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Process Simulation of Syngas Purification by Gas Permeation Application

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Nowadays, syngas production from renewable energy sources particularly by methanation process has taken great interest. The aim of the process is energy saving by converting surplus produced energy into a truthful chemical product. Methanation reactor outlet stream contains a gas mixture which is not feasible to be used directly in distributing grids, where a higher purity of methane is necessary to obtain the highest power density. To reach the different grades of methane (for heat, electricity and vehicle fuels applications), various purification levels should be provided for syngas. For use as a fuel, elimination of carbon dioxide and water is needed, because water affects negatively on the mechanical components within the vehicles' engine equipment. Moreover, CO_2 removal should be carried out to enhance heat quality of methane and cause less pollution in the atmosphere. In the current study, the performance of a combination of flash separator and hollow fiber membranes for syngas purification was studied. For this purpose, a flash separator model was implemented to condense water from the wet feed. Then for the elimination of CO_2 from methane, a hollow fiber membrane system was considered. Therefore, a unit operation user model in FORTRAN was developed to incorporate into Aspen Plus® V8.6. Different designs and arrangements of membrane modules were compared, and the best result was to purify methane up to 98 %vol. obtained using a two-stage gas permeation system with recycle streams. The model scheme can be beneficial in the design and performance analysis of a complex methanation plant system prior to practical realization.

1. Introduction

Production of methane by methanation catalytic reaction was fully presented in one of the previous papers of the authors (Sharifian and Harasek, 2015). It was reported that the product stream contains approximately 50 % water, 33 % methane (as the main product), 12 % carbon dioxide and 5 % the rest (CO and H_2) (Sharifian et al. 2016). Purification of syngas allows a wider variety of applications, either for heat and electricity, or as vehicle fuels. Especially, for use as a fuel, purification is needed to elimination of carbon dioxide (CO_2) and water, because water affects the mechanical components within engine equipment. Moreover, CO_2 should be removed in order to enhance heat quality of methane and cause less pollution in the atmosphere. This gas mixture is not feasible to be directly used in distributing grids, where higher methane purity is essential to obtain the highest power density. Thus, after methanation reactor, purification of methane is needed to make it usable for grid connection. The goal of purification section is to reach methane percentage of higher than 98 % and less than 2% for the rest components. In the current study, gas permeation membrane system has been applied for methane purification. Membrane is an interesting tool for separation of homogeneous mixtures when a huge bulk of feed in a continuous system is available. Among many recent researches on gas permeation systems, Razavi et al. (2016) modeled CO_2 removal from N_2 by a hollow fiber membrane. Darebkhani et al. (2018) presented a semi-empirical study on CO_2 removal from CH_4 injected from combustion unit. Dalane et al. (2019) also developed a model in Aspen HYSYS for subsea natural gas dehydration process using membrane.

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2. Syngas purification

2.1 Flash separation (water removal)

One of the common methods for water removal from a gas mixture is flash separation. This application can be more useful when gas components have completely different thermodynamic properties from water. Through this method, gravity is implemented in a vertical cylinder to let the liquid phase settle at the bottom of that, where it is withdrawn. The feed to a vapor–liquid separator (either be a liquid or gas) is flashed into vapor and liquid as it enters the separator. Then, the vapor phase passes through the gas outlet valve in top of the flash column excluding liquid droplets. Figure 1 presents the effects of temperature changes on the water removal performance of methanation product stream using a flash separator column at 50 bar pressure. It can be found that the lower temperature leads to smaller mole fraction of water in the vapor phase which is more desirable. Moreover, mole fraction of methane as the main product rises up when the flash column operates at low temperatures.

