

# Process integration aspects of the design of a gas separation system for the upgrade of crude Synthetic Natural Gas (SNG) to grid quality in a wood to methane process

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## Abstract

The present paper investigates the prospects of process integration of the biogenic production of crude synthetic natural gas (SNG) and its upgrade to grid quality. At the example of a separation by means of a membrane cascade, a holistic design approach targeting the overall process performances is presented. Compared to a design obtained from an isolated approach, it is shown that a considerable reduction of the size and cost of the separation system is possible if a tight process integration is considered in the system design.

**Keywords:** SNG, process integration, CO<sub>2</sub> separation, membrane system design

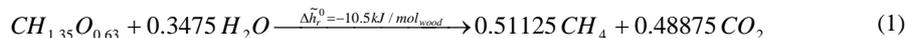
## 1. Introduction

Among the possible routes for producing fuels from biomass, thermochemical processing is one of the most promising options since a complete conversion of lignocellulosic biomass is achieved. In these processes, the reactive steps are performed at high temperature and a viable process integration is crucial to obtain an efficient conversion. Several recent studies have investigated suitable technology and processes for SNG production (Mozaffarian and Zwart, 2003; Duret et al. 2005; Gassner and Maréchal, 2005; Heyne et al., 2008; Luterbacher et al., 2008), the necessary gas upgrading step has however not received much attention. The present paper investigates this issue in more detail and aims to identify the advantages of a tight integration of the reactive steps with a gas separation system by membranes.

## 2. Problem statement

### 2.1. Crude SNG production

Representing the biomass as a chemical molecule with the carbon atom as reference, the conceptual design of its conversion into methane is based on Equation (1):



Technically, the most envisaged route is to gasify the biomass and convert the producer gas into methane. Prior to gasification, the raw material is dried to below 20-25%wt humidity in order to prevent excessive losses due to water evaporation. From the current state of research and process development (Mozaffarian and Zwart, 2003; Stucki, 2005), it is expected that the first installations will be based on indirectly heated fluidised bed gasification of FICFB-type that has been developed and commercialised by (Hofbauer

et al., 2002). Due to the presence of dust, tars and catalyst poisons like sulphur compounds, the producer gas is cleaned before entering a catalytic fluidised bed reactor, where it is converted at 300-400°C to methane.

The stoichiometric equation (Eq. 1) shows that the overall conversion of wood to methane is exothermic and releases about 450 kJ/kg<sub>wood</sub> of heat. This net release is distributed over the gasification and methanation reactions. The first one is endothermic and requires heat at high temperature, whereas the second one is exothermic and releases heat at lower temperature. The process thus requires additional energy and the quality of the process integration will define the overall process efficiency. The process is pinched at the gasification temperature and about 200 - 250 kW of high temperature heat at 850 – 900°C are typically required to convert 1 MW of wood to crude SNG.

The expected gas compositions of the producer gas and the crude methanation product computed with a previously developed process model (Duret et al., 2005; Gassner and Maréchal, 2005) are reported for methanation at atmospheric pressure in Table 1.

	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub> O
Gasification	2.2	10.9	38.8	25.5	18.6	0.5	3.5
Methanation	-	44.8	5.9	0.1	45.1	1.0	3.1
- without H <sub>2</sub> O, CO <sub>2</sub>	-	86.4	11.3	0.3	-	2.0	-
- without H <sub>2</sub> O, CO <sub>2</sub> , H <sub>2</sub>	-	97.4	-	0.3	-	2.3	-
Grid specifications		> 96	< 4	< 0.2		< 6	-8°C

Table 1: Cold gas compositions and upgrading requirements (in % vol).

