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Simulation of Methanol Production from Biogas: Impact of Feedstock Composition and Stoichiometric Number Adjustment

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ABSTRACT

Biogas offers a promising biogenic carbon source for renewable methanol, but differences in CH_4/CO_2 ratio across feedstocks and possible upstream CO_2 handling can shift syngas stoichiometry away from the methanol synthesis target range. This work quantifies how biogas composition and reformer operation influence the stoichiometric number (SN) and the associated conditioning requirement needed to meet methanol synthesis targets. A steady-state Aspen Plus® model of an integrated biogas-to-methanol process is used as the analysis framework. A base-case operating point is defined, followed by parametric evaluation of biogas CH_4/CO_2 ratio, reformer temperature, reformer pressure and steam-to-methane (S/C) ratio. The studied CH_4/CO_2 ratio range covers CO_2-rich to CH_4-rich cases that may occur across sites and upgrading levels. The resulting SN shifts are tracked and converted into a quantitative correction requirement to maintain the methanol design target (SN = 2.01). Temperature determines the upper limits of conversion and SN, while pressure and S/C ratio have secondary effects once high-temperature operation is reached. By comparison, the CH_4/CO_2 ratio has the strongest influence on syngas composition, defining H_2-deficiency and H_2-excess regimes. Methanol production increases as SN approaches the required target range but shows diminishing gains beyond it, indicating limited benefit from excess hydrogen under fixed synthesis conditions.

Keywords: biomethanol, biogas, stoichiometric number, eSMR

INTRODUCTION

International shipping is entering a transition period driven by tightening greenhouse-gas regulations and the need to reduce transport emissions. The International Maritime Organization (IMO) reports that international shipping emitted close to one billion tonnes of CO_2 in 2018 and that emissions are expected to grow with the continued rise of maritime trade [1]. To counter this, the IMO and the European Union (EU), among other stakeholders, have implemented measures to support the decarbonisation of marine transport, thus increasing the push for sustainable alternative fuels [2, 3].

Among the available alternatives, methanol has attracted strong interest as a practical short-term option for maritime decarbonisation. Methanol is in liquid form at ambient conditions, it can be stored and handled using established infrastructure, and it is already being used in dual-fuel marine engines [4]. The key point, however, is that methanol's decarbonisation benefit depends on how it is produced. When synthesised from renewable or biogenic carbon sources (biomethanol), methanol can offer substantially lower life-cycle emissions compared to conventional marine fuels [5]. Despite this potential, large-scale renewable methanol production remains limited and requires process configurations that combine robust syngas generation with efficient synthesis and purification.

Biogas-based methanol production is particularly attractive because it relies on biogenic carbon, but it also introduces an important process challenge: biogas composition varies widely with feedstock and digester operation. Biogas typically contains a significant amount of both CH_4 and CO_2. In steam methane reforming (SMR) of biogas, the inlet carbon balance directly shapes the outlet H_2, CO, and CO_2 levels. Hence, changes in feed CH_4/CO_2 ratio strongly influences the resulting syngas composition and its suitability for downstream methanol synthesis [6]. In practice, this means that plants for biogas-based methanol production should be designed to handle varying feed conditions.

A lower direct-emissions route to generate syngas is electrified steam methane reforming (eSMR). In eSMR, high-temperature reforming heat is supplied electrically rather than by fuel combustion, which can reduce direct CO_2 emissions from syngas generation when the electricity is renewable or from other low-carbon sources [6]. However, electrifying the heat supply does not by itself guarantee a syngas composition suitable for methanol synthesis. The syngas composition at the reformer outlet remains sensitive to reformer temperature, pressure, and steam-to-carbon ratio and, critically, the CH_4/CO_2 ratio of the biogas feed, so syngas stoichiometry must be adjusted to meet methanol synthesis requirements.

Syngas quality for methanol synthesis is commonly assessed using the stoichiometric number (SN), $(H_2-CO_2)/(CO+CO_2)$, which reflects the balance between H_2 and carbon oxides (CO_x) in the synthesis gas. Stoichiometric methanol synthesis is equivalent to SN = 2, since this corresponds to the hydrogen-to-CO_x balance required by the overall methanol synthesis stoichiometry. Hence, values close to 2 are typically preferred for methanol production. When SN > 2, the syngas is hydrogen-rich, whereas SN < 2 indicates a carbon-rich mixture with insufficient hydrogen for the synthesis stoichiometry. For biogas reforming, external adjustment through the addition of H_2 or CO_2 (or, alternatively removal of CO_2 or H_2) may be necessary to meet the SN required for methanol synthesis.

