines driven by the steam produced in recovering heat from the raw synthesis gas mixture. Where the oxygen containing-gas is substantially pure oxygen, for metallurgical reasons it is preferably fed to the

reformer at a temperature below about 250°C, more preferably below 100°C, especially below 50°C.

The feed-gas is compressed and pre-heated, if necessary, and fed to an autothermal reformer having burner means where it is mixed with the oxygen-containing gas and possibly steam and non-catalytically partially oxidised in a flame combustion zone beneath the burner means. Typically the feed gas is fed to the reformer at a temperature greater than 450°C and at a pressure in the range 2 to 100, preferably 5 to 60 bar abs. The oxygen-containing gas is fed to the burner at a temperature below about 250°C and preferably at a pressure typically 1-5bar above the pressure of the feed-gas. The amount of oxygen used to partially oxidise the hydrocarbon feedstock effects the temperature of the raw synthesis gas mixture and hence its composition. In general, increasing the amount of oxygen, thereby increasing the temperature of the raw synthesis gas mixture leaving the autothermal reformer, causes the $[H_2]$ / [CO] ratio to decrease and the proportion of carbon dioxide to decrease. Decreasing the required amount of oxygen is advantageous as this means that a smaller, and hence cheaper, air separation unit can be employed to produce the oxygen. The amount of oxygen-containing gas added is preferably such that 40 to 90 moles, preferably 50 to 70 moles of oxygen (O_2) are added per 100 gram atoms of hydrocarbon feedstock fed to the reformer, i.e. an oxygen to hydrocarbon ratio of 0.5 to 0.7.

The partially oxidised gas mixture formed in the combustion zone is then contacted with a reforming catalyst that catalytically-reforms the gas mixture towards an equilibrium composition based upon the temperature, pressure and composition of the partially oxidised gas mixture. Steam reforming reactions occur, generating hydrogen. The reforming catalyst is preferably disposed as one or more fixed beds of catalyst, e.g. between 1 and 5 beds, underneath the flame-combustion zone. In an autothermal reformer the beds may be 1 to 5 metres in depth.

The reforming catalyst is a transition metal catalyst, preferably a first or second row transition metal catalyst, more preferably a nickel or cobalt catalyst, which may be supported on a suitable refractory support such as alumina, calcium-aluminate, magnesia, zirconia or the like. One or more transition metal reforming catalyst may be used in the bed or beds. Preferably the reforming catalyst comprises a supported nickel catalyst. The catalyst support may be in the form of rings or cylindrical multi-hole pellets but are preferably clover-leaf multi-hole or fluted-cylindrical multi-hole pellets of e.g. alumina or calcium aluminate. Such supports provide a reduced pressure drop through the bed of catalyst than rings or cylindrical multi-hole pellets.

The raw synthesis gas mixture comprising hydrogen, carbon oxides, steam and any unreacted hydrocarbon and inerts such as nitrogen or argon introduced by the oxygen-containing gas will be at a temperature in the range 900 to 1100°C. Cooling and subsequent separation of

condensed water from the raw synthesis gas mixture is required to provide a synthesis gas suitable for use in synthesis processes such as methanol synthesis, ammonia synthesis or liquid hydrocarbon synthesis, e.g. by the Fischer Tropsch process.

In the present invention at least part of the raw synthesis gas mixture is recycled to the partial oxidation step prior to separation of condensed water. The part of the raw synthesis gas mixture that may be recycled to the partial oxidation step will depend for example, upon the composition of the oxygen-containing gas, and may be in the range 1 to 99% by volume, preferably in the range 10 to 70% by volume, more preferably 10 to 35% by volume. The raw synthesis gas mixture may be recycled directly by direct injection into the autothermal reformer or may be mixed with the feed-gas or steam. Accordingly the feed-gas may comprise a mixture of hydrocarbon and raw synthesis gas mixture, steam and raw synthesis gas mixture, hydrocarbon, steam and raw synthesis gas mixture or pre-reformed gas (optionally with added steam) and raw synthesis gas mixture. Alternatively, the raw synthesis gas may be combined with the hydrocarbon/steam mixture prior to any prereforming step.

