



Evaluation of Steam Reforming Based on Carbon Number in Natural Gas Processing

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Abstract. The methanol production process through the reforming unit is a crucial step in converting natural gas into synthesis gas, which is used as the primary feedstock in synthesizing high-quality methanol (grade AA). Periodic evaluation of the reforming unit performance is essential to ensure process optimization and the synthesis of gas quality. This study uses Aspen HYSYS software simulations to analyze the effect of operating conditions and natural gas feedstock characteristics on reforming unit performance. The analysis was carried out by comparing the composition of natural gas at two different periods, identifying the key parameters that affect methane conversion, and evaluating the effect of temperature and pressure on synthesis gas quality. The results showed increased operating temperature and pressure contributed to increased methane conversion and H₂/CO ratio. High methane content in the feed plays a vital role in the efficiency of the reforming reaction, although the presence of other compounds can inhibit the process. The results showed that on May 31, with better operating conditions, syngas with a composition of 67.64% were produced compared to 67.28% on July 24. However, the increased feed flow rate on May 31 led to higher energy consumption. The conclusion of this study confirms the importance of optimizing operating parameters such as temperature, pressure, and feed composition to improve methanol production efficiency and yield. In addition, the balance between methane and C₂⁺ hydrocarbons in natural gas largely determines the efficiency of methanol synthesis.

Keywords: Aspen HYSYS, Methanol, Synthesis gas, Steam reforming, Unit reformation

1 Introduction

Methanol synthesis has almost always been based on Cu/ZnO₂/Al₂O₃ catalysts since 1970. A natural gas-based methanol plant consists of three components: preparation, synthesis, and distillation. Typically, the syngas component accounts for about 60% of

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the investment. Methanol can be obtained from several processes such as pyrolysis of wood, synthesis from a mixture of hydrogen gas and carbon oxide and partial oxidation of methane. Commercially, methanol is produced from the reaction of syngas (CO , CO_2 , dan H_2) obtained or produced from natural gas. Methanol has proven useful for direct use as a fuel in methanol fuel cells (DMFC) or after reforming. In addition, methanol is used to produce chemicals such as formaldehyde (CH_2O), acetic acid (CH_3COOH), dimethyl ether (DME, CH_3OCH_3) and others [1].

In the early 1930s, there was an increasing demand for octane petrol. Research into methods and techniques to increase the number of octane fractions in the boiling point range of petrol attracted attention. Any process that increases octane will increase the demand for higher octane petrol, as pure (distillate) petrol often has a very low octane. Many people use a process called thermal reforming, but to a much lesser extent than thermal cracking. Thermal reforming is a natural progression of the older thermal cracking process, where heavier oils are converted into gasoline, whereas reforming converts (reforms) gasoline into higher octane petrol. The equipment for thermal reforming is basically the same as thermal cracking, but the temperature used is higher [2].

The methanol production process consists of several main units, one of which is the reforming unit. The reforming unit plays an important role in converting natural gas into synthesis gas, which will then be used as the main raw material for methanol synthesis. The quality of synthesis gas produced by the reforming unit will greatly affect the performance and productivity of the methanol synthesis unit, including its ability to produce high purity methanol (grade AA).

The reforming process in methanol plants aims to convert feed gas into syngas (synthesis gas), which is then used as feedstock for methanol synthesis. In this process, there are two main stages, namely primary reforming and secondary reforming, each of which has an important role in ensuring the efficiency and effectiveness of syngas production. Primary reforming is the initial stage where the feed gas, which usually consists of a mixture of light hydrocarbons such as methane, is reformed into syngas with the help of steam (water vapor) at high temperature and pressure. This process is carried out in the primary reformer reactor, where the reaction is endothermic, where heat is required to break down the hydrocarbon molecules into carbon monoxide (CO), hydrogen (H_2), and a small amount of carbon dioxide (CO_2). Catalysts commonly used in primary reforming are nickel-based, which are effective in supporting this reforming reaction. After the primary reforming stage, the syngas produced still contains residual hydrocarbons that have not been fully converted. At this stage, the syngas coming out of the primary reformer is mixed with air or supplemental oxygen before entering the secondary reformer reactor where in methanol synthesis air will be the reactant while in ammonia air can be used as a nitrogen source. The aim is to increase the conversion of the remaining hydrocarbons into syngas. This reaction is usually exothermic, which means it produces heat. Secondary reforming also helps in balancing the hydrogen to carbon monoxide (H_2/CO) ratio in the syngas according to the needs of the subsequent methanol synthesis process [3].

