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CO-PRODUCTION OF AMMONIA, METHANOL, AND/OR POWER FOR EXPORT

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RESUME

Récemment, on a commandé une grande unité industrielle pour la production d'ammoniac et de méthanol. De plus, plusieurs projets en vue de la production intégrée d'ammoniac et de grandes quantités d'énergie sont étudiés sérieusement.

Cette communication décrit les schémas de procédé pour les unités de production intégrée en terme de coûts de production et de rendement énergétique. Des matières premières légères (gaz naturel) et lourdes (produits pétroliers lourds ou charbon) seront examinées.



INTRODUCTION

Recently a large grassroots plant for combined production of ammonia and methanol was contracted. Also, several projects for integrated production of ammonia and large amounts of power are being seriously considered.

The paper will describe process schemes for integrated production units and discuss the advantages which can be obtained in terms of production cost and energy efficiency. Both light feedstock (natural gas) and heavy feedstock (heavy oil products or coal) will be considered.

PROCESS SCHEME

Almost all natural gas based plants are based on the overall process scheme shown in Figure 1 introduced more than 30 years ago, featuring desulphurization, primary (fired tubular) and secondary reforming, two-step shift conversion, carbon dioxide removal, methanation and synthesis. Over the years this process scheme has been gradually improved by introduction of new technology in the individual process steps, by overall optimization of the process lay-out, and by extensive integration between the process units and the steam and power system.

A general view of ammonia technologies including the Topsøe Ammonia Technology seems to be that it is a mature technology where little or no new development is taking place. However, in reality the technology is constantly being improved by introduction of new developments, both new process concepts and new designs of equipment, catalysts, etc.

DESIGN CONSIDERATIONS (Cf. Figure 2)

For the very first time worldwide a grassroots plant for co-production of ammonia and methanol has been contracted. Earlier co-production plants have been made as add-on units, where ammonia plants have been revamped to be able to produce both ammonia and methanol from the synthesis generated in the front-end, or where an ammonia synthesis unit is added to a methanol or ethylene plant, using hydrogen-rich off-gas as feed with necessary nitrogen produced in an air separation unit. It is generally known that revamp of a plant puts a number of restrictions on the process design, simply because a number of equipment has to be reused.

When a new plant is designed all the equipment can be designed for the optimal operating conditions, and no restrictions due to reuse of existing equipment are present.

In principle a co-production plant is a plant having a front-end which is common for two synthesis units, i.e. the ammonia and the methanol synthesis. This means that the design of the front-end must be made to fulfill the most demanding requirements of the two synthesis units.

Although it is not the purpose of the present presentation to compare in detail the energy consumption for various types of feedstocks, it may be appropriate to indicate typical ranges. As the consumption figures and investment costs are lowest in natural gas based plants, it is not surprising that plants based on natural gas completely dominate the industry today.

Typical figures are shown in Table 1.

Table 1 - Different Feedstocks

Energy Consumption	Gcal/MT Product
Coal	9.5 - 10.0
Fuel oil	8.0 - 8.5
Naphtha	7.0 - 7.75
Natural gas	6.5 - 7.0

One of the most important factors in the production cost is the capital related costs. In general only about 10-15% of the production cost can be related to the feed and fuel consumption. This means that the energy consumption is not of very big importance to the plant owners.

Having fixed the production cost which will be almost constant independently of whether ammonia or methanol is processed, the plant owner has a very big advantage because it is possible to maximize the production of the product giving highest profit.

Overall it is, however, the reliability of the plant which is the most important factor for the production cost.

Co-production Units

For more than 50 years Topsøe has been active in supplying technology for plants producing ammonia, methanol, and other kinds of synthesis gases. As such the know-how involved in design of co-production facilities is well established within the company, and Topsøe has been involved in a number of projects for co-production units where the first unit was started up in 1993. Figure 3 shows references for co-production units.

Recently a large grassroots plant to be erected in Malaysia for combined production of ammonia and methanol was contracted based on Topsøe process design. In the following the various possible process schemes will be discussed, and in particular the process scheme used for this project will be described in further detail.

All the process steps used in the new grassroots plant are well-proven in Topsøe ammonia and methanol plants in the sense that you have a complete ammonia plant in combination with a complete methanol plant back-end with synthesis and product purification utilizing the ammonia plant front-end.