Cooling may be effected on the raw synthesis gas mixture to reduce the thermal burden on the recycling equipment. In some synthesis processes, e.g. the manufacture of hydrogen and ammonia, it is preferred that the raw synthesis gas mixture is partially cooled, e.g. to below about 450°C, prior to cooling to below the dew-point and separation of condensed water, so that the partially-cooled raw synthesis gas mixture may be subjected to the water gas shift reaction. The water-gas shift reaction can be used to convert carbon monoxide to carbon dioxide and increase the hydrogen content of the synthesis gas. The water-gas shift reaction may be performed for example, using an iron-based high-temperature shift catalyst at about 450°C, or a copper-based low-temperature shift catalyst at about 230°C. Cooling may be performed by means such as steam raising boilers and other forms of heat-exchange apparatus known to those skilled in the art. Cooling may extend to below the dew-point of the steam in the raw synthesis gas mixture, i.e. the temperature at which water condenses from the pressurised raw synthesis gas mixture. The temperature of the dew-point will be dependant upon the operating pressure of the process, but typically, the dew-point will typically occur in the range 20 to 60°C.

Cooling the raw synthesis gas mixture may however necessitate a subsequent re-heating step using heat exchange equipment after the recycling equipment in order to bring the recycled raw synthesis gas mixture to a temperature suitable for feeding to the partial oxidation step. Furthermore, cooling without separation of condensed water requires that an increased amount of oxygen-containing gas is required for the partial oxidation step compared to the situation had it not been cooled. Similarly, performing the water-gas shift reaction on the partially-cooled raw synthesis gas mixture prior to recycle may require an increased amount of oxygen-containing

gas at the partial oxidation step. Furthermore, if the raw synthesis gas mixture is cooled to below its dew-point, additional heat will be required to vapourise the condensed water. Accordingly, in a preferred embodiment, the raw synthesis gas mixture is recycled to the partial oxidation step prior to a cooling step. Recycle of raw synthesis gas mixture prior to the cooling step also has the benefit that lower steam ratios may be employed than would otherwise be necessary, e.g. a steam ratio of 0.2 to 0.6 may be achieved. Furthermore, such a recycle reduces the need for a pre-reformer, and may eliminate the need for it with light hydrocarbon gases such as natural gas. It will be understood that some cooling of the raw synthesis gas mixture may occur by radiative losses from the recycling equipment and/or connecting pipework, but it is preferred that the raw synthesis gas mixture is fed to the partial oxidation step at a temperature in the range 600-1100°C, preferably 800-1100°C.

Accordingly, the recycle equipment is preferably fabricated using suitable heat-resistant materials. Raw synthesis gas mixture recycle may be affected by suitable recycle equipment operatively connected to the autothermal reformer such as compressors or circulators with suitable flow-control valves, however we have found a particularly suitable method for recycle is by means of an ejector. Thus in a preferred embodiment the recycle equipment comprises an ejector operatively connected to the autothermal reformer. An ejector works on the Venturi principle whereby a driving fluid, such as a gas under pressure, is passed through a constriction into an expansion region in which the fluid is at a lower pressure than the fluid in the constriction. Using a suitably pressurised driving fluid, the difference in pressure between the lower pressure expansion region and the pressure of the raw synthesis gas mixture results in the desired recycle. Because a pressure drop occurs through the autothermal reformer apparatus an ejector is able to effect recycle of the raw synthesis gas mixture using the pressurised feed-gas or steam as the driving fluid. The ejector also provides efficient mixing of the driving fluid and the raw synthesis gas mixture.

In the present invention, the ejector is external to the autothermal reformer. The driving fluid therefore may be steam or the feed-gas, said feed-gas comprising the hydrocarbon feedstock and optionally steam or a pre-reformed gas mixture comprising hydrocarbon, steam, hydrogen and carbon oxides. Because the cooling step typically may provide high-pressure steam, preferably, the driving fluid is a steam-containing gas.