Types of reforming include some of the main approaches used by the industry. One is catalytic reforming, which uses catalysts such as platinum to increase the octane

value of naphtha, a light fraction of petroleum. The catalyst breaks down long-chain hydrocarbons into smaller, branched molecules, which have a higher-octane value. Steam reforming without a catalyst simply uses high heat to convert long-chain hydrocarbons into hydrocarbons with different structures; it produces synthesis gas consisting of hydrogen and carbon monoxide and is often used in hydrogen production [2].

Reforming is essential in methanol production as it provides synthesis gas, or syngas, consisting of hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). In catalytic reactions, this synthesis gas serves as the base material for methanol manufacture. Therefore, the main goal of methanol manufacturing is to produce high-quality synthesis gas from hydrocarbons, such as natural gas or naphtha, which is ideal for subsequent reactions. In addition, the reforming process also produces hydrogen, which is essential for reactions that produce methanol from carbon monoxide. Reforming makes methanol manufacture more efficient, reduces energy wastage, and increases production yields by providing the right synthesis gas [4].

The endothermic nature of the reforming reaction means that it absorbs heat during the reaction. To maintain the reaction at the desired rate, this negative reaction and the high output temperatures typically associated with reforming process conditions require a large supply of heat energy. As a result, heat must be continuously introduced into the system to maintain the required temperature and allow the reaction to proceed properly. This heat supply is usually carried out in industrial practice by means of heated or fired reactors, where fuel is burned to generate sufficient heat for the reforming process. This method allows precise control of the reaction temperature, which is crucial for achieving maximum conversion of the feedstock into the desired product, such as synthesis gas. In steam reforming there are several reactions, namely:

Table 1. Steam Reforming Reactions [4]

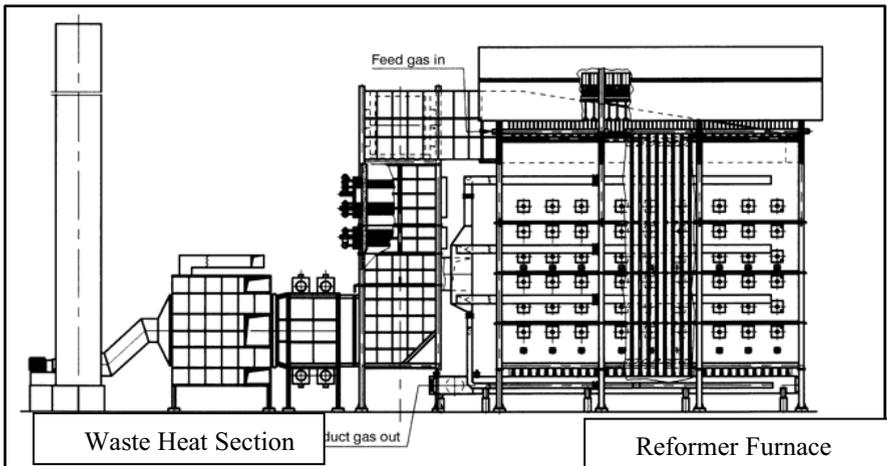
Reaction		$-\Delta H_{298}^0$	$\frac{\text{kJ}}{\text{mol}}$
R1	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	-206	
R2	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	-165	
R3	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	-247	
R4	$CO + H_2O \leftrightarrow CO_2 + H_2$	41	
R5	$C_nH_m + nH_2O \leftrightarrow nCO + (n + 0.5m)H_2$	<0	

In addition to the steam reforming reaction, carbon can also be formed according to the reaction in Table 2.

Table 2. Carbon-Forming Reactions [4]

Reaction		$-\Delta H_{298}^0$	$\frac{\text{kJ}}{\text{mol}}$
R6	$\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$	-75	
R7	$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$	172	
R8	$\text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O}$	131	
R9	$\text{C}_n\text{H}_m \rightarrow n\text{C} + 0.5m\text{H}_2$	<0	

Catalyst properties are usually determined by severe operating conditions, such as temperatures of 450-950°C and vapour partial pressures of up to 30 bars. The surface area of nickel determines the intrinsic activity of the catalyst. As shown in Fig. 1, the catalyst is fed into several high-alloy reforming tubes placed in a furnace. The tubular reformer has various tube and burner arrangements to choose from [4].