## 2.2. Design problem definition

According to the new Swiss directive for the supply of biogas to the natural gas grid, unlimited amounts of gas can be fed to the grid if its methane content is higher than 96% vol and the CO<sub>2</sub>, H<sub>2</sub> and CO content less than 6, 4 and 0.2% vol respectively, while having a dew point at grid pressure (50 bar) lower than -8°C (SVGW, 2007). Assuming that nitrogen can not be easily separated from methane, Table 1 also shows the maximum obtainable purities after complete removal of water, carbon dioxide and hydrogen. Provided that an ideal separation process for removing CO<sub>2</sub> from the SNG is used, the hydrogen concentration is expected to rise to around 11%. The CH<sub>4</sub> purity will be at best around 86%, and at least some of the unconverted hydrogen must be removed. The identification of the minimum energy requirements of the process furthermore adds a supplementary aspect to the design problem. Gasification has a relatively important heat demand at high temperature, which is usually supplied by burning producer gas and therefore reduces the methanation flow. In the combined heat and power application for which the gasification technology has originally been developed, few other fuel alternatives are present. However, in an SNG plant that necessarily suffers from a non-ideal separation, depleted gas streams from the SNG upgrading section could be used instead of the intermediate product. The condition for this is that its flame temperature is sufficiently higher than the gasification temperature. If the depleted gas is too diluted, it must in any case be treated in a catalytic combustion to eliminate the residual methane due to its high environmental impact as a greenhouse gas.

From these considerations, it is obvious that the design of the separation system is not a trivial problem. It requires the development of an appropriate multicomponent separation system, while also considering possible cost and energy savings originating from the trade-off between using the producer gas or a depleted gas as hot utility. In the framework of the actions aimed to climate change mitigation, rather pure carbon

dioxide (95% minimum) may also represent a valuable by-product. If sequestration instead of venting the separated carbon dioxide is targeted, care must be taken not to dilute this by-product with nitrogen from combustion with air. A possible option is thereby to use oxygen produced by electrolysis in the catalytic combustion, whose by-produced hydrogen could be supplied to the methane synthesis and would increase the SNG output (Gassner and Maréchal, 2008b). A general block flow diagram of these different upgrading options is given on Figure 1.

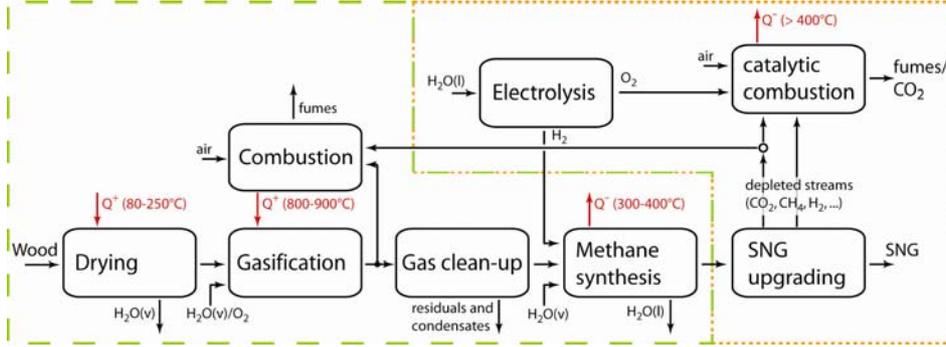


Figure 1: Block flow diagram of the crude SNG production (dashed) and upgrading (dotted) units.

### 3. Process integration study

#### 3.1. Modelling

According to the applied design methodology (Gassner and Maréchal, 2008a), its thermodynamic part is divided into an energy-flow and an energy-integration model. In the energy-flow model, the thermodynamic conversions occurring in the different process units are modelled with a commercial flowsheeting tool (Belsim SA, 2007). The heat requirement of the process units is transferred to the energy-integration model, where the energy conversion and heat transfer system is determined by a mixed integer linear programming model targeting minimum operating costs with respect to the minimum approach temperature constraints. The thermodynamic conditions are then considered as design targets for the process equipment, which is then rated and costed by design heuristics and data from existing experimental and pilot plant facilities.

In order to investigate the impact of process integration on the optimal design of the separation system and the reactive sections of the plant, multi-stage membrane separation has been chosen among the identified candidate technologies for a detailed modelling. According to the theory of gas separation by membranes, a practical description of the permeation process through a membrane is to consider the difference of partial pressure in the bulk as driving force (Hwang and Kammermeyer, 1975). Using a phenomenological constant termed permeability  $P_i$ , the permeation of species  $i$  is described as:

$$\frac{dn_{i,p}}{dA} = \frac{P_i}{\delta} \cdot (p_{i,r} - p_{i,p}) \quad (2)$$

where  $n_{i,p}$  is the partial molar flow of  $i$  that permeates the membrane,  $A$  the membrane area,  $\delta$  its thickness, and  $p_{i,r}$  and  $p_{i,p}$  the partial pressure on the retentate and permeate side, respectively. The selectivity  $\alpha_{i,j}$  of the membrane between two different species  $i$  and  $j$  is defined by the ratio of their respective permeabilities  $P_i/P_j$ .