Using an ejector to effect recycle has the advantage that there are no moving parts and that the equipment may be fabricated to tolerate high temperatures. The amount of raw synthesis gas mixture that is recycled using an ejector may be controlled by altering the pressure of the driving fluid but preferably the amount is controlled by by-passing a portion of the driving fluid, e.g. feed-gas, around the ejector or by using a variable throttle ejector having an adjustable

constriction. Control valves may be employed in the by-pass line where the temperature of the raw synthesis gas mixture is below 650°C.

The present invention provides an autothermal reforming process with increased versatility and economy in respect of steam and oxidant and provides a synthesis gas of appropriate composition for a number of synthesis processes, particularly for the synthesis of liquid hydrocarbons by e.g. the Fischer Tropsch process.

The invention is illustrated by reference to the accompanying drawings in which;

Figure 1 is a diagrammatic flowsheet of one embodiment of the invention whereby recycle of raw synthesis gas mixture is effected by means of an ejector.

In figure 1, a pressurised hydrocarbon/steam mixture, prepared for example by saturation of a natural gas feedstock by hot water in a saturator, is fed via line 10 to a heat exchanger 12 where it is heated to between 400-700°C and then fed via line 14 to a pre-reformer 16 containing a bed of a supported nickel pre-reforming catalyst 18. The hydrocarbon/steam mixture undergoes partial steam reforming whereby some methane is reformed and higher hydrocarbons are converted to methane. The pre-reforming reaction is endothermic and the pre-reformed gas mixture, comprising methane, steam, carbon oxides and hydrogen is fed via line 20 to a heat exchanger 22 where it is heated to >400°C and fed via line 24 as the driving fluid to an ejector 26 wherein the pre-reformed gas mixture passes through a constriction into an expansion region thereby creating a lower pressure region that may be used to effect recycle of a raw synthesis gas mixture stream fed to the ejector 26 via line 28. The mixed pre-reformed gas and raw synthesis gas mixture are then fed via line 30 as the hydrocarbon-containing feed-gas to the top of an autothermal reformer 32. Substantially pure oxygen at a temperature of <250°C is fed via line 34 to burner means 36 located at the top of the autothermal reformer. Non-catalytic partial oxidation of the feed-gas occurs underneath the burner in a flame-combustion zone 38. The resulting partially oxidised gas stream is then passed through a bed of a supported nickel reforming catalyst 40 that brings the composition of the partially-oxidised gas mixture towards equilibrium thereby generating a raw synthesis gas mixture comprising hydrogen, steam and carbon oxides at a temperature in the range 900-1100°C. The raw synthesis gas mixture leaves the reformer 32 via line 42. The recycle line 28 from line 42 conveys the part of the raw synthesis that is recycled to the ejector 26. The remaining raw synthesis gas mixture is cooled in one or more heat exchangers 44, such as a steam raising boiler followed by further heat exchangers that cool the raw synthesis gas mixture to below the dew-point of the steam. The cooled raw synthesis gas mixture is then fed via line 46 to a separator 48 wherein the condensed water is separated from the synthesis gas. The condensed water is taken from the separator 48 via line 50 and may be recycled, e.g. to a saturator. The synthesis gas leaves the separator 48 via line 52 and is fed to a synthesis process, e.g. a Fischer-Tropsch process.

The invention is further illustrated by reference to the following calculated example based upon the process depicted in Figure 1 and comparative examples 1-3 having modifications described below to the process as depicted in figure 1.

Four cases were examined based on an autothermal reformer operated under conditions suitable to generate synthesis gas for synthesis of liquid hydrocarbons via the Fischer-Tropsch process. In all four cases the following conditions were fixed;

1. The hydrocarbon feedstock was desulphurised natural gas, at a fixed flowrate of 5000 kmol/h. The steam flowrate was fixed at 2809 kmol/h. The feedstock steam ratio was 0.525.
2. The natural gas at 400°C and steam at 250°C were mixed at circa 27bar abs. and heated up to 520°C in the heat exchanger 12.
3. The mixed natural gas/steam mixture was pre-reformed in pre-reformer 16 where the higher hydrocarbons were reformed to give a pre-reformed gas at circa 490°C and 26.5 bar abs.
4. The heat exchanger 22 was operated in each case to achieve a feed-gas temperature in line 24 of 650°C.
5. Oxygen was provided to the burner 36 at a temperature of 200°C and at a variable flowrate to achieve a raw synthesis gas mixture exit temperature of 1050°C.