**Fig. 1.** Reformer Furnace and Waste Heat Section [4]

In the reforming process, catalysts, such as the commonly used nickel, accelerate the reaction between methane and water vapour to produce hydrogen (H_2) and carbon monoxide (CO). This process is essential for the production of synthesis gas. In addition, these catalysts lower the required operating temperature, improve energy efficiency, and reduce coke formation, which can damage the catalyst and reduce the effectiveness of the process. Due to the balance between H_2 and CO in the synthesis gas, the gas ratio is very important for methanol synthesis. The H_2/CO molar ratio should be around 2:1 for ideal methanol synthesis. This ratio ensures that enough hydrogen is available to convert carbon monoxide to methanol through the catalytic reaction carried out in the

methanol synthesis reactor under specific conditions. If the H_2/CO ratio is not suitable, methanol production efficiency may decrease, and more unwanted by-products, such as carbon dioxide (CO_2), may result. Therefore, to guarantee an economical and efficient methanol synthesis process, the use of effective catalysts and proper control of the synthesis gas composition are essential [5].

The characteristics of the natural gas feedstock greatly affect the performance of the reforming unit. Since methane is the main component converted into synthesis gas, natural gas with a high methane (CH_4) content is suitable for steam reforming. The reason why natural gas with low content of heavy hydrocarbons such as ethane, propane and butane is preferred is that heavy hydrocarbons can increase coke formation on the catalyst, which reduces the reforming efficiency. Removal of sulphur compounds from natural gas before reforming is essential as sulphur compounds, such as hydrogen sulphide (H_2S), can poison the catalyst and lower the efficiency of the process. In addition, inert gases such as nitrogen (N_2) and helium (He) present in natural gas do not participate in the reforming reaction but can reduce the concentration of H_2 and CO in the synthesis gas and increase the energy requirement for heating. In addition, the presence of carbon dioxide (CO_2) in natural gas can affect the performance of the water-gas shift reaction, which converts part of the carbon monoxide into hydrogen and CO_2 and affects the H_2/CO ratio in the synthesis gas. Therefore, in order to guarantee high efficiency and optimal yield in the reforming process, proper selection and purification of natural gas is essential [4].

2 Materials and Methods

This research methodology is a decision-making process to obtain a comparison of natural gas content to produce optimal synthesis gas for methanol synthesis. This research aims to obtain a good natural gas content to be processed into syngas based on steam reforming results. This comparison takes into account the carbon number aspect of all aspects that can affect the steam reforming unit.

Table 3. Thermodynamic Conditions and Flow Rates of Each Pre-Reformer Stream 24 July 2024

Name	Natural Gas	Purge Gas	Steam
Vapor Fraction	1	1	1
T (°C)	22.3	38.2	252.0711273
P (Bar)	30.88	79.9	40.5
Molar Flow (Nm^3/H)	59948.6600	2800	95602.6730
Mass Flow (Kg/H)	46156.8562	624.4413073	76840
Heat Flow (Kcal/H)	-41270988.8005	-202135.2854	-240499454.5977

Table 4. Mole Fraction of Components for each Stream at Pre-Reformer 24 July 2024

Mole Fraction	Natural Gas	Purge Gas	Steam
CO ₂	2.06	1.91	0
CH ₄	95.55	13.61	0
N ₂	0.07	0.23	0
Etana	1.05	0	0
Propana	0.71	0	0
i-Butana	0.15	0	0
n-Butana	0.19	0	0
i-Pentana	0.07	0	0
n-Pentana	0.04	0	0
N-Heksana	0.12	0	0
CO	0	0.82	0
H ₂	0	83.43	0
H ₂ O	0	0	100

Table 5. Thermodynamic Conditions and Flow Rates of Each Pre-Reformer Stream 31 May 2024

Name	Natural Gas	Purge Gas	Steam
Vapor Fraction	1	1	1
T (°C)	22.3	38.2	252.0711
P (Bar)	30.88	79.9	40.5
Molar Flow (Nm ³ /H)	57331.0000	2805	96622.8993
Mass Flow (Kg/H)	47359.4482	750.3824857	77660
<i>Heat Flow (Kcal/H)</i>	-42500051.7831	-	-
		381973.5602	243065950.5994

Table 6. Mole Fraction of Components for each Stream in the Pre-Reformer 31 May 2024

Mole Fraction	Natural Gas	Purge Gas	Steam
CO ₂	3.54	2.67	0
CH ₄	91.12	17.62	0
N ₂	0.07	0.42	0
Etana	2.28	0	0
Propana	1.62	0	0
i-Butana	0.35	0	0
n-Butana	0.44	0	0
i-Pentana	0.17	0	0
n-Pentana	0.11	0	0
N-Heksana	0.3	0	0
CO	0	1.07	0
H ₂	0	78.22	0
H ₂ O	0	0	100

Feed composition is an important factor affecting the pre-reforming process. The higher the heavy hydrocarbon (C_2^+) content in the feed, the higher the temperature and pressure required to achieve the desired conversion. This is because heavy hydrocarbons are more difficult to decompose compared to methane (CH_4).