The objective of this work is to quantify how biogas composition and reforming conditions influence synthesis gas stoichiometry and the downstream adjustment required to meet methanol design targets. The analysis is focused on steady-state behavior to give clear insight into the relationship between CH_4/CO_2 variability, reformer operation, and stoichiometric control. Specifically, an integrated Aspen Plus® model of a biogas-to-methanol process (eSMR → syngas conditioning → methanol synthesis loop → purification) is used to map how changes in CH_4/CO_2 ratio shift SN and to determine the magnitude and direction of the required conditioning action needed to reach the target SN used for methanol synthesis.

A CH_4/CO_2 ratio range of 1-5 is used as a bounding design range to cover differences across biogas sources and the effect of upstream CO_2 handling, rather than day-to-day variability for a single digester. Hence, the main focus is the syngas production. Process design, optimization, energy use, and cost are not covered in this study.

METHODS

Process Modeling and Simulation

Initially, a steady-state Aspen Plus® base-case model was developed to represent the integrated biogas-to-methanol pathway. The flowsheet comprises biogas compression and preheating, mixing with steam, syngas generation in the eSMR reactor, SN adjustment through addition of H_2 or CO_2, a methanol synthesis loop with recycle/purge, and downstream purification. To calculate thermodynamic properties, Peng–Robinson (PR) was used for the reforming section, Redlich-Kwong-Soave with modified Huron-Vidal mixing rules (RKSMHV2) for the high-pressure methanol synthesis loop, and the non-random two-liquid model (NRTL) for the low-pressure separation section. The main assumptions and key model parameters for the reformer and methanol reactor are listed in Table 1, while Figure 1 illustrates the overall biogas-to-methanol model in more detail.

Table 1: Reformer and methanol reactor key parameters and assumptions.

Block name	Block type	Parameter	Value
ESMR	RGibbs	Calculation mode: chemical equilibrium	
		Operating temperature	950 °C
		Operating pressure	25 bar
		Pressure drop	1 bar
BWR	RPlug	Reactor temperature	230 °C
		Reactor Pressure	75 bar
		Number of tubes	1100
		Length	7 m
		Diameter	0.04m
		Pressure drop	Ergun eq.
		Particle density	1775 kg/m^3
		Particle diameter	5.5 mm

A simplified biogas composition of 60 % CH_4 and 40 % CO_2 (60/40 biogas) was chosen for the base case, with a feed rate of 145 tonne/day. The biogas is compressed to the reformer pressure in a three-stage compressor with intercooling. The compressed biogas is then mixed with 172.7 tonnes/day steam to reach an H_2O/CH_4 (S/C) ratio of 3, selected to suppress carbon formation and ensure stable reforming. In the base case, the eSMR was operated at 950 °C and 25 bar. A target of SN = 2.01 was chosen for the methanol synthesis, potentially adding H_2 or CO_2 downstream to meet this requirement. A value