The front-end is based on two-step reforming featuring fired tubular and secondary reforming. Shift section comprises high and low temperature shift, CO₂-removal section is based on the Benfield system with two-stage regeneration.

Before the final decision was taken about which process lay-out to be selected for the methanol synthesis and methanation system, the optimum reaction conditions for the methanol synthesis were studied carefully.

As can be seen from the curve in Figure 4, the pressure is a significant factor having a great impact on the carbon conversion into methanol.

Overall it is, however, a matter of considering the energy efficiency versus the investment cost. As such 3 different process lay-outs will be considered in the following:

1) Low Pressure Co-production

The process lay-out shown in Figure 5 is also sometimes termed *clean-up methanolation*.

In this process lay-out the co-production units are inserted between the CO₂-removal unit and the methanator. Partial by-passes are arranged to provide the necessary CO and CO₂ for the methanol reaction, but since the methanol reaction is disfavoured by low pressure there will be a limit as to how much CO + CO₂ can be permitted to continue unconverted to the methanator. Since this limit is rather low, the methanol production potential of this lay-out is very limited, and in this particular case not sufficient.

2) Side Stream in Front-end

With this lay-out (Figure 6) a fraction of the synthesis gas is extracted upstream the high temperature shift, cooled and sent to a methanol converter and returned downstream the high temperature shift. The cooling/reheating is

necessary to reduce the water content of the synthesis gas. Water in the concentration normally seen at the inlet of a high temperature shift will adversely effect the methanol equilibrium and catalyst durability.

The production rate of methanol is determined by the split ratio upstream the high temperature shift.

At this location in the ammonia plant, the concentrations of the active components ($\text{CO} + \text{CO}_2$) are high, but the overall pressure is low. Consequently, the conversion is less than desirable. By inserting a compressor before the methanol reactor it is possible to increase the pressure and thereby the conversion.

Some parties suggest taking the side stream from between the primary and secondary reformer to avoid nitrogen, which is inert to the methanol synthesis. This is, however, not preferable, partly because the tie-in is more tedious and expensive, and partly because the inert nitrogen to a large extent is substituted by unconverted methane which also is inert.

3) High Pressure Co-production

In this lay-out (Figure 7) the co-production unit is located between the two casings of the synthesis gas compressor, i.e. at higher pressure than the previous scheme. It is possible to operate at high concentrations of $\text{CO} + \text{CO}_2$ giving a high production rate.

Topsøe has concluded that the high pressure scheme is the most attractive, and this scheme is described in more detail below.

PROCESS DESCRIPTION OF THE HIGH PRESSURE CO-PRODUCTION UNIT

Methanol Production

The co-production unit consists of two methanol synthesis reactors followed by a high pressure methanator. In the front-end of the ammonia plant the low temperature shift, the CO_2 absorber and the high temperature shift are equipped with by-passes to control the amounts of CO and CO_2 in the synthesis gas for the desired methanol production. A high CO/CO_2 ratio is desired. A certain minimum of CO_2 is required, however, due to catalyst kinetics.

The synthesis gas is compressed in the first synthesis gas compressor casing and led to the first methanol synthesis reactor. The reactor is a boiling water type reactor, necessitated by the strongly exothermic methanol reaction. The catalyst is located in a number of tubes. The reactor is cooled by boiling water on the shell side. The reactor is operated in a once-through fashion; recirculation is not required because of the high pressure. The second methanol reactor is an inexpensive adiabatic reactor applicable because the majority of the reaction heat is absorbed in the first reactor.

The gas outlet the reactors is cooled in a feed/effluent exchanger and a water cooler. After the second reactor and cooler it enters a combined water scrubber/methanol separator.

The synthesis gas exit the water scrubber methanol separator is preheated in a feed/effluent exchanger and in a trim heater before entering the methanator. The methanator exit gas is cooled, and condensate is separated before the synthesis gas is passed to the second casing of the synthesis gas compressor.

Installing the co-production unit between the compressor casings ensures that ammonia will not leak to the methanol synthesis or methanol to the ammonia synthesis loop through the traditional leak between the final compression stage and the recirculator stage.