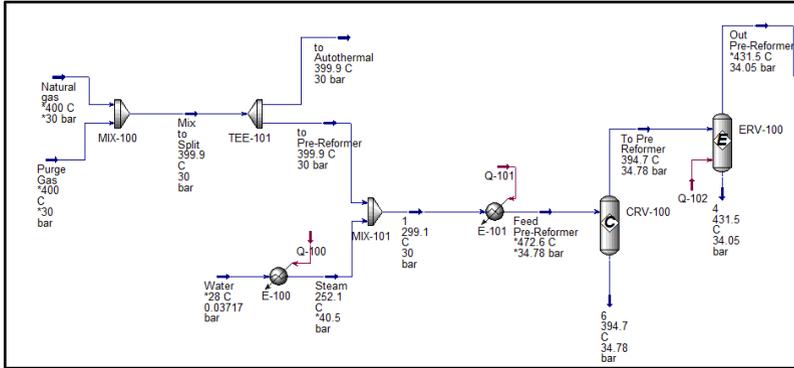


Fig. 2. Hysys Simulation of Pre-Reformer Unit



Fig. 3. One of the Pre-Reforming and Conversion Reaction Mechanisms included

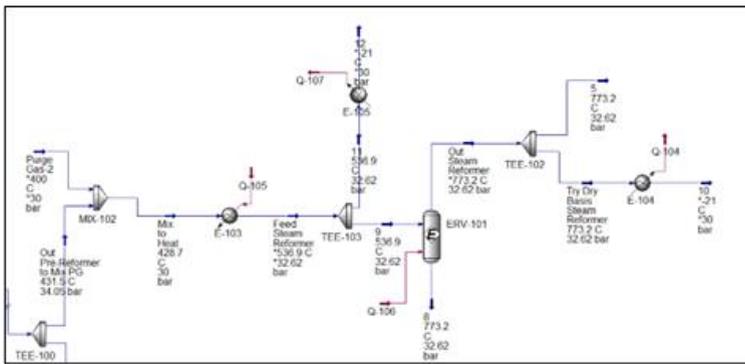


Fig. 4. Hysys Simulation for Steam Reformer Unit

The fluid package's used are Peng-Robinson with ideal vapour assumption. The selected reactor is a conversion reactor that is useful for converting long-chain hydrocarbon gas (C_2^+) into short-chain hydrocarbon gas, and the other reactor is an equilibrium reactor used for water gas-shift reactions. The initial input data included the reaction mechanism, stoichiometric coefficients and conversion rates of the base components for each reaction and the flow rate of each component. Components with sulphur content were ignored as they are very small. The reactions that occur are largely endothermic adiabatic so that the reaction requires heat which is characterised by the exit gas temperature being lower than the inlet gas temperature.

3 Results and Discussions

3.1 Effects of Different Inlet Gas Composition and Flow Rate in The Pre-Reformer

Table 7. Thermodynamic Conditions and Flow Rates of Each Pre-Reformer Inlet and Outlet

Name	Feed Pre-Reformer	Out Pre-Reformer	Feed Pre-Reformer	Out Pre-Reformer
	(24 July 2024)	(24 July 2024)	(31 May 2024)	(31 May 2024)
Vapor Fraction	1	1	1	1
T (°C)	472.6500	431.48	476	441
P (Bar)	34.78	34.05	35.12	34.4
Molar Flow (Nm ³ /H)	143664.3153	148438.8552	143397.1004	149595.1634
Mass Flow (Kg/H)	112672	112672	115080	115080
Heat Flow (Kcal/H)	-260388057.1568	-260048647.5906	-264184753.6714	-263856956.3539

Table 8. Mole Fraction of Components for each Stream in the Pre-Reformer Inlet and Outlet