As the permeation is described by a set of  $i$  differential equations of the same type as Eq. 2, its resolution depends on the flow pattern of the membrane. Except for the simple case of perfectly mixed permeate and retentate chambers, no analytic solutions have been reported for multicomponent systems, but some simplified analytic or numeric procedures have been suggested. For flowsheet calculations, a simplified algebraic design model for hollow-fiber modules in counter-current operation developed and validated by Pettersen and Lien (1994) proves to be appropriate and has been implemented in the process model.

With the properties of commercially available membranes (Table 2), a single membrane stage is generally not sufficient to reach the required purity and an acceptable recovery of the crude SNG. Several membrane stages must therefore be cascaded, and a multitude of possibilities for the feed location, membrane connections and intermediate product withdrawals to be used as hot utility exist. From a first screening of all the possible cascades schemes, a superstructure of the most promising flowsheets has been defined (Figure 2) and is subjected to the process optimisation.

$P_{CO_2}$	9 barrer	$\alpha_{CO_2,H_2}$	3.42 -
$\delta$	1000 Å	$\alpha_{CO_2,CH_4}, \alpha_{CO_2,CO}, \alpha_{CO_2,N_2}$	21.1 -

Table 2: Properties of commercial cellulose acetate membranes (Bhide and Stern, 1993; Phair and Badwal, 2006). 1 barrer =  $7.5 \cdot 10^{-18} \text{m}^2/\text{s} \cdot \text{Pa}^{-1}$ .

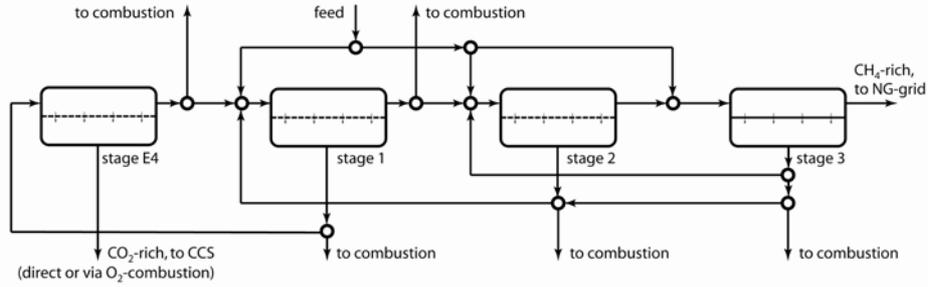


Figure 2: Superstructure of the membrane system.

### 3.2. Comparison of different levels of process integration

#### 3.2.1. Approach

In order to investigate the influence of the level of integration on the process performance, the separation system is optimised by applying two different strategies. In a first approach, only the isolated performance of the separation system is considered in the optimisation, which represents a sequential design of the production and separation steps without considering the possible synergies resulting from the integration. For this purpose, the thermo-economic indicators are defined to only assess the performance of the separation system. According to its system boundary represented by the dotted line on Figure 1, the performance of the separation is evaluated by its energy efficiency (Eq. 3) and the total cost for the crude SNG separation (Eq. 4):

$$\mathcal{E}^{sep} = \frac{\Delta h_{SNG}^0 \dot{m}_{SNG}^-}{\Delta h_{crudeSNG}^0 \dot{m}_{crudeSNG}^+ + \dot{E}^{sep,+}} \quad (3); \quad C_p^{sep} = C_{I,d}^{sep} + C_M^{sep} + C_{el}^{sep} + C_{RM}^{sep} \quad (4)$$

In these equations,  $\Delta h^0$  terms the heating value of the streams,  $\dot{m}$  their mass flows and  $\dot{E}$  the electricity consumption. The superscript <sup>sep</sup> stands for the separation system, and <sup>-</sup> and <sup>+</sup> refer to positive output and input terms, respectively.  $C_{I,d}$ ,  $C_M$ ,  $C_{el}$  and  $C_{RM}$  represent the depreciated investment, maintenance, electricity and raw material's cost. For the separation system, the latter is calculated by the difference of the energy content between the crude and grid quality SNG. The energy in the depleted streams is therefore considered as lost.