The methanol production can easily be decreased by reducing the by-pass over the shifts and CO_2 absorber and thus depriving the methanol synthesis of its CO and CO_2 feedstock.

Methanol Purification

The crude methanol product will contain water and certain by-products at levels which will not be acceptable for most uses. Therefore, a purification unit is required.

The lay-out and energy consumption of the distillation unit depends on the required specification for the purified product, in this case a two-column lay-out is applicable.

The heat input required for the two-column distillation for product quality US Federal Grade AA, the most often encountered commercial specification, is approx. 1.2 Gcal/MT methanol, equivalent to approx. 2300 kg/MT methanol of low pressure steam (3.5 kg/cm² g).

The lay-out of the two-column distillation unit as shown in Figure 8 is described in the following. In the first column, the stabilizer column, the various low boiling compounds, in particular dimethyl-ether, are separated from the methanol/water mixture. In the second column, the concentration column, water and methanol are separated, and high boiling compounds, in particular higher alcohols, are concentrated and removed. Vapour from the top of the stabilizer column is cooled in an overhead condenser, and the vapour/liquid mixture is collected in an overhead accumulator. Volatile gases leaving the top of the accumulator are sent to the fuel or flare header.

From the bottom of the stabilizer column raw methanol is pumped to the concentration column. In this column, water is separated at the bottom. Part of the water can be recycled to the top of the stabilizer column to improve the separation of the various low boiling compounds. Higher alcohol impurities are withdrawn in a small purge stream in the lower part of the column. Methanol product is removed several trays below the top and cooled in the methanol product cooler before it is transferred to the methanol shift tank for analysis of the quality. After successful analysis the methanol product is transferred to the methanol storage tank. Vapour from the top of the concentration column is condensed in an overhead condenser and returned to the column through an overhead accumulator.

INTEGRATED PRODUCTION OF AMMONIA AND/OR POWER AND STEAM

Since an ammonia or a co-production plant includes a number of rather large compressors and is often combined with downstream facilities requiring large amounts of steam it is an obvious choice to select a gas turbine as driver for one of the big compressors in combination with a steam generator utilizing the hot exhaust gas from the gas turbine. The steam may be used for other drivers or for power production for export, possibly supplemented with steam from other sources.

The integration of such an installation can be done in several different ways depending on the actual site requirements.

A very flexible lay-out is a system where a gas turbine drives the process air compressor. The hot exhaust gas can be sent either to the by-pass stack or to a boiler producing high pressure steam at 110 bar, 5250C (cf. Figure 9).

The unit should be equipped with a diverter damper in the exhaust gas duct and the boiler should preferably be able to produce steam even though the gas turbine trips. In this way the boiler after the gas turbine can be used as a start-up boiler as well as an « auxiliary boiler » producing steam to close the steam balance. Depending upon how fast steam is required in case of a trip of the secondary reformer the boiler can be equipped with either a forced draft fan or an induced draft fan to assure a stable supply of combustion air to the boiler in case of gas turbine trip.

Gas turbines can utilize a variety of fuels and the integration of gas turbine can be done in a number of ways utilizing also f.inst. purge gases from the process plant as fuel.

If the requirements for power for export is significant, the gas turbine can be equipped with a power generation unit coupled via an auxiliary gearbox to the gas turbine shaft. This power production normally covers the requirements for power in the ammonia plant itself. Since the gas turbine will normally run on part load when driving the process air compressor, the addition of the auxiliary power generation unit will increase the load on the gas turbine resulting in a higher overall efficiency.

By producing high pressure steam in the boiler after the gas turbine and utilizing the steam for power production 15 MW of power can easily be exported from a 1500 MTPD ammonia plant.

CONCLUSION

- \$ Energy efficient grassroots co-production plant
- \$ Flexible process lay-out
- \$ Product flexibility
- \$ Integrated power/steam production possible

It has been possible to design a very energy efficient co-production plant. A better energy efficiency as well as a higher flexibility can be achieved when a new plant is designed compared to a revamp situation.

Changing market situations can be handled because the flexibility in product output is present.

Due to the very flexible process lay-out, it is possible to integrate the ammonia/co-production plant with the steam and power system.