Comparative example 1 – no recycle of raw synthesis gas mixture (base case)

The scheme is as depicted in Figure 1 but without ejector 26 and recycle line 28.

The pre-reformed gas mixture is the hydrocarbon-containing feed-gas to the autothermal reformer. It is fed to the autothermal reformer at 650°C and circa 25.5 bar abs.
The raw synthesis gas mixture is produced at a pressure of 25 bar abs.
The reformed gas is cooled in heat exchangers 44, e.g. firstly in a waste heat boiler, cooling the gas to 350°C that raises steam at 105 bar abs. from boiler feed water at its bubble point. The synthesis gas is then cooled in further heat exchangers down to 50°C, at which temperature most of the water content of the synthesis gas has been condensed. The process condensate is then separated in the separator 48 and sent for reuse. The synthesis gas, which has a H_2:CO ratio of 2.10:1 is then fed via line 52 to the Fisher Tropsch synthesis loop.

Comparative example 2 – recycle of cooled and de-watered synthesis gas

The scheme is as depicted in Figure 1 but without ejector 26 and recycle line 28. Rather a recycle of cooled, de-watered synthesis gas is taken from line 52, via a compressor to the pre-reformed gas mixture in line 20 (prior to heat exchanger 22).

20.3% volume of the cooled, de-watered synthesis gas is recycled from line 52 back to the pre-reformed gas mixture in line 20. Hence the hydrocarbon-containing feed-gas in line 24 is a mixture of pre-reformed gas and de-watered synthesis gas which has been heated in heat exchanger 22 to 650°C and is at a pressure of circa 25.5 bar abs. Because the synthesis gas is cool, this increases the overall heat input required. The compression requirements are modest, with the recycled cold de-watered synthesis gas being available at circa 23 bar abs.

The remaining 79.7% vol. synthesis gas is fed via line 52 to the Fisher Tropsch synthesis loop. Due to the changed composition of the cooled, de-watered synthesis gas compared to the raw synthesis gas mixture, the product raw synthesis gas mixture has a different composition from that with no recycle (H_2:CO ratio = 2.02) and therefore produces less final product in the Fischer-Tropsch process. Furthermore, as the recycle gas passes through the autothermal reformer and has a sensible heat demand, the required oxygen flow to achieve 1050°C is greater than the oxygen flow without recycle.

Comparative example 3 – recycled hydrogen separated from cooled, de-watered synthesis gas

The scheme is as depicted in Figure 1 but without ejector 26 and recycle line 28. Rather a recycle of cooled, de-watered synthesis gas is taken from line 52 to a hydrogen-separation unit utilising e.g. membranes, to provide a hydrogen-rich gas and a hydrogen-depleted cold, de-watered synthesis gas. The hydrogen-rich gas is recycled via a compressor to the pre-reformed gas mixture in line 20 (prior to heat exchanger 22) while the hydrogen-depleted, cool, de-watered synthesis gas is returned to line 52.

This arrangement further also requires that the cold, de-watered synthesis gas is re-heated above the dew point prior to the hydrogen separation unit to prevent contamination of the membranes with moisture. The membranes remove about 17.6% by volume of the total hydrogen production, which is recycled to the pre-reformed gas mixture. As the hydrogen is the permeate, it is at lower pressure, e.g. ca. 5 bar abs. and requires compression to the feed pressure of circa 25.5 bar abs. This is a greater compression duty than that of comparative example 2. The remaining synthesis gas (which consists of the synthesis gas bypassing the recycle plus the membrane retentate) is fed via line 52 to the Fisher Tropsch synthesis loop. The recycled cold hydrogen-rich gas is combined with the pre-reformed gas mixture in line 20

and these form the hydrocarbon-containing feed-gas to the autothermal reformer. This mixture is fed via line 24 to the autothermal reformer at 650°C and circa 25.5bar abs. Again, because the synthesis gas is cool, this increases the overall heat input required.