In contrast to this approach targeting only the separation performance, a second set of indicators that represent the whole system performance is defined. The overall system efficiency (Eq. 5) and the production cost for grid-quality SNG (Eq. 6) are used:

$$\varepsilon = \frac{\Delta h_{SNG}^0 \dot{m}_{SNG}^- + \dot{E}^-}{\Delta h_{wood}^0 \dot{m}_{wood}^+ + \dot{E}^+} \quad (5); \quad C_p = C_{I,d} + C_M + C_{OL} + C_{el} + C_{RM} \quad (6)$$

With this formulation, the energy efficiency accounts for the possibility of co-producing electrical power  $\dot{E}^-$ , and the production cost includes the cost of operating labour  $C_{OL}$ . Furthermore, the raw material's cost  $C_{RM}$  considers only the expenses for wood, which implies that the depleted gas is treated on-site and might provide useful heat for the system. Since the evaluation of these overall properties in the separation design requires knowledge and data of the whole system, this approach represents a simultaneous design of the crude SNG production and its upgrading. The dotted and dashed parts on Figure 1 are thus considered simultaneously, and advantages due to the process integration with respect to the energy and material streams are accounted.

### 3.2.2. Optimisation results and discussion

In order to generate a complete set of optimal configurations, a multi-objective optimisation of the product recovery, power consumption and investment cost as objectives is performed, where the membrane system layout, the stage cuts and its operating pressures are used as decision variables. Figure 3 shows the obtained performance indicators for the best system layouts of the superstructure. From these plots, considerable qualitative and quantitative differences in the performance of the isolated membrane cascade and the overall system is observed. The isolated optimisation clearly suggests a 3 stage countercurrent cascade with about 94% of SNG recovery in the separation step. However, from an overall system point of view, it is sufficient to only recover about 84% of the crude SNG in a less costly system with only one recycle loop. For the overall system, a mediocre performance of the separation step is not penalising. With a non-negligible fraction of methane and hydrogen in the depleted stream (20% vol in total), its flame temperature remains sufficiently high to supply heat above the high temperature pinch, and less producer gas must be used for this purpose. Due to the advantageous process integration, considerably less electrical power is consumed in the separation (67 instead of 82 kW<sub>el</sub>/MW<sub>SNG</sub>) and a much smaller membrane system (230 instead of 363 m<sup>2</sup>/MW<sub>crudeSNG</sub> in total) is required.

## 4. Conclusions

By implementing a thermo-economic model for multicomponent membrane gas separation in a process model for SNG production, the process integration of the gas separation with its production has been investigated. It has been shown that a holistic approach provides a qualitatively different and more advantageous process design than separately addressing the crude SNG production and its separation. Using the residual methane and hydrogen in the depleted stream as fuel for the process, it is possible to considerably reduce the size and cost of the gas upgrading system.

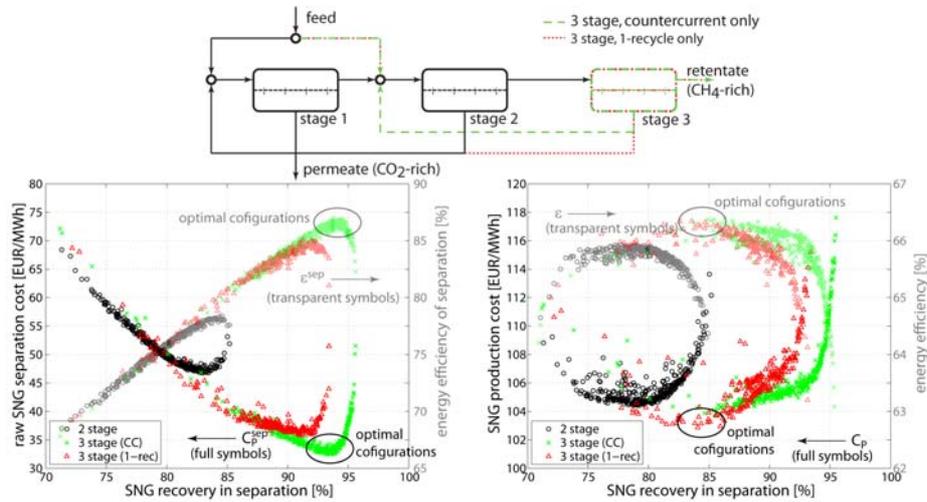


Figure 3: Performance of the separation system (left) and the overall process (right).

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