Figure 1 - Process Scheme for Production of Ammonia

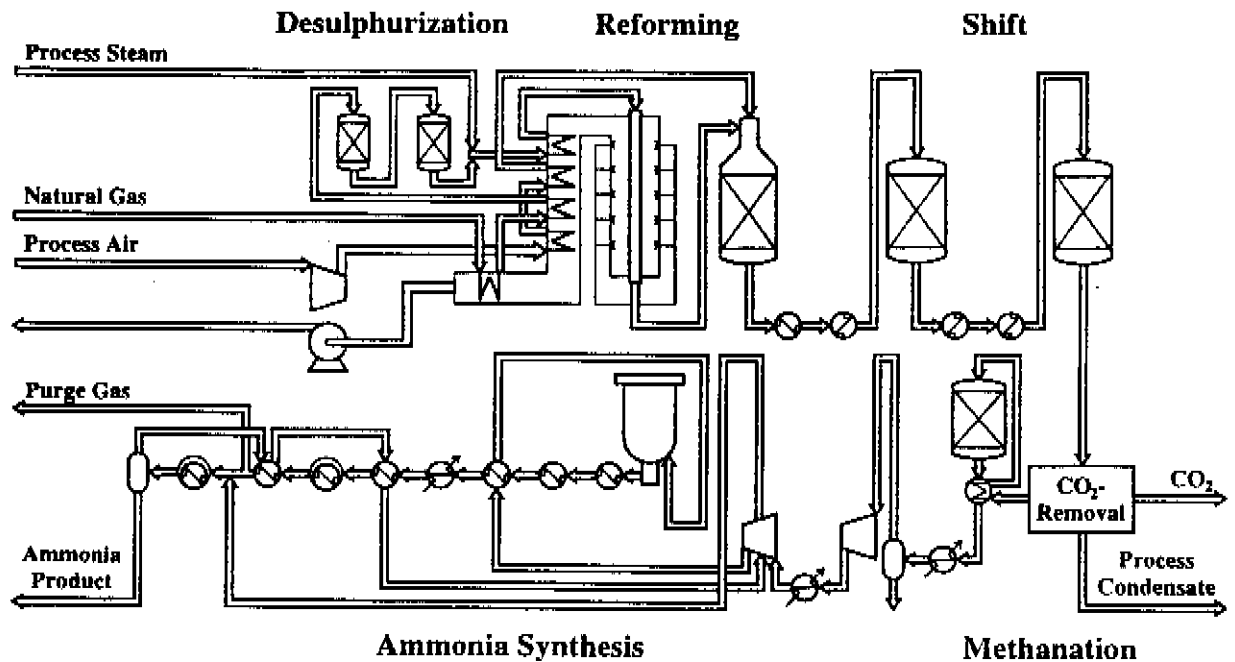


Figure 2 - Design Considerations

Design Considerations

- \$ Feedstock characteristics
- \$ Energy efficiency
- \$ Production cost
- \$ Plant flexibility and reliability

Design Considerations

Many plant owners have a desire to be flexible towards changing demands in the fertilizer market. Being able to diversify the products from a process, to assure that the given raw materials are always processed into the most profitable products, is therefore of great interest to the industry today.

Figure 3 - Co-production Units

- **Co-production of Methanol**
 - revamp (add-on unit)
 - grassroots plant
- **Experience**
 - 72 MTPD methanol and 286 MTPD ammonia unit, Middle East, start-up 1993
 - 363 MTPD methanol and 907 MTPD ammonia unit, USA, start-up 1994
 - 100 MTPD methanol and 600 MTPD ammonia unit, China, under design and implementation
 - 200 MTPD methanol and 1125 MTPD ammonia, Malaysia, under design and implementation

