

Title: Method for the control of pressure in a loop for the preparation of ammonia or methanol

The present invention is directed to the method for the control of pressure in a loop for the preparation of ammonia or methanol. More particular, the invention makes use of the anti-surge control valve of a compressor and/or a compressor flow regulation valve for the recirculation of an ammonia or methanol loop recirculation gas at varying flow of fresh ammonia or methanol synthesis gas.

As an example, ammonia synthesis gas is conventionally prepared by subjecting hydrocarbon feed of natural gas or higher hydrocarbons to endothermic steam reforming reactions in a fired tubular steam reformer by contact with a steam reforming catalyst. The primary reformed gas is then fed into a secondary adiabatic reformer, wherein part of hydrogen and residual amounts of hydrocarbons in the gas are partial oxidized with air or oxygen enriched air in presence of a secondary reforming catalyst. From the secondary reformer, raw synthesis gas containing hydrogen, nitrogen, carbon monoxide and carbon dioxide formed during reaction of the feedstock in the above steam reforming reactions and nitrogen introduced into the gas through addition of air in the secondary reforming step.

The primary and secondary steam reforming can in large scale ammonia or methanol synthesis plants be replaced by autothermal reforming (ATR).

Recently, use of renewable energy in the ammonia or methanol synthesis has become more available. As an example,

combination of electrolysis of water operated on renewable energy, such as wind power and solar energy for the production of hydrogen by electrolysis of water and air separation for the production of nitrogen has been envisaged for the preparation of ammonia synthesis gas. The thus produced hydrogen and nitrogen are combined in stoichiometric ratios to form synthesis gas for ammonia production.

The problem when using renewable energy in the ammonia or methanol synthesis is that the supply of energy varies depending on the natural variations of for instance wind and sun. As a result, the flow of fresh methanol or ammonia synthesis gas produced by means of renewable energy can vary substantially.

Because of relatively low single pass conversion rates of ammonia or methanol synthesis gas in the respective converters caused by equilibrium limitations, a large loop recycle stream of unconverted synthesis gas is required in the loops.

To substitute converted hydrogen and nitrogen in the unconverted synthesis gas, a make-up gas of fresh ammonia synthesis gas must constantly be added into the loop recycle gas. Similar, to the ammonia synthesis, converted hydrogen and carbon oxides must be substituted in the methanol synthesis loop with fresh hydrogen and carbon oxides containing synthesis gas.

In case of large and frequent load variations because of varying flow of fresh synthesis gas to the synthesis loop, the mechanical stress caused by pressure variations

introduced by the load variations will lead to unreferenced mechanical stress conditions that may cause mechanical failures of pressure bearing equipment. The temperature variations, however, will be limited.

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Such operating conditions are especially relevant when the production is dependent on a variable flow of feedstock such as it is the case for green ammonia or methanol production.

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Traditionally an ammonia and methanol loop does not feature a dedicated pressure control. In case of reduced feed flow to the loop, the loop pressure will drop. Thereby the conversion will reduce to a point eventually matching the make-up flow. In case of increasing feed flow, the pressure and the conversion will increase. Since the load of a traditional ammonia and methanol plants tends to be stable over long periods, the absence of a pressure control does not normally represent a problem.

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For a given ammonia converter/loop configuration a possible way to control the loop pressure is varying the H/N ratio in the in the fresh ammonia synthesis gas, i.e. the make-up gas can to decrease the reactivity of the gas. In some cases, it is also possible to vary the contents of inerts in the loop by reducing the purge flow, but this is seldom relevant for green ammonia production where the make-up gas is very low in inerts. In practice, however, it is difficult to control loop pressure with this method.

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We have found that the amount of feed gas to the ammonia and methanol reactor can be controlled by the anti-surge control of the recirculator (loop recycle compressor). The antisurge or kickback valve is typically a fast reacting control element for protection against surge resulting in vibrations and thus damage of the compressor.

Pursuant to the above finding, the present invention provides a method for the control of pressure in a loop for the preparation of ammonia or methanol comprising the steps of

- (a) providing a fresh ammonia or methanol synthesis gas;
- (b) providing a loop recirculation gas;
- (c) providing a loop recirculation compressor with an anti-surge valve and/or a compressor flow regulation valve;
- (d) providing an ammonia or methanol synthesis loop;
- (e) adding the fresh ammonia or methanol synthesis gas into the loop recirculation gas;
- (f) pressurizing the loop recirculation gas from step (e) in the loop recirculation compressor; and
- (g) monitoring pressure in the ammonia or methanol synthesis loop,

wherein flow of the loop recirculation gas through the anti-surge valve and/or the recirculation compressor flow regulation valve is controlled to obtain a substantially constant pressure in the ammonia or methanol synthesis loop.

In case of slow load variation (days or weeks), the method according to the invention can be supplemented by control of the temperature in a high pressure ammonia or methanol

loop separator. Thereby reactivity of the loop recirculation loop gas flowing to the ammonia converter can be reduced when the concentration of ammonia in the feed gas is increased. Higher temperature leads to less reactivity and higher loop pressure.

Thus, in an embodiment of the invention the method comprises the further step of controlling temperature in a loop separator arranged in the loop for the preparation of ammonia or methanol.

The loop separator separates liquid ammonia or methanol product from the unconverted gas effluent from the synthesis converter at equilibrium between gas and liquid at the given pressure and temperature. At constant pressure and higher temperature gives higher content of product in unconverted gas to be recycled back to the synthesis converter. This will lower the potential conversion per pass since the synthesis reaction is limited by equilibrium resulting in reduced capacity of the synthesis loop at constant pressure.

