

VOL. 61, 2017



DOI: 10.3303/CET1761135

Guest Editors: Petar S Varbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš Copyright © 2017, AIDIC Servizi S.r.I. **ISBN** 978-88-95608-51-8; **ISSN** 2283-9216

Innovative Methanol Synthesis Process by Using Exergy Recuperative Pressure and Heat Circulation Modules

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The demand for methanol will continue increasing methanol is attractive as fuel applications and chemicals. To reduce energy requirements for the methanol synthesis, it is necessary to investigate a whole process and to retrofit it with energy saving processes. Recently, the authors developed a self-heat recuperation technology (SHR) for saving energy and developed the exergy recuperative pressure and heat circulation modules to expand SHR to the pressure recovery. In this paper, the feasibility of applying exergy recuperative pressure and heat circulation modules to the methanol synthesis process was investigated and an innovative process for methanol synthesis process was developed from the energy saving point of view. By installing exergy recuperative pressure and heat circulation modules to the methanol synthesis process, the energy consumption of the process can be greatly reduced.

1. Introduction

Global methanol demand is about 72 Mt/y. The demand for methanol will continue to increase since methanol is attractive as fuel (Horng et al., 2006) and chemical applications (Manenti et al. 2014). Currently, most methanol is produced from fuel, especially natural gas and coal by steam reforming and gasification reactions. At first, CH₄ from the fuel is mixed with steam and reformed to CO and hydrogen with a catalyst (Puerari et al., 2014). Then, a methanol and water mixture is produced from CO and hydrogen. From CO₂ utilization point of view, methanol production from CO₂ has been recently investigated (Luu et al, 2016). However, the conversion ratio of these reactions is not high enough. Many investigators have managed to produce a catalyst that achieves high conversion from reactant to product in the reactor such as modification of commercial based catalysts (Vanden Bussche and Froment, 1996) and newly developed organocatalysts (Sabet-Sarvestani et al., 2017) or applied the heat recovery technology using combined heat and power (CHP) for increasing energy efficiency of the plants (Azadi et al., 2016).

Recently, self-heat recuperation technology was developed by authors (Kansha et al., 2009). In this technology, the latent heat as well as the sensible heat of the process stream can be circulated without any heat addition, leading to a reduction in the energy requirement of several chemical processes by using compressors and self-heat exchangers based on exergy recuperation. As a result, the heat of the process stream is perfectly circulated, and thus exergy loss during heat transfer can be minimized (Kansha et al., 2013). This self-heat recuperation technology is suitable for thermal and separation processes and can be applied to several chemical processes for energy savings. Kansha et al. (2014) have proposed a methanol synthesis demonstration plant referred as LPMEOH[™] Demonstration Unit (Heydorn et al., 2003) based on self-heat recuperation. In this study, plant was designed by focusing to maximize internal heat circulation duties.

This study investigated the feasibility of pressure and heat circulation modules by expanding self-heat recuperation technology to an industrial methanol synthesis process based on actual plant data.

2. Methanol synthesis process

Methanol is produced from reformed carbon monoxide and hydrogen from a fuel mixture together with a catalyst. After the reactions take place in the reactor, the product mixture from the reactor contains the methanol product as well as water because of the sub-reactions, in addition to reactant gases. For product separation from the reactant recycle stream, the product mixture from the reactor is fed through a gas-liquid separator to achieve high reaction conversion. The product crude methanol that contains the methanol and other components is fed into the distillation processes to purify the methanol. Methanol synthesis process is composed by two main sections, reaction section and distillation section.

2.1 Reaction section

Figure 1 shows a flow diagram of the actual industrial reaction section of the targeted methanol synthesis process. Feed gas which composed of CO, CO₂ and hydrogen is supplied as Make-up gas to the reaction section and compressed by compressor (stream 1). This stream is mixed with recycled gas (stream 9) and heated by heat exchanger (stream 2). Stream 2 is supplied to a reactor, in which methanol synthesis reactions are taken place. These methanol synthesis reactions are represented by the following reactions;

CO(g) + 2H₂(g)↔ CH₃OH(g)
$$ΔH_{298} = -90.55 \text{ kJ mol}^{-1}$$
 (1)

$$CO_2(q) + H_2(q) \leftrightarrow CO(q) + H_2O(q)$$
 $\Delta H_{298} = +41.12 \text{ kJ mol}^{-1}$ (3)

where ΔH_{298} is the heat of reaction at standard temperature and pressure, i.e. 298 K and 1 atm. Eq(1) and Eq(2) are CO and CO₂ hydrogenation reaction and Eq. (3) is the reverse water–gas shift reaction (Farsi and Jahanmiri, 2011). Therefore, overall reaction in the reactor is exthothermic reaction. This reaction heat is recovered by steam generation in industry. In fact, boiler feed water (BFW) is supplied to the reactor and steam is generated (middle pressure steam: about 3 MPa) by using reaction heat in Figure 1. The reactions isothermally take place at about 245 °C. Stream 3 is the product methanol and unreacted gas mixture. The heat of this stream is exchanged with the heat of feed stream (stream 2) for recovering a part of reaction heat. After that, stream 3 is cooled by cooler to condense methanol (stream 4) and provided to the separator (high pressure separator). In the separator, condensed methanol (stream 5) is separated from unreacted gas mixture (stream 6). Stream 5 is depressurized by valve and supplied to purification section as crude methanol. A part of unreacted gas is purged as purge gas (stream 7) for a fuel in the plant. Most of unreacted gas is recycled (stream 8) to adjust the pressure by circulator (stream 9). According to Le Chatelier's principle, high pressure condition is preferable for this methanol synthesis. In fact, methanol synthesis reaction takes place at about 10 MPa in industry.