Figure 4 - Pressure Dependence of Methanol Equilibrium Conversion

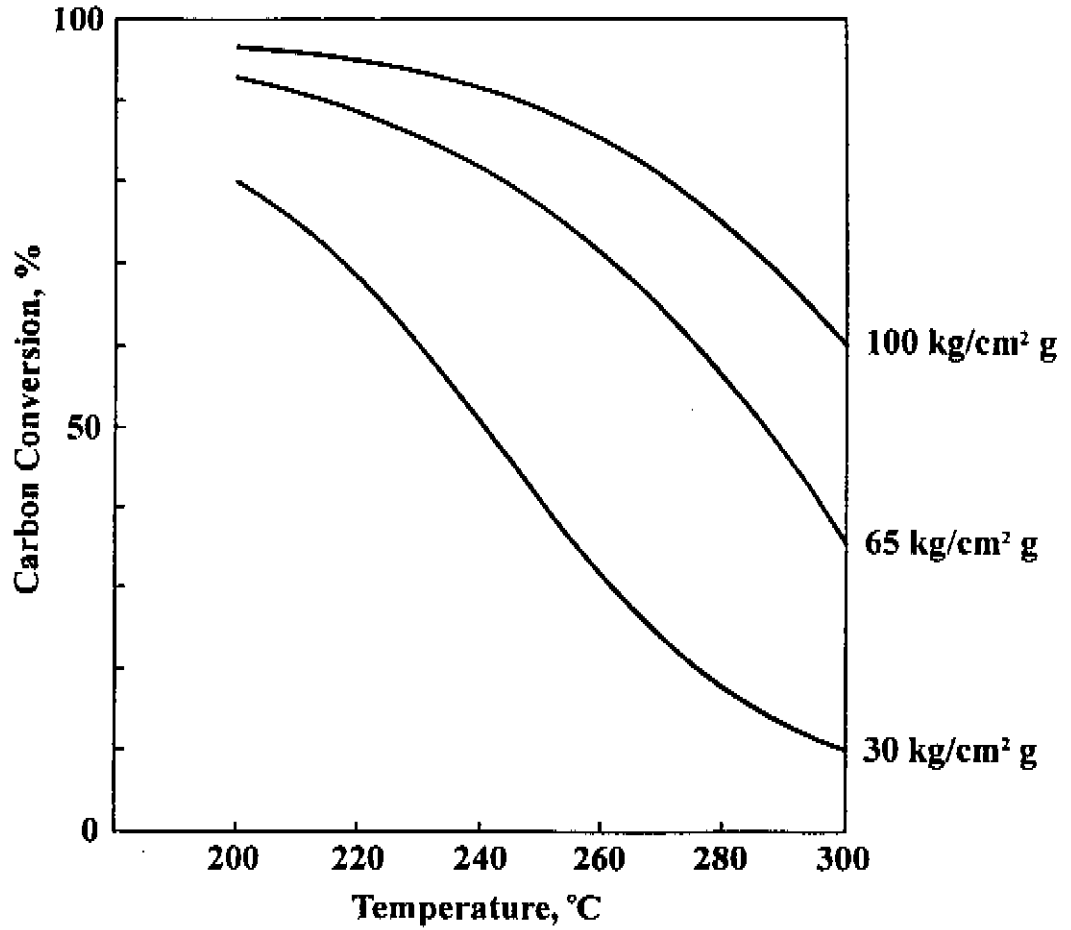