Furthermore, due to the changed composition of the recycled synthesis gas compared to the raw synthesis gas mixture, the product raw synthesis gas mixture has a different composition (H_2:CO ratio = 2.01:1) and therefore produces less final product in the Fischer-Tropsch process. As the recycle gas passes through the autothermal reformer and has a sensible heat demand, the required oxygen flow to achieve 1050°C is greater than the oxygen flow without recycle.

Example 1 – Recycle of raw synthesis gas mixture by means of an ejector

The scheme is as depicted in Figure 1.

21.6% by volume of the hot raw synthesis gas mixture is recycled via line 28 back to the re-heated pre-reformed gas mixture in line 24 (i.e. after it has passed through heat exchanger 22). The compression requirements are very low for this recycle duty, with the recycled gas being available at circa 25 bar abs. in line 28 and the feed pressure to the ATR is circa 25.5 bar abs in line 30. The compression power is supplied by an ejector 26 driven by the re-heated pre-reformed gas at 650°C. The pressure of the re-heated pre-reformed gas is 27.0 bar abs in line 24 compared to the comparative example 1 pressure of 25.5 bar abs, a modest increase in the feed-gas feed pressure. The remaining 78.4% vol raw synthesis gas mixture is cooled in the heat exchangers 44, and because the cooling is performed after the recycle stream 28 is split off, the cooling duties are the same as comparative example 1. The recycled raw synthesis gas mixture is at 1050°C and when mixed with the pre-heated pre-reformed gas 24 (650°C) forms the hydrocarbon-containing feed-gas for the autothermal reformer at approximately 750°C. As the recycled raw synthesis gas mixture does not flow through the heat exchanger 22 the overall heating duty is the same as that in comparative example 1.

Since the composition of the recycled raw synthesis gas mixture is exactly the same as the autothermal reformer effluent, and it is recycled at full temperature, the product raw synthesis gas mixture has exactly the same composition (H_2:CO ratio = 2.10) as the comparative example 1. Therefore, Example 1 produces the same final Fischer-Tropsch product as the base case but with no increase in sensible heat demand in the autothermal reformer or, the required oxygen flow to achieve a raw synthesis gas mixture temperature of 1050°C.

The results are summarised in the following table;

	Comparative 1 (base case)	Comparative 2	Comparative 3	Example 1
Natural gas flow kmol/hr	5000	5000	5000	5000
Steam flow kmol/hr	2809	2809	2809	2809
Oxygen flow kmol/hr	2803	2907	2854	2804
Feedstock steam:carbon ratio	0.525	0.525	0.525	0.525
Potential $(CH_2)_n$ FT product rate kmol/hr	4684	4539	4544	4684
Product H_2:CO ratio	2.10	2.02	2.01	2.10
Total heating load MW	39.9	59.9	51.6	39.8
Total cooling load MW	198	236	220	198
Steam raised Te/hr	335	404	374	335
Feed-gas pressure Bar abs	25.5	25.5	25.5	27.0
ATR Steam:carbon ratio	0.436	0.436	0.435	0.580
Carbon-potential $(P[H_2])^2/P[CH_4]$ bar abs.	0.26	3.82	3.36	4.17

The above table shows that comparative example 1 (no recycle) has a reaction quotient for the methane cracking reaction of 0.26. A low value of the reaction quotient indicates that carbon formation is thermodynamically possible. At a temperature of 650°C, the equilibrium reaction quotient is 3.25, i.e. a value less than 3.25 may lead to thermal cracking of the feed gas. Therefore, the base case scheme could potentially give rise to carbon formation from methane cracking should there be an active surface present for this reaction. Although each of the comparative examples has a reaction quotient above the equilibrium value, Example 1 has the highest reaction quotient of all the examples and therefore is the furthest from the equilibrium value. Furthermore, the steam to carbon ratio of the hydrocarbon-containing gas as it flows into the autothermal reformer is the same for all the comparative examples but is higher for Example 1. Therefore, this case exhibits an additional improvement over and above the comparative examples, as the additional steam will further suppress the formation of carbon.