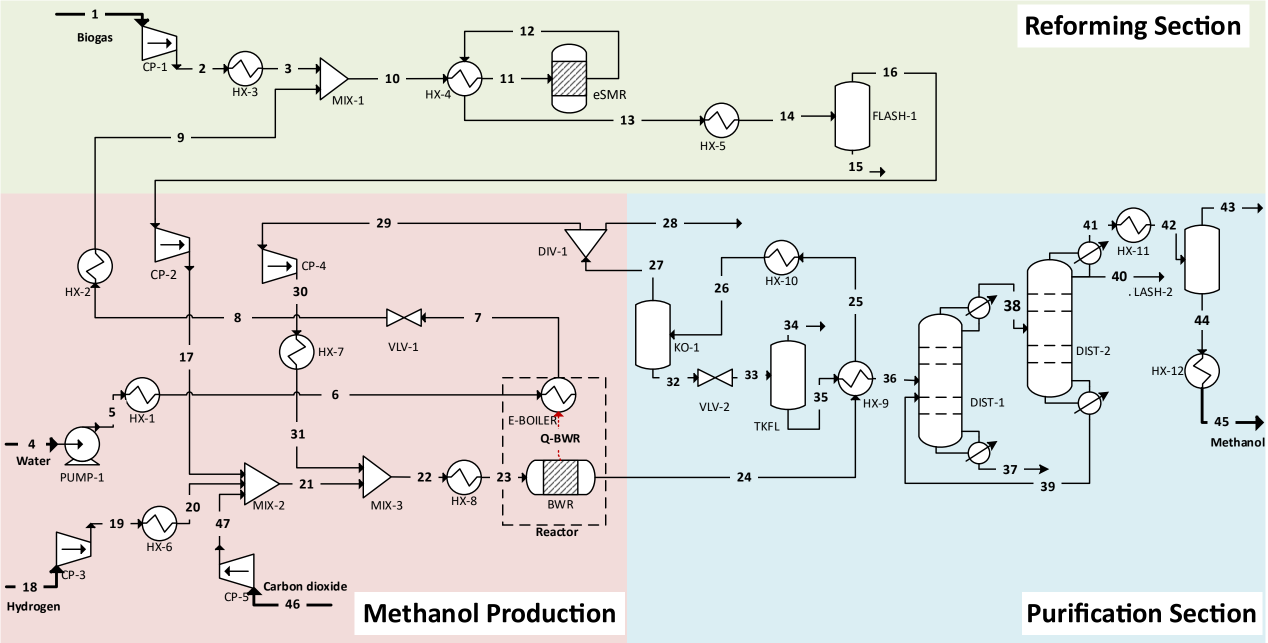

Figure 1: Detailed flowsheet for the biogas-to-methanol production base case

slightly above 2 was chosen as the reaction kinetics benefit from high H_2 partial pressure, and the catalyst benefits from a reducing atmosphere.

The eSMR operating temperature and pressure were selected based on the parametric sensitivity results, while the methanol reactor temperature and pressure were chosen to reflect industrial operating ranges reported by Nyári et al. [7]. The methanol synthesis catalyst and kinetic data were taken from Van-Dal et al. [8].

Reforming Section

The eSMR reactor was modelled in Aspen Plus® using an RGibbs equilibrium block. This choice is consistent with electrically heated reforming concepts, where heat is supplied rapidly and uniformly, minimizing thermal gradients and enabling operation close to thermodynamic equilibrium, as reported by Wismann et al. [9]. The following reforming reactions were modeled:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

In conventional reforming processes aimed at H_2 production, a water–gas shift (WGS) unit is often added to increase H_2 yield. However, when producing methanol, SN plays the key role. Since the WGS reaction generates 1 mol CO_2 for every 1 mol H_2 produced, it has no net effect on SN and mainly adds extra equipment and utility demand. Therefore, a WGS unit was not included in the model.

Methanol Synthesis and Purification

The methanol reactor was modelled in Aspen Plus® using an RPlug reactor to represent a fixed-bed boiling water reactor (BWR). This reactor concept was selected because the exothermic reaction heat can be recovered as steam, which can be integrated to support the upstream steam demand in the reforming section. In addition, the BWR configuration provides effective temperature control, enabling operation close to the optimal reaction temperature.

The reactor kinetics were implemented using the Vanden Bussche-Froment model due to its validity at high-pressure [7], making it suitable for commercial operating conditions. The following reactions were modeled:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{3}$$

$$CO + 2H_2 \leftrightarrow CH_3OH \tag{4}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{5}$$

A recycle-to-fresh ratio of 4 was chosen, balancing conversion gains against increased compression duty. The reactor geometry was tuned to achieve a superficial gas velocity near 0.4 m/s, supporting hotspot mitigation while maintaining reasonable residence time and heat transfer performance in the catalyst bed.