Figure 5 - Low Pressure Co-production

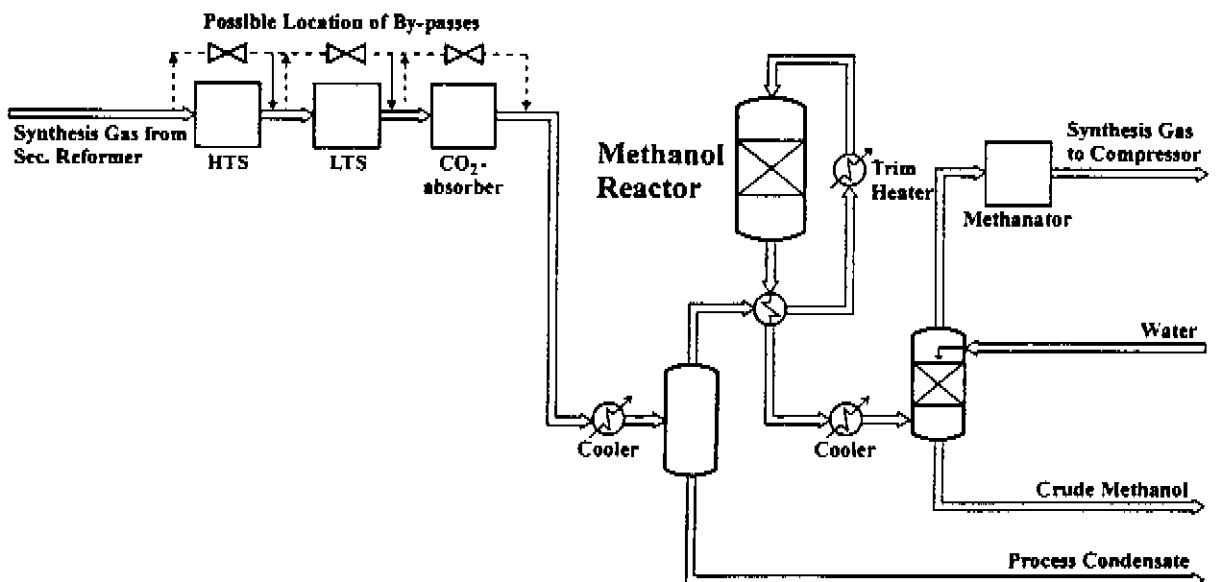


Figure 6 - Side Stream In Front-end