Mole Fraction	Feed Pre-Reformer (24 July 2024)	Out Pre-Reformer (24 July 2024)	Feed Pre-Reformer (31 May 2024)	Out Pre-Reformer (31 May 2024)
CO ₂	0.69	2.26	1.14	3.14
CH ₄	30.74	30.25	28.60	30.05
N ₂	0.02	0.02	0.03	0.03
Etana	0.34	0	0.71	0
Propana	0.23	0	0.50	0
i-Butana	0.05	0	0.11	0
n-Butana	0.06	0	0.14	0
i-Pentana	0.02	0	0.05	0
n-Pentana	0.01	0	0.03	0
N-Heksana	0.04	0	0.09	0
CO	0.01	0.03	0.02	0.04
H ₂	1.25	6.23	1.19	6.27
H ₂ O	66.55	61.20	67.38	60.47

From the two dates simulated there are some differences between the composition and flow rate data. The flow rate itself on 24 July has an increase of 0.19% compared to 31 May. From Table 7, the Pre-Reformer feed flow rate increased from 143397.1004 Nm³/H on 31 May. to 143664.3153 Nm³/H on 24 July. which shows an increase of 0.19% The feed composition on both dates also has a different C₂⁺ content on 31 May has a C₂⁺ content of 2.32% and on 24 July of 5.27% indicates a heavier burden for the pre-reformer to convert C₂⁺ completely The flow carbon number of natural gas on 31 May was 2734.3107 mol/h while 24 July was 2723.0182 mol/h with a difference of 11.2925 mol/h Although the difference is small. This difference can affect the efficiency and final result of the reaction. especially in processes that are sensitive to the amount of carbon. With 2734.3107 mol/h. the reaction may be slightly more efficient than with 2723.0182 mol/h. as more carbon is available for conversion to product. With a higher carbon flow. methanol or hydrogen production may increase slightly. The temperatures obtained in the two-simulation data are also different where 31 May has a higher temperature of 441°C compared to 24 July at 431.48°C. as well as a much higher pressure of 34.05 bar for 24 July and 34.45 bar on 31 May. Although the 31 May feed flow rate was lower than the above data showing a decrease in CH₄ and an increase in CO and H₂ the productivity of the pre-reformer was maintained thanks to the increase in operating temperature and pressure. However, the increase in pre-reformer temperature on 31 May also required more energy.

Feed composition is an important factor affecting the pre-reforming process. The higher the heavy hydrocarbon (C₂⁺) content in the feed, the higher the temperature and pressure required to achieve the desired conversion. This is because heavy hydrocarbons are more difficult to decompose compared to methane (CH₄). Conversely, methane-rich feeds require lower temperatures and pressures for pre-reforming in the data obtained accordingly where on 24 July the C₂⁺ value was lower than the C₂⁺ value on 31 May so the temperature and pressure on 24 July was lower.

The pre-reformer output gas will be mixed with some purge gas and then fed to the steam reformer. The steam reformer aims to continue the methane reforming reaction from the pre-reformer output into syngas (CO, CO₂, and H₂). The reaction that occurs in the steam reformer is entirely endothermic. In this steam reformer, natural gas is converted into syngas which consists of the majority of H₂, CO₂, and CO.

3.2 Output Effect of Pre-Reforming

Table 9. Thermodynamic Conditions and Flow Rates of Each Steam Reformer Inlet and Outlet

Name	Feed Steam	Out Steam	Feed Steam	Out Steam
	Reformer	Reformer	Reformer	Reformer
	(24 July 2024)	(24 July 2024)	(31 May 2024)	(31 May 2024)
Vapor Fraction	1	1	1	1
T (°C)	536.91	773.1800	546	776
P (Bar)	32.62	29.82	32.92	29.99

Name	Feed Steam Reformer (24 July 2024)	Out Steam Reformer (24 July 2024)	Feed Steam Reformer (31 May 2024)	Out Steam Reformer (31 May 2024)
Molar Flow (Nm ³ /H)	157939.0252	196573.2583	159285.1634	198598.3367
Mass Flow (Kg/H)	114790	114791.0272	117672	117672
Heat Flow (Kcal/H)	-252537361.6545	63252607.8882	-256846286.7144	64086673.3185

Table 10. Mole Fraction of Components for each Stream in the Steam Reformer Inlet and Outlet

Mole Fraction	Feed Steam Reformer (24 July 2024)	Out Steam Reformer (24 July 2024)	Feed Steam Reformer (31 May 2024)	Out Steam Reformer (31 May 2024)
CO ₂	2.24	5.50	3.11	5.83
CH ₄	29.25	13.68	29.29	13.60
N ₂	0.04	0.03	0.05	0.04
Etana	0	0	0	0
Propana	0	0	0	0
i-Butana	0	0	0	0
n-Butana	0	0	0	0
i-Pentana	0	0	0	0
n-Pentana	0	0	0	0
N-Heksana	0	0	0	0
CO	0	6.18	0.10	6.65
H ₂	10.88	41.92	10.65	41.57
H ₂ O	57.52	32.69	56.79	32.32