Claims.

1. A reforming process comprising the steps of;
   (a) partially oxidising a feed-gas comprising a hydrocarbon feedstock with an oxygen-containing gas,
   (b) bringing the composition of the resulting partially oxidised gas stream towards equilibrium by passing said partially oxidised gas stream over a reforming catalyst to provide a raw synthesis gas mixture,
   (c) cooling said raw synthesis gas mixture and
   (d) separating condensed water from the raw synthesis gas mixture,
   characterised in that prior to the step of separating the condensed water from the raw synthesis gas mixture, part of said raw synthesis gas mixture is recycled to the partial oxidation step.

2. A process according to claim 1 wherein the feed-gas comprises a pre-reformed gas mixture.

3. A process according to claim 1 or claim 2 wherein the part of raw synthesis gas mixture that is be recycled to the partial oxidation step is in the range 1 to 99% by volume.

4. A process according to any one of claims 1 to 3 wherein the reforming catalyst comprises a supported nickel catalyst.

5. A process according to any one of claims 1 to 4 wherein the raw synthesis gas mixture is cooled to below 450°C and subjected to the water gas shift reaction prior to separation of condensed water.

6. A process according to any one of claims 1 to 5 wherein the raw synthesis gas mixture is recycled prior to the cooling step.

7. A process according any one of claims 1 to 6 wherein the raw synthesis gas mixture is recycled to the partial oxidation step by means of an ejector.

8. A process according to claim 7 wherein the ejector is driven by the feed gas.

9. A process according to claim 7 or claim 8 wherein the ejector is driven by a steam containing gas.

10. A process according to any one of claims 1 to 9 wherein the oxygen containing gas is substantially pure oxygen and is fed to the process at a temperature below 250°C.