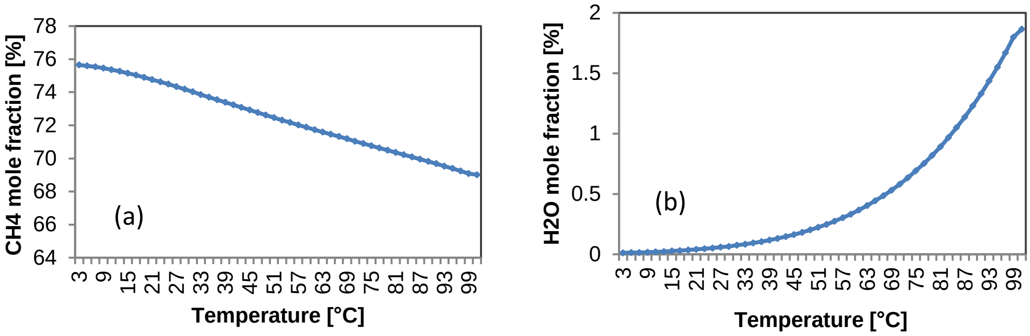

Figure 1: Mole fraction of component (a) CH_4 and (b) H_2O in the vapor phase, 50 bar pressure and various temperature values

Figure 2 illustrates the influences of pressure changes on the purification performance at the temperature of 4 °C. It can be seen that at the constant temperature, upper operating pressure leads to lower water mole fraction and higher methane mole fraction in vapor stream which is what exactly is needed in this process.

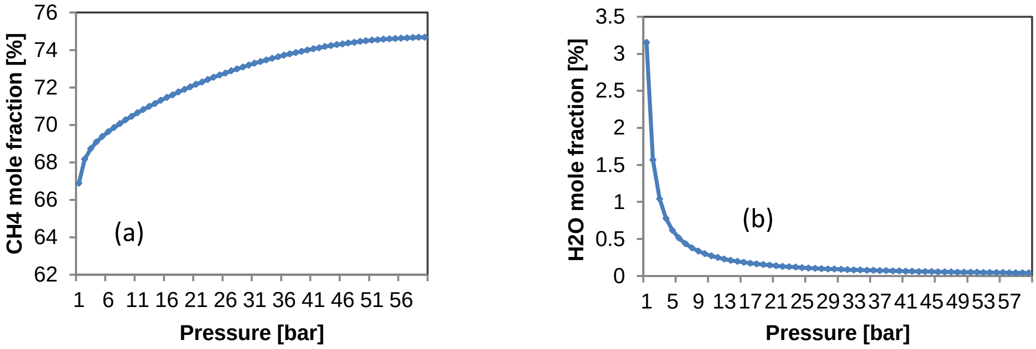

Figure 2: Mole fraction of component (a) CH_4 and (b) H_2O in the vapor phase, temperature of 4 °C and various pressure values

2.2 Membrane gas separation

After water removal process as the primary step of purification which is based on differences in liquefying temperatures, methane composition enhanced up to 80 % (see Table 1).

The next step is using a membrane separator to increase the purity of methane. Study of gas separation processes has a very long background in chemical engineering; however, membrane gas separation technology is developed within the last three decades. Easy plant operation, negligible environmental impacts, small maintenance cost and low weight equipment are of the most important advantages of membrane gas separation processes (Drioli and Romano, 2001). Membrane process is utilized in a wide range of environmental applications like organic vapor removal from polluted air, methane recovery from landfill gas (Rautenbach and

Welsch, 1993), natural gas processing, biogas purification, enhanced oil recovery and flue gas treatment (Chung et al., 2003).

There are numerous mathematical models and calculation methods for multicomponent gas separation systems available in the literature, and also various models which are widely accepted as the most practical representation of multicomponent gas separation in hollow fiber membranes (Pan, 1986).

Table 1: The components' percentages after water removal

Component	Symbol	Percentage [%]	
		before flash	after flash
Water	H_2O	45-55	0-1
Methane	CH_4	27-35	75-85
Carbon dioxide	CO_2	5-15	5-15
Hydrogen	H_2	1-5	1-5
Carbon monoxide	CO	0-1	0-2

This study is based on a mathematical model and a numerical solving technique for an asymmetric hollow fiber membrane gas module for separation of multicomponent mixtures and its implementation in a commercial simulator (Aspen Plus® V8.6). For this purpose, a gas permeation system (GP) has been developed and validated for a multicomponent system, then it is incorporated into Aspen plus for implementation in syngas purification after methanation process in a flowsheet (Sharifian et al., 2016).