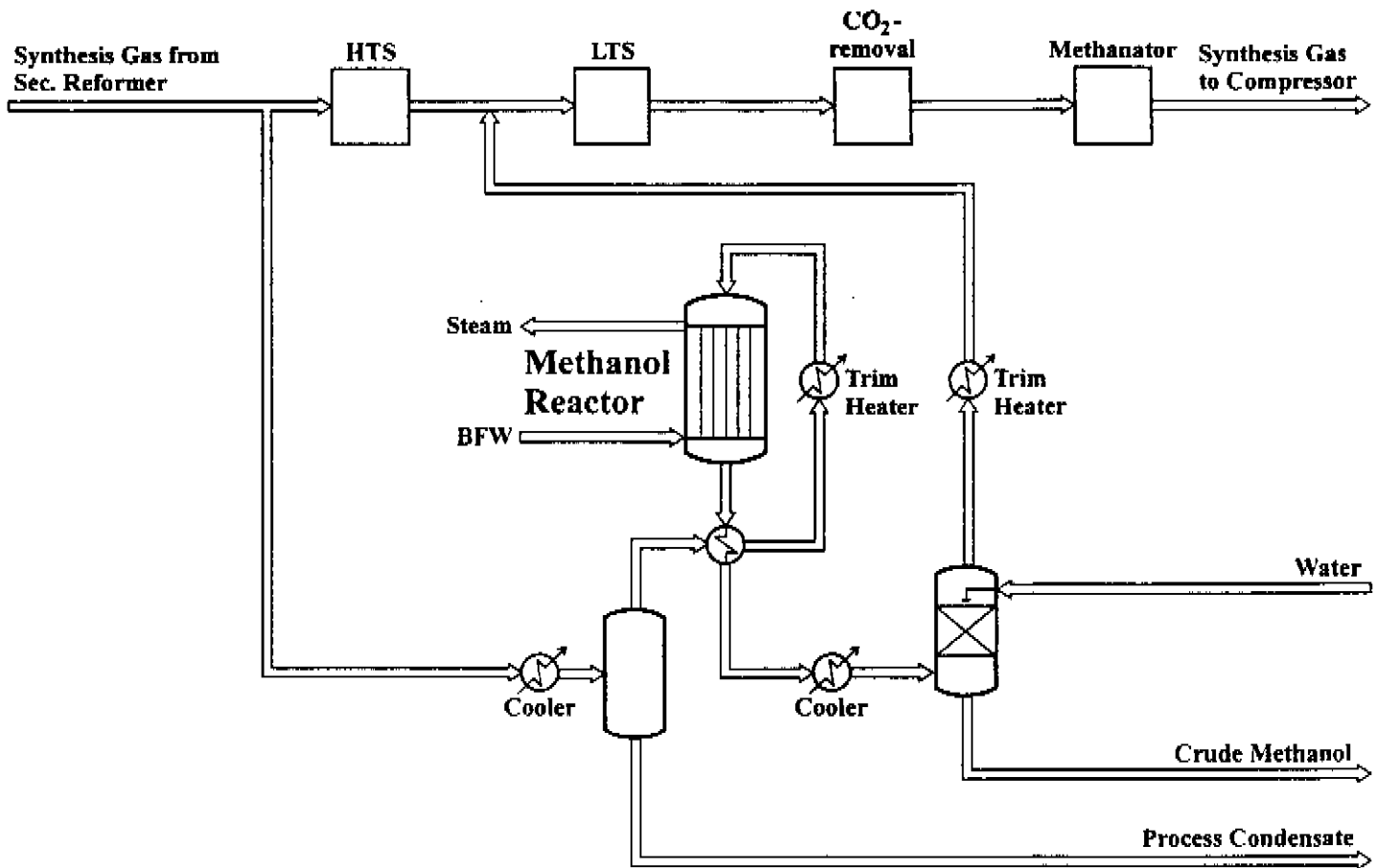


Figure 7 - High Pressure Co-production

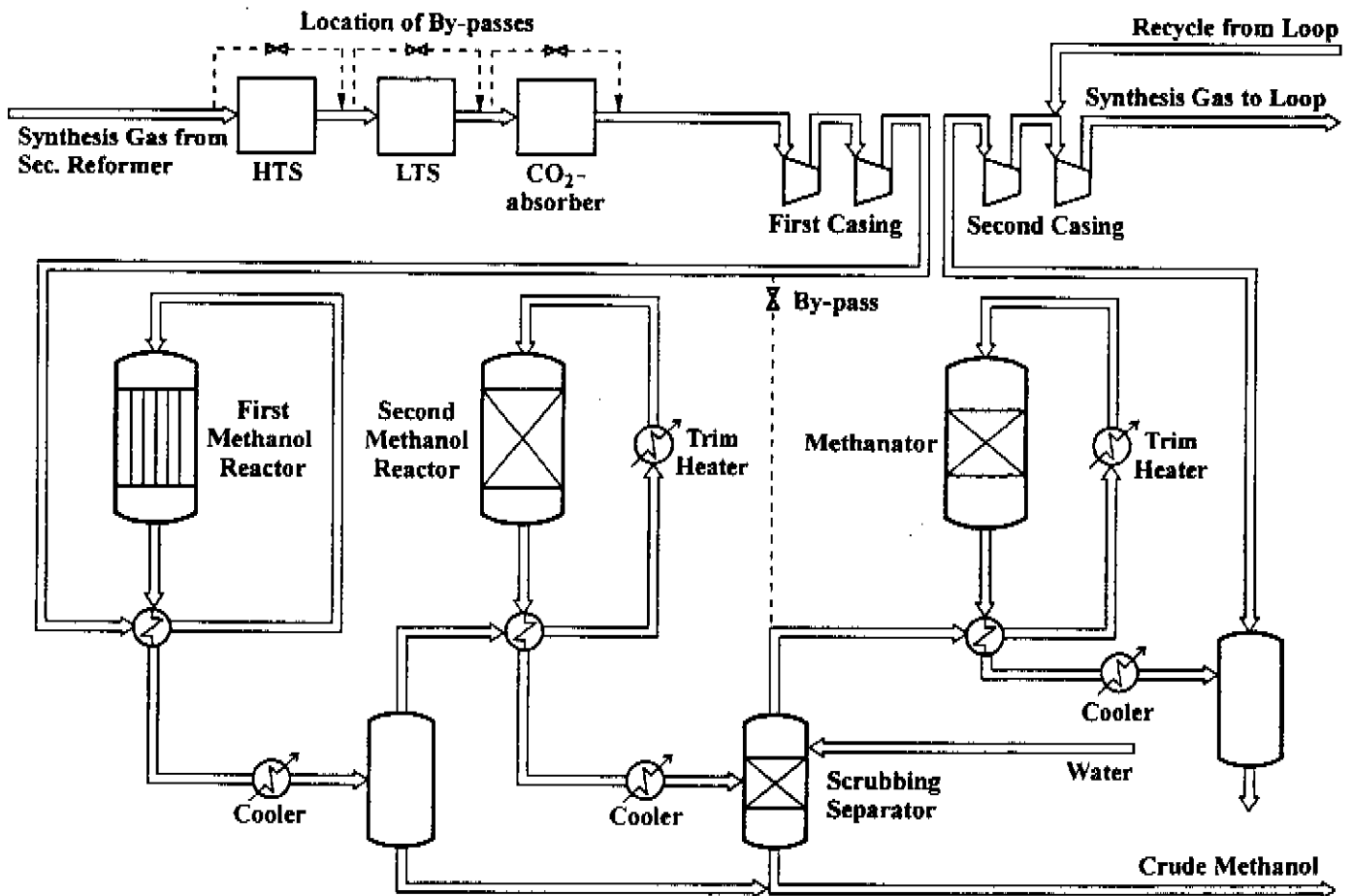