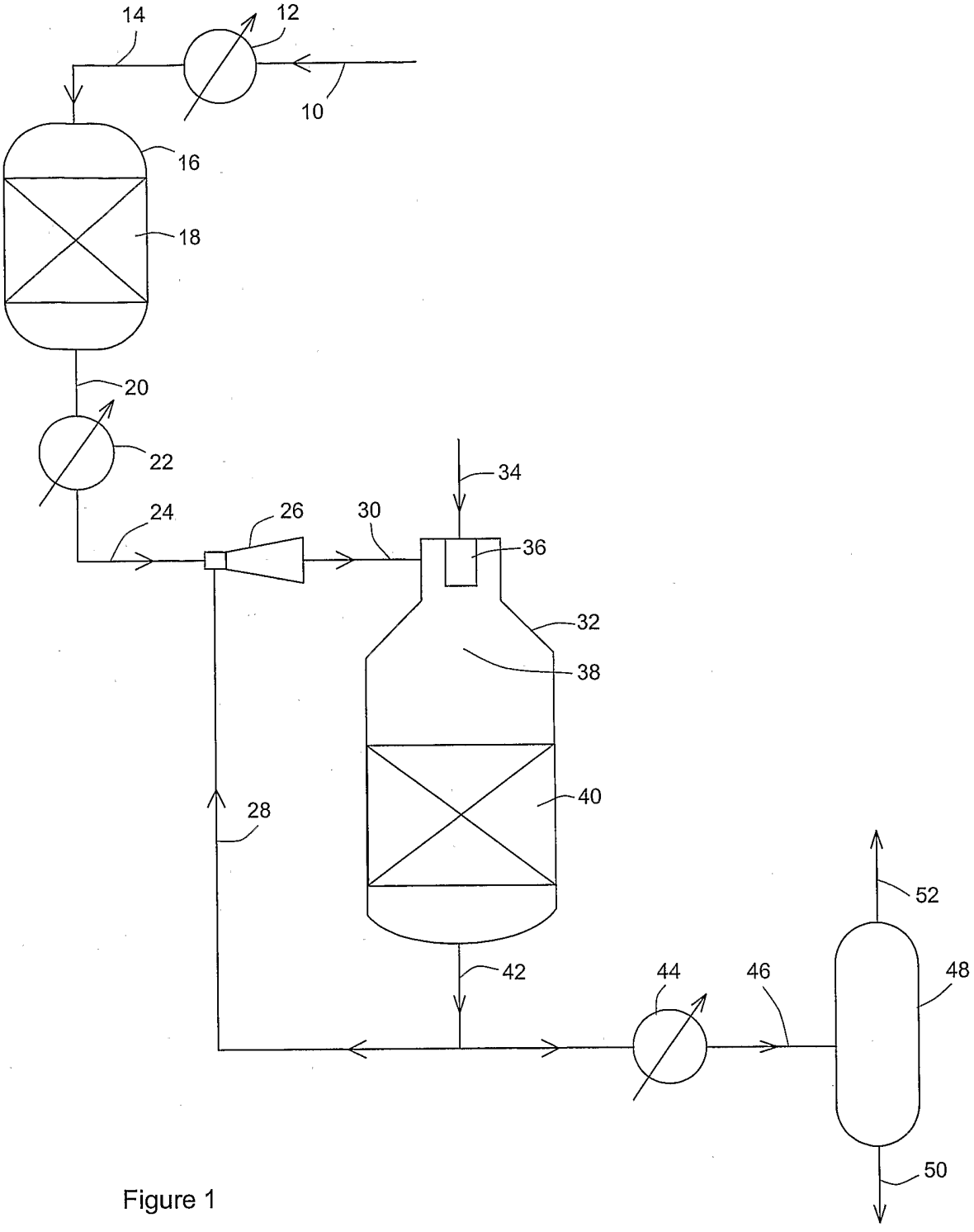

Figure 1

INTERNATIONAL SEARCH REPORT

ıational Application No
PCT/GB2004/002407

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/38

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)
IPC 7 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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 0 723 930 A (TEXACO DEVELOPMENT CORP) 31 July 1996 (1996-07-31) the whole document	1,3,4,6 2,5,7-10
Y	CHRISTENSEN R S ET AL: "IMPROVE SYNGAS PRODUCTION USING AUTOTHERMAL REFORMING" HYDROCARBON PROCESSING, GULF PUBLISHING CO. HOUSTON, US, 1 March 1994 (1994-03-01), pages 39-42,44,46, XP000199938 ISSN: 0018-8190	2,10
A	the whole document	1
A	EP 0 989 094 A (TOPSOE HALDOR AS) 29 March 2000 (2000-03-29) the whole document	1,2,10

-/--

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

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 September 2004	08/09/2004

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, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Engelen, K

INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB2004/002407

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00/03126 A (SAIGNE MICHEL ; SOYEZ WERNER (BE); NORSK HYDRO AS (NO); FJELLHAUG HENR) 20 January 2000 (2000-01-20) the whole document	5
A	EP 0 287 238 A (ICI PLC) 19 October 1988 (1988-10-19) cited in the application	1,6-9
Y	the whole document	7-9
A	GB 2 265 380 A (SHELL INT RESEARCH) 29 September 1993 (1993-09-29) page 2, line 15 - page 5, line 4; figure 1	1,7-9
A	WO 01/46068 A (PIETERSE COEN WILLEM JOHANN ; SEVENHUIJSEN ERIC (NL); WENTINCK HENDRIK) 28 June 2001 (2001-06-28) the whole document	1
P,X	EP 1 400 489 A (KELLOGG BROWN & ROOT INC) 24 March 2004 (2004-03-24) the whole document	1,6-10
P,A	WO 03/062141 A (SMAGGASGALE GILLIAN HELEN ; RYTTER ERLING (NO); STATOIL ASA (NO); GRIS) 31 July 2003 (2003-07-31) the whole document	1,4-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