One of the advantages of the invention is that energy for operating various equipment for the preparation of ammonia synthesis gas can be renewable energy generated by windmills, solar cells, hydraulic energy or other renewables.

Preferably, the equipment comprises one or more electrolysis units, such as solid oxide electrolysis cells.

Thus, in an embodiment of the invention, hydrogen contained in the fresh ammonia or methanol synthesis gas is provided by means of electrolysis of water.

5 In further an embodiment, nitrogen contained in the fresh ammonia synthesis gas is provided by means of air separation.

10 In still an embodiment of the invention, the fresh methanol synthesis gas is provided by co-electrolysis of water and carbon dioxide.

15 In further an embodiment of the invention, the fresh ammonia synthesis gas is prepared in a solid oxide electrolysis cell of water and air.

Fig. 1 shows a typical configuration of the make-up gas compressor, recirculator and synthesis loop.

20 If the antisurge valve is open, then less flow will pass on to the reactor. During start-up where the synthesis reactor is heated up by circulating gas in the loop and having the start-up heater ignited then the antisurge will initially be fully open in order to protect the recirculator from
25 surge and to reduce the flow rate to the reactor for easy control of the heating up phase.

30 The same valve (antisurge valve) is used simultaneously as compressor protection and flow control valve to the reactor. This is feasible as the two functions are never contradictory and in any case the machine protection will

overrule all other set point to the valve. This concept is well proven for start-up of the synthesis.

5 Using renewable energy for production of synthesis gas will provide fluctuations throughout a day in feed gas flow rate resulting in many and possibly also abrupt synthesis pressure fluctuations. This can be smoothed out or even eliminated by the method according to the invention.

10 In normal operation, the recirculator antisurge valve can be used for control of the loop pressure. At full capacity the valve will remain closed and if less make up gas is available then the recirculation gas flow will be reduced correspondingly by controlled opening of the valve.

15 This will limit the conversion of synthesis gas in the loop to exactly the amount of make-up gas available resulting in keeping the same amount of gas in the loop and thus constant loop pressure.

20 There might be an understanding of the loop pressure is also controlled by the make-up compressor speed, but this is not the case as the make-up gas compressor will deliver the required pressure for a given conversion in the loop.

25 Since the method of the invention controls the conversion in the loop to maintain a constant loop pressure then the make-up gas compressor will follow the loop requirement. The only way the make-up gas compressor can do that and
30 still be within its operating window (flow versus discharge

pressure) is by opening its own antisurge valve(s) to compensate for the lower make-up gas flow available (see figure 1 and 2).

5 There could be cases where it is not allowed to use the antisurge valve for loop pressure control valve. Then the alternative would be to install a control valve in parallel without jeopardizing the compressor surge protection as the
10 antisurge valve opening is still governed by the compressor requirement measured as resulting flow from two control valves to the suction of the recirculator (see Fig. 2).

Since the conversion equilibrium temperature remains constant, a control which ensure the ratio between make-up gas
15 and converter feed gas remains constant will nearly eliminate pressure and temperature fluctuations in the converter and ammonia loop.

Because the anti-surge valve has a security function, the
20 flow from the compressor discharge side to suction side may additionally or completely be regulated by means of compressor flow regulation valve during feed gas flow variations.

25 The examples of Fig. 1 and 2, will have a limitation on the turn down of the gas flow since the minimum flow to the converter will depend on the pressure drop ratio between the converter and the anti-surge valve.

30 Fig. 3 shows a configuration where the gas flow to the converter can be controlled down to a zero flow by means of a loop pressure controller and optionally a small bypass

valve. When reducing or closing the loop pressure controller, the synthesis gas in the synthesis reactor is retained in the reactor and maintains the reactor pressure. This will allow the loop pressure to be controlled down to very low load and still keep the loop pressure up and the converter in hot conditions. This is important in the case where suddenly the renewable energy and thus synthesis gas production comes back from low load to high load, then the conversion of synthesis gas into ammonia or methanol can take place essentially instantaneous.

Fig. 4 shows a similar process layout as shown in Fig. 3, where one or more valves are foreseen to control converter inlet flow, recirculator anti-surge flow, and make-up gas compressor anti-surge flow. The module of the make-up gas is controlled by a ratio controller of hydrogen and nitrogen flow in ammonia synthesis gas by controlling the nitrogen flow rate relative to the hydrogen flow rate. With many fluctuations perhaps daily in energy supply, and thus directly impacting the hydrogen flow rate and also the nitrogen flow rate, the measurement of hydrogen and nitrogen flow might get a bit off set at each fluctuation. A small change in the make-up gas module will be amplified in the module of the loop recirculation gas and for this reason it is desirable to improve the module controller by having a near real-time analyzer on the make-up gas. Typically, a common gas chromatography analyzer is used for multiple sampling point leading to long tubing from each sampling point to the analyzer, which results in long cycle time for each analysis. Long cycle time of 10-20 min. is not suitable for adjustment of the module controller. A real-time analyzer can provide a cycle time of 10-20 sec. and the

module controller can act in time before a wrong module gets amplified in the loop resulting in loss of capacity and/or pressure increase when high capacity is required.

- 5 In the figures, A defines an analysis point, F a flow measurement point, and P a pressure measurement point.