2.3 Design Strategy

The design of process is one of the important assessment parts in chemical systems. Design of a gas permeation process contains an appropriate operating condition and module arrangement. The most common and simplest design of a gas permeation separator for purification of methane after water removal step is a single stage arrangement without any recycle stream. Although industrial scale systems usually involve sets of single stage separators in parallel, in many cases multistage arrangements including a recycle flow are utilized. The design of multistage application usually contains two or three modules which are connected in different schemes in order to increase the main product purity and decrease the percentages of loss. There are many cases in the literature (He et al. 2014) which are based on CO_2 removal from natural gas in various flow patterns, applications and designs (Ohs et al. 2016). For calculation of a module some parameters such as inner and outer diameters, active length, permeance of species and actual pressure values in both sides are needed. Table 2 presents the recommended characteristics for a typical module which can be implemented in a gas upgrading system. Using Aspen Plus® as a commercial and user friendly tool helps user to define all operating parameters in the flowsheet. In our case, the permeance of components is chosen from our pilot plant system fact sheet. However, in further researches, these data can be specified based on the system demands and desirable product conditions and feed composition.

Table 2: The module characteristics for gas upgrading system

Parameter	Value
Membrane type	asymmetric hollow fiber membrane
Flow pattern	co-current flow
Inner diameter [µm]	300
Outer diameter [µm]	500
Active length [m]	0.5
Permeance [10^{-10} mol/s m^2 Pa]	CO_2: 311.4 CO: 12.8 H_2: 971.0 CH_4: 12.4 H_2O: 3348.2

Four process designs were chosen for simulation to evaluate the performance of membrane for methane purification in power-to-gas system. Apart from the single stage permeator, design of multistage system is very vital when separation strategy is not chosen yet. Figure 3 shows three different arrangements of two-stage permeators. In the first one (Figure 3 a), there is no recycle flow; it is the simplest configuration in order to enrich the main component in the retentate flow. In Figures 3 b and c, a recycle flow is used to reduce the valuable product losses in the permeate stream.

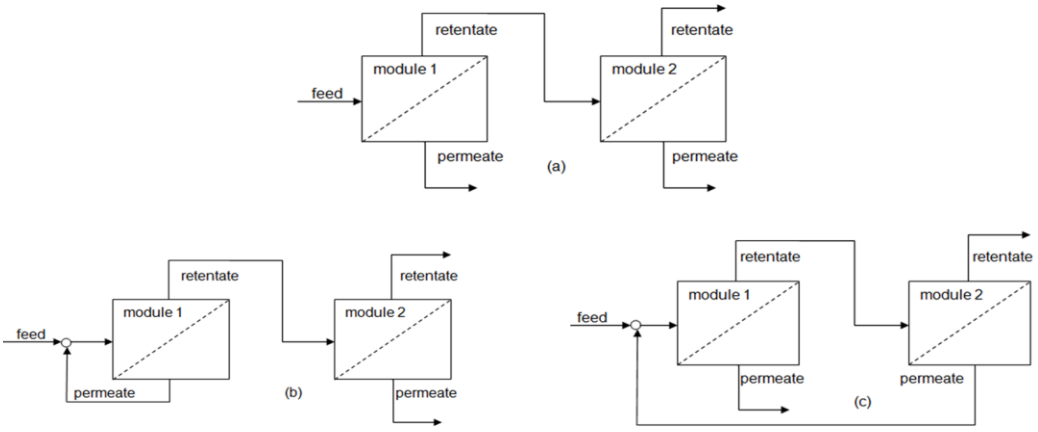

Figure 3: Schematics of design configuration of two stage permeator system (b, c) with or (a) without recycle stream

All the process layouts presented in Figure 3 have been implemented in Aspen Plus to evaluate the post processing of methanation process. This part of study focuses on the purity of methane as the main product, low carbon dioxide concentration in outlet stream and small methane losses. Comparison of the results (Table 3) shows that the first design (without recycle) leads to good methane fraction in outlet stream. At the same time, it has the highest methane losses rate among other designs.