rnational Application No
CT/GB2004/002407

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0723930 A	31-07-1996	US 5496859 A	05-03-1996
		AU 692974 B2	18-06-1998
		AU 4218996 A	08-08-1996
		BR 9600210 A	07-10-1997
		CA 2163615 A1	29-07-1996
		EP 0723930 A2	31-07-1996
		IN 184751 A1	23-09-2000
		NO 955160 A	29-07-1996
EP 0989094 A	29-03-2000	DK 121198 A	26-03-2000
		CN 1249267 A	05-04-2000
		DE 989094 T1	14-08-2003
		EP 1426329 A1	09-06-2004
		EP 0989094 A2	29-03-2000
		JP 2000185904 A	04-07-2000
		KR 2000023408 A	25-04-2000
		NO 994653 A	27-03-2000
		TW 486515 B	11-05-2002
		US 2001008621 A1	19-07-2001
		ZA 9906123 A	06-04-2000
WO 0003126 A	20-01-2000	WO 0003126 A1	20-01-2000
		AT 249572 T	15-09-2003
		AU 744197 B2	21-02-2002
		AU 8753898 A	01-02-2000
		BR 9815946 A	28-02-2001
		CA 2337394 A1	20-01-2000
		DE 69818111 D1	16-10-2003
		DE 69818111 T2	03-06-2004
		EE 200100019 A	17-06-2002
		EP 1105625 A1	13-06-2001
		ES 2206972 T3	16-05-2004
		HU 0102620 A2	28-11-2001
		ID 28247 A	10-05-2001
		JP 2002520533 T	09-07-2002
		NO 20006618 A	22-12-2000
		NZ 509572 A	31-10-2003
		PL 345658 A1	02-01-2002
		RU 2213051 C2	27-09-2003
		SK 392001 A3	06-08-2001
		US 6505467 B1	14-01-2003
EP 0287238 A	19-10-1988	IN 172368 A1	03-07-1993
		AT 58512 T	15-12-1990
		AT 67153 T	15-09-1991
		AU 598123 B2	14-06-1990
		AU 1448088 A	13-10-1988
		AU 589527 B2	12-10-1989
		AU 7326887 A	03-12-1987
		CA 1272602 A1	14-08-1990
		CA 1299088 C	21-04-1992
		DE 3766311 D1	03-01-1991
		DE 3864721 D1	17-10-1991
		EP 0254395 A2	27-01-1988
		EP 0287238 A2	19-10-1988
		IN 178329 A1	29-03-1997
		IN 173499 A1	21-05-1994
		JP 1721596 C	24-12-1992

INTERNATIONAL SEARCH REPORT

Information on patent family members

rnational Application No
PCT/GB2004/002407

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0287238 A		JP 4006841 B	07-02-1992
		JP 63282410 A	18-11-1988
		JP 2079044 C	09-08-1996
		JP 6094225 A	05-04-1994
		JP 7117221 B	18-12-1995
		NO 872207 A ,B,	30-11-1987
		NO 881572 A ,B,	14-10-1988
		NZ 220346 A	27-07-1989
		NZ 224141 A	26-02-1990
		US 4788004 A	29-11-1988
		US 4938685 A	03-07-1990
		US 5048284 A	17-09-1991
		US 5110563 A	05-05-1992
		ZA 8802425 A	22-02-1989
		CA 1331696 C	30-08-1994
		DE 68914051 D1	28-04-1994
		DE 68914051 T2	21-07-1994
		EP 0351094 A1	17-01-1990
		JP 1818424 C	27-01-1994
		JP 5024844 B	09-04-1993
		JP 62295993 A	23-12-1987
		JP 2070928 A	09-03-1990
		JP 2757966 B2	25-05-1998
GB 2265380 A	29-09-1993	CA 2091748 A1	24-09-1993
WO 0146068 A	28-06-2001	AU 2170201 A	03-07-2001
		WO 0146068 A1	28-06-2001
		EP 1244599 A1	02-10-2002
		JP 2003517985 T	03-06-2003
		US 2002192154 A1	19-12-2002
EP 1400489 A	24-03-2004	US 2004057898 A1	25-03-2004
		CA 2435960 A1	23-03-2004
		EP 1400489 A1	24-03-2004
		JP 2004115365 A	15-04-2004
WO 03062141 A	31-07-2003	WO 03062141 A1	31-07-2003