Downstream purification was represented by a flash

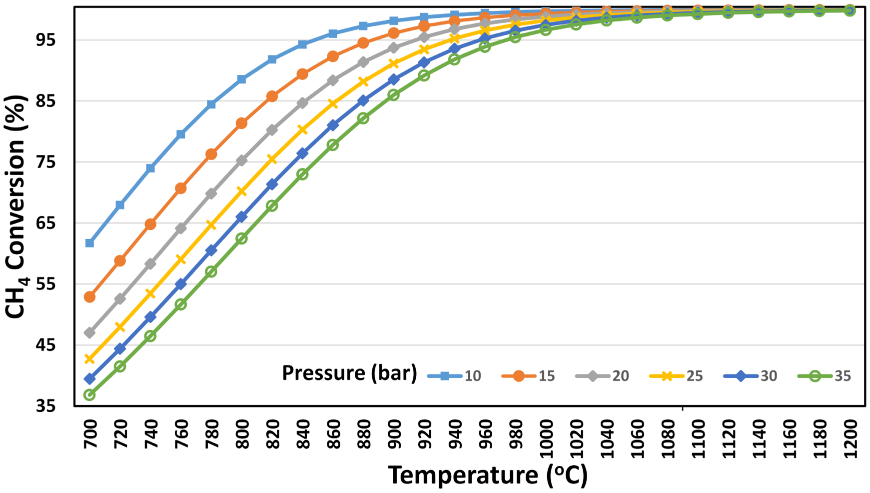

Figure 2. CH_4 conversion as function of reformer temperature for different reformer pressures (60/40 biogas, S/C = 3).

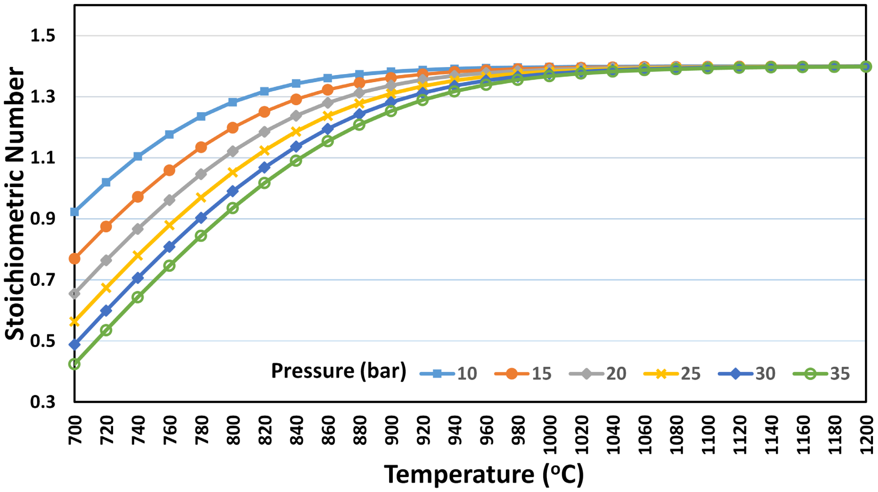

Figure 3. Reformer-outlet SN as a function of reformer temperature for different reformer pressures (60/40 biogas, S/C = 3).

separation (for non-condensable removal) followed by two distillation columns to obtain fuel-grade methanol (99.85 wt%) [10]. The purification section is included to close the overall process and verify the reported fuel-grade methanol purity, but it is not the main focus of this work.

Parametric Analyses

Parametric analyses were performed on a molar basis using the base-case model to examine how changes in feed composition, S/C ratio, reformer temperature and reformer pressure influence reformer-outlet syngas composition and downstream methanol production. Differences between the reformer outlet SN and the methanol design target were assessed to indicate the extent of composition adjustment required to reach the target stoichiometry, i.e., the amount of H_2 or CO_2 added (or removed, depending on the availability of the corresponding resources) to reach the target SN.

RESULTS AND DISCUSSION

Base Case Model

In the base case, the CH_4 conversion in the eSMR reactor was 96.2%, resulting in syngas with SN = 1.36. In order to reach SN = 2.01, 6.8 tonne/day green H_2 was added downstream. The final methanol production in the base case was 151 tonne/day. Table 2 summarises key overall conversion metrics for the base case model.