The second design leads to a smaller methane fraction in the outlet and the worst overall performance in comparison with the other configurations belongs to this design. It is shown that the third arrangement has a good feasible agreement with our demands. Therefore, the last one has been incorporated into the complete flowsheet.

The survey on different schematics shows that the two-stage separation systems have smaller CH_4 losses in comparison with the single stage. Thus, the first permeate stream contains the high amount of CO_2 and H_2 which can be injected in fresh feed stream for methanation process. In addition, permeate stream of the second module which mostly involves methane can be recycled before the first permeator.

Table 3: Comparison of the performances of different two stage permeator designs in syngas purification (Figure 3)

Design configuration	CH_4 fraction [%]	CH_4 loss [%]	CO_2 mole fraction [%]
a	98.5	10.0	0.10
b	95.7	7.2	0.13
c	98.0	8.1	0.11

3. Complete flowsheet

An integration of gas upgrading system after methanation process is carried out in a complete flowsheet. This system involves different models and specifications which have to be considered. PENG_ROB method has been implemented as the base property method which can be chosen in Properties section of Aspen Plus® V8.6. This property method is comparable with the RK-SOAVE property method. It is highly recommended for gas-processing, refinery and petrochemical systems. The PENG-ROB property method can also be utilized for non-polar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulfide and hydrogen.

3.1 Specifying blocks

The flowsheet (Figure 4) consists of the following blocks: a pre-heater which is used to increase the temperature of feed up to the operating set point condition. It was implemented using an isentropic single stage compressor unit operation model, COMPR to raise the flow pressure up to 10 bar.

Heat exchanger plays a vital role in the flowsheet of the process. Prior to reactor, a pre-heating operation is needed to prepare the reactant. Also, after methanation process, the product stream temperature has to be reduced to 4 °C for water removal. HEATER block performs these types of single phase or multiphase calculations. Heater produces one outlet stream, with optional water stream. The heat duty specification may be provided by a heat stream from another block. If user enters one specification (temperature or pressure) on the Specifications sheet, HEATER uses the sum of the inlet heat streams as duty specifications. Otherwise, heater uses the inlet heat stream only to calculate the net heat duty.

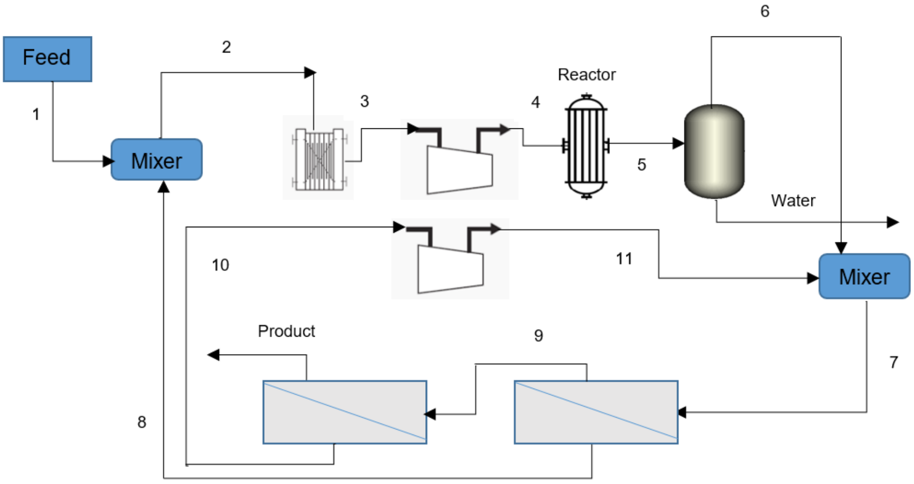

Figure 4: A schematic of methanation process and purification of natural gas using Aspen Plus® V8.6 flowsheet

The RGIBBS reactor model is chosen for methanation process. As it was addressed before (Sharifian and Harasek, 2015), this model verified very well the process of CO2 and CO hydrogenation.