Figure 1: A flow diagram of the reaction section of the targeted methanol synthesis process

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2.2 Purification section

In industry, crude methanol from reaction section is purified by distillation as shown in Figure 2. Crude methanol from reaction section is supplied to distillation column as stream 1. In the first distillation column, light ends gas, small amount of hydro carbon gas such as methane and ethane is separated from crude methanol. The bottoms of this distillation (stream 3) is supplied to the next distillation for separating product methanol (stream 4) and heavy ends which is heavier hydro carbon compounds such as dimethyl ether (stream 5).



Figure 2: A flow diagram of the purification section of the targeted methanol synthesis process

3. Simulation results

A simulation was conducted using PRO/II Ver. 9.0 (Invensys, SimSci) to examine the energy required for the self-heat recuperative methanol synthesis process and to compare it to that of the actual industrial methanol synthesis process. In this simulation, the Soave-Redlich-Kwong modified (SRK-M) was selected for the thermodynamics data and 100 % adiabatic efficiency was assumed for the compressors. In addition, the minimum temperature difference for the heat exchangers was fixed at 30 K and 10 K for the heat exchangers in the reaction section and in the distillation section respectively. The heat and pressure losses from the system are negligible. The product methanol rate was 10 t/d. The conditions of the feed (Make-UP Gas) were fixed at 45 °C and 2.0 MPa. The reaction conditions were fixed at 245 °C as isothermal reactor and 10.0 MPa. Table 1 shows the representative stream conditions of the reaction in this process as outlined in Figure 2.

Stream No.	1	2	3	4	5	6	7	8 (= 9)
Flow Rate [kg-mol/h]	59.74	191.17	164.65	164.65	18.85	145.80	14.38	131.42
Temperature [°C]	45	245	245	45	45	45	45	45
Pressure [MPa]	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Composition								
CO ₂	0.09	0.04	0.02	0.02	0.01	0.02	0.02	0.02
CO	0.14	0.05	0.01	0.01	0.00	0.01	0.01	0.01
H ₂	0.73	0.81	0.76	0.76	0.00	0.85	0.85	0.85
Methane	0.03	0.08	0.10	0.10	0.01	0.11	0.11	0.11
N ₂	0.00	0.01	0.01	0.01	0.00	0.01	0.01	0.01
H ₂ O	0.01	0.00	0.03	0.03	0.28	0.00	0.00	0.00
Methanol	0.00	0.00	0.08	0.08	0.70	0.00	0.00	0.00
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table	1:	Stream	conditions
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By following these assumptions and settings, energy required for the reaction section of the conventional and proposed process were examined as shown in Figure 3 and 4. The conventional process required 79 kW (= 39 + 40) for compression works and 59 kW heat was supplied from reaction heat. Thus, 258 kW heat was recovered by steam generation. On the other hand, the proposed process required 106 kW (= 72 + 60 - 26) for compression and expansion. All of exothermic reaction heat (317 kW) can be recovered by steam generation.

Next, energy required for the purification section of the conventional and proposed process were examined as shown in Figure 5 and 6. In this part, over all process temperature is close to ambient temperature. Therefore, the minimum temperature difference in the heat exchanger was set to 10 K. The feed stream was crude methanol which contains 70 mol% methanol. The number of stages of the first and second distillation columns were set to 61 and 80 to satisfy the product methanol composition. Feed stages of distillation columns were set to 20 and 30 from top. To examine the energy consumption of the conventional and proposed process, process simulation was conducted. It can be seen from Figure 5 that the first distillation column was required to 89 kW for the bottom reboiler and that the second distillation column required for 381 kW for the bottom reboiler in the conventional purification section. On the contrary, it can be seen from Figure 6 that the first distillation column was required to 7 kW for the compressor and that the second distillation column required for 75 kW for the compressor in the conventional purification section. The comparison of energy consumption among the conventional and proposed processes was summarized at Table 2. It can be understood that the proposed process required for only 1/3 of energy consumption of the conventional process. Furthermore, the steam generation amount of the proposed process was larger than that of the conventional process. By following the design theory of the pressure circulation module, a part of cooler duty should be recovered by stream 8 in reaction section of the proposed process.



Figure 3: A flow diagram and energy consumption of the conventional reaction section



Figure 4: A flow diagram and energy consumption of the proposed reaction section

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Figure 5: A flow diagram and energy consumption of the conventional methanol purification process



Figure 6: A flow diagram and energy consumption of the proposed methanol purification process

		Conventional Process	Proposed Process
Reaction	Heat [kW]	0	0
	Work [kW]	79	106*
Purification	Heat [kW]	470	0
	Work [kW]	0	82*
Total [kW]		549	188
Steam generation [kW]		258	317

Table 2: Summary of Energy Consumption

*Net Energy Required (Compressor - Expander), Adiabatic efficiency: 100 %

4. Conclusions

In this paper, the feasibility of applying exergy recuperative pressure and heat circulation modules to the methanol synthesis process was investigated and an innovative process for methanol synthesis process was developed from the energy saving point of view. The use of exergy recuperative pressure and heat circulation modules for methanol synthesis led to a drastic reduction in the energy consumption of the industrial process. This phenomenon shows that a new process design methodology using exergy recuperative pressure and heat circulation modules has further energy saving potential for other chemical processes.

Acknowledgments

This work was supported by the "Advanced Low Carbon Technology Research and Development Program" of the Japan Science and Technology Agency.

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