Figure 8 - Methanol Purification

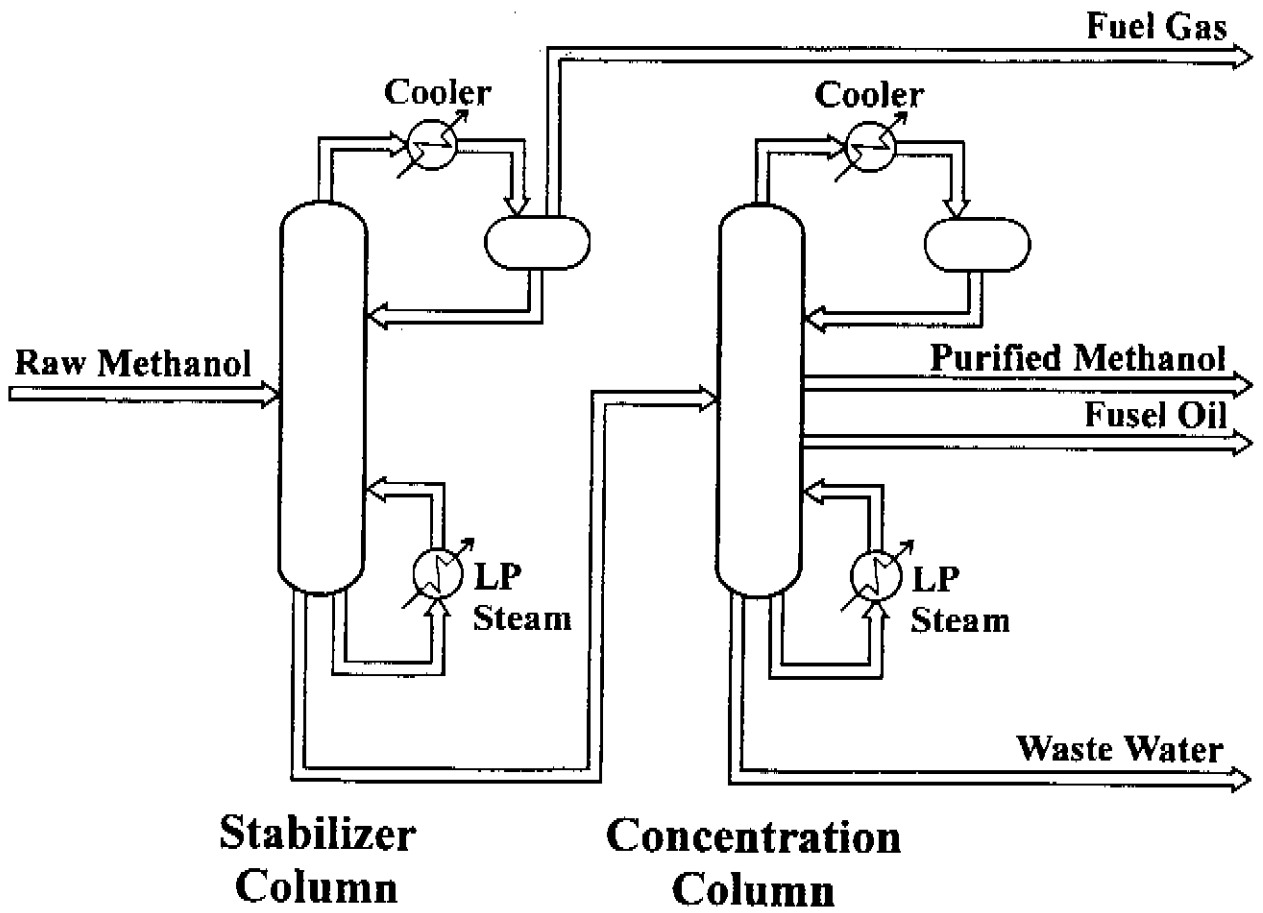


Figure 9 - Gas Turbine Integration