As default, RGIBBS is based on the assumption that all the species of solution are distributed in all phases. In this study, both vapor and liquid phases are considered. In addition, it is assumed that the model considers all components as products. In the Setup specification, the products sheet can be defined to assign different sets of species to each solution phase. Furthermore, different thermodynamic property methods can be selected for each phase. The temperature of 250 °C and pressure of 10 bar are the main operating conditions of this model which calculates at the phase and chemical equilibrium point.

MIXER is another important block which is used in the flowsheet (Figure 4). Mixer combines the material streams (or heat or work streams) into one outlet.

Table 4: Streams specification related to Figure 4

Stream NO	1	2	4	5	6	7	8	9	10	Product
Mole Fraction										
CO_2	0.2	0.197	0.197	0.001	0.015	0.013	0.09	0.005	0.04	trace
CO	0	trace	trace	Trace	trace	trace	trace	trace	trace	trace
H_2	0.8	0.797	0.797	0.017	0.075	0.085	0.60	0.041	0.387	0.018
CH_4	0	0.005	0.005	0.332	0.923	0.901	0.39	0.956	0.605	0.982
H_2O	0	trace	trace	0.649	trace	trace	trace	trace	trace	trace
Total mole flow, kmol h^{-1}	4.02	4.07	4.07	2.47	0.54	0.56	0.04	0.52	0.02	0.50
Temperature, ˚C	25	24	250	250	4	4	4	4	4	4
Pressure, bar	1	1	10	10	50	50	1	50	1	50

After methanation process water removal is very important. FLASH is provided in Aspen Plus library to perform rigorous 2- (vapor liquid) or 3- (vapor liquid liquid) phase equilibrium calculations. In 3-phase FLASH, one vapor outlet stream, one liquid outlet stream, and an optional water decant stream are produced. This model can be used to model flash separations, evaporators, knock out drums, and any other single stage separators especially vapor-liquid deputation with different evaporation points. This separation will be performed by suddenly changes in the operating conditions (mostly pressure and temperature). In our study, water must be removed from the natural gas stream. Thus, relatively high pressure and low temperature are needed to liquefy the high percentage of water which is available in the product stream (60 %). Flash separation is performed at the pressure of 50 bar and temperature of 4 °C, and then the waste water stream can be found from bottom and the enriched vapor product from the top.

USER model which can be found in CUSTOMIZE ribbon Manage Library is the last block for purification (membrane separation system). As mentioned before, through this study a two-stage module purification including recycle streams -one from the first block to methanation process and another from the second block to the first module- was chosen (Figure 4). Table 4 is related to the result streams of the flowsheet (Figure 4).

4. Conclusion

Purification of methane after methanation process is the main aim of this manuscript. Enrichment of natural gas makes it usable for gas grid distribution. Some methods to reach small enough fractions of carbon dioxide and carbon monoxide and also the highest purity for methane in the outlet of methanation process as well as an efficient water removal process were discussed. First of all, a flash separation was chosen in order to remove water from the product stream. After this part, by demand of H_2 and CO_2 removal, the necessity of using a membrane gas separation was shown up. There was no built-in model related to gas permeation application in Aspen Plus V8.6®. Thus, a new FORTRAN user model has been developed for multi-component gas permeation asymmetric hollow fiber membrane system. This model worked like other built-in models in Aspen Plus® V8.6 library and can be used for design, optimization and sensitivity analysis of single gas permeation and multistage systems as well. Comparison of the results of different designs and arrangements showed that the two-stage separation system without recycle has the highest loss for valuable product. In the two-stage with recycle, the first permeate stream contained high amount of CO_2 which can be injected to the fresh feed of methanation process. Whereas, the second module permeate stream can be implemented as a recycle stream before the first permeator because of the high fraction of CH_4. Finally, a complete flowsheet including methanation of carbon dioxide and purification of product was designed.

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