At initial conditions (24 July), the feed composition was dominated by methane (29.25%) with a flow rate of 157939.0252 Nm³/h, steam reformer feed temperature of 536.91°C, and pressure of 32.62 bar. This resulted in high methane conversion in the steam reformer (41.81%). However, on 31 May, several changes occurred, such as an increase in methane content to 29.29%, an increase in feed flow rate to 159285.1634 Nm³/h, and an increase in steam reformer feed temperature to 546°C, and operating pressure increased to 32.92 bar. These changes resulted in an increase in methane conversion in the steam reformer to 42.13%. However, the synthesis gas production rate increased due to the increase in feed flow rate.

The influence of operating temperature and pressure on steam reformer performance is significant. But it must be seen in relation to the feed composition. On 24 July, the steam reformer feed temperature was 536.91°C and the operating pressure was 32.62 bar. The feed composition at that time was dominated by methane (29.25%), which can facilitate efficient methane reforming reactions at high temperatures. This resulted in a lower methane conversion compared to 31 May in the steam reformer, where on 24 July it was only about 41.81% and on 31 May it was 42.13% and at the temperature

and pressure on 31 May it had a higher value, the decrease in feed temperature caused the methane reforming reaction rate to decrease, so the methane conversion in the steam reformer dropped. In addition, the increase in other contents in the feed, which have slower reforming reaction rates than methane, also decreased the overall effectiveness of the reforming reaction. To improve the performance of the steam reformer, options such as increasing the feed temperature and adjusting the feed composition to increase the H_2/CO ratio can be considered.

The steam reforming process for synthesis gas production is influenced by several key factors, including feed composition, feed temperature and operating pressure. Feed composition is the most important factor, where the methane content is the main component that determines the efficiency of the reforming reaction. The higher the methane content in the feed, the more efficiently the reforming reaction runs. However, the presence of other compounds such as ethane, propane, or natural gas can inhibit the reforming reaction and decrease methane conversion. Higher feed temperatures can promote faster reforming reaction rates, thereby increasing methane conversion. Higher temperatures also favor a water gas shift reaction towards more hydrogen production. However, too high a temperature can accelerate catalyst deactivation and increase energy consumption. Higher operating pressure, on the other hand, tends to increase methane conversion and H_2/CO ratio in the synthesis gas. An increase in pressure shifts the reaction equilibrium towards the formation of more products. However, increased pressure also increases the energy requirement for compression, so energy efficiency needs to be considered.

In general, feeds with high methane content can be operated at lower temperatures to achieve optimal methane conversion and hydrogen production. While for feeds with low methane content, higher operating temperatures are required. In the above simulation, it can be compared that 24 July has a lower temperature with the amount of energy used of 63252607.88 Kcal/h while 31 May has a higher temperature with the amount of energy used of 64086673.31 Kcal/h, where the methane composition is lower on 24 July so that the temperature on 24 July should be higher but this can also be influenced by the incoming flow rate so that the temperature on 31 May is higher than 24 July because the 31 May flow rate is greater than the 24 July flow rate.

4 Conclusion

Good natural gas for methanol production should have high total carbon, including C_2^+ hydrocarbons (ethane, propane, butane, pentane, hexane) and carbon dioxide (CO_2). Although methane (CH_4) is the main component of natural gas, its too high proportion can reduce the carbon fraction of C_2^+ and CO_2 . This results in low total carbon available for methanol synthesis. When the composition of natural gas is dominated by CH_4 , the efficiency of the methanol synthesis process decreases, resulting in reduced methanol production. To increase methanol production yield, it is important to have a proper balance between CH_4 and C_2^+ and CO_2 hydrocarbons in natural gas.

From the composition and flow rate of the input gas on 24 July and 31 May the hysys simulation results show with a high amount of methane and also a larger flow rate produces better syngas where the composition of syngas produced on 31 May is around 67.64% with a flow rate of 198598.33 Nm³/h compared to the composition of syngas produced on 24 July around 67.28% with a flow rate of 196573.25 Nm³/h but has the amount of energy used more due to the greater flow rate, so it can be compared on 31 May and 24 July the gas composition and flow rate is better on 31 May.

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