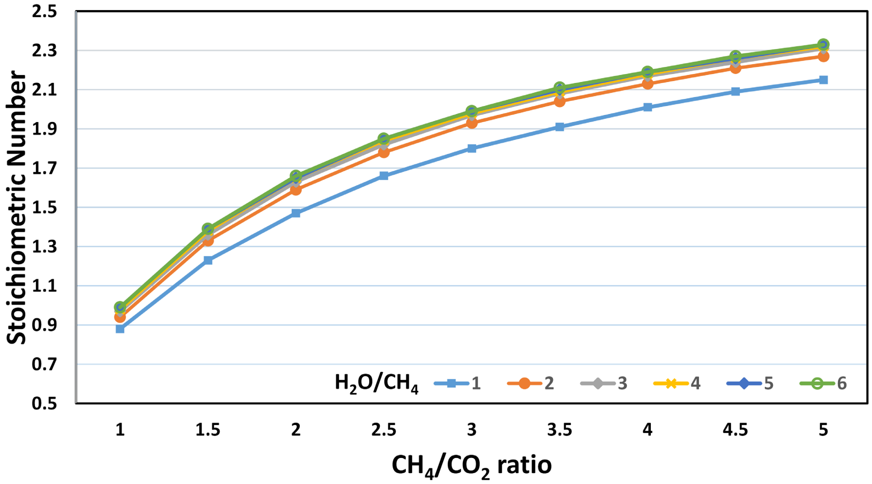

Figure 4. SN as function of biogas CH_4/CO_2 ratio for different S/C ratios (950 °C, 25 bar).

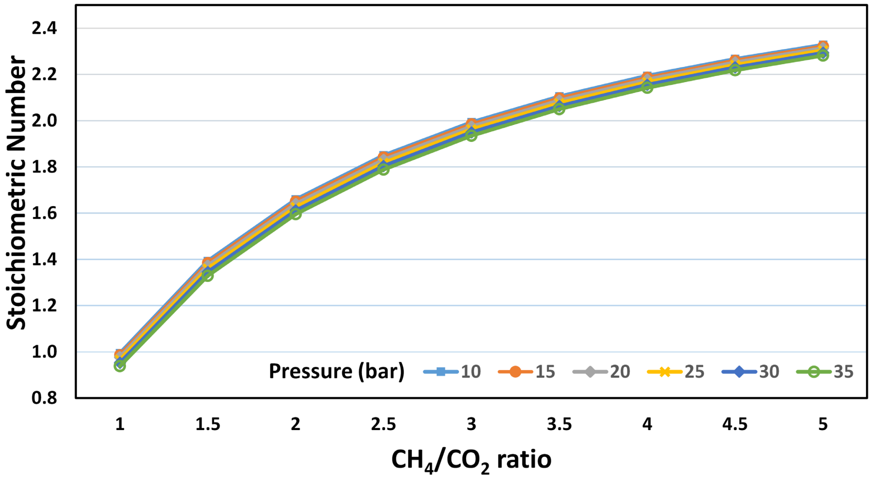

Figure 5. SN as function of biogas CH_4/CO_2 ratio for different reformer pressures (950 °C and S/C = 3).

Table 2: Base case conversion for the methanol section.

Parameter	Value
CO conversion (%)	98.8
CO_2 conversion (%)	87.9
H_2 conversion (%)	93.6
Biogas to methanol conversion (%)	92.9

Parametric Analysis

Figures 2 and 3 first establish the combined influence of temperature and pressure on reformer performance for the 60/40 biogas feed at S/C = 3. As expected for an equilibrium-limited endothermic reformer, increasing temperature increases CH_4 conversion and shifts the outlet composition towards higher H_2 production, which is directly reflected in a higher SN.

Pressure acts in the opposite direction, suppressing conversion and lowering SN, with the effect most evident at the lower end of the temperature range. At sufficiently high temperatures, the conversion and SN curves converge across pressures, indicating that moderate pressure changes have a diminishing influence. This behaviour motivates the selection of 950 °C as a reference operating point for the remaining parametric analysis, where conversion and SN are close to their upper-limit values, and pressure sensitivity is limited. This does, however, come at the cost of high energy input to the reformer.

With the reformer temperature fixed at 950 °C, Figures 4 and 5 highlight the role of feed composition through the biogas CH_4/CO_2 ratio. Figure 4 shows SN as a function of the CH_4/CO_2 ratio at constant reformer temperature (950 °C) and pressure (25 bar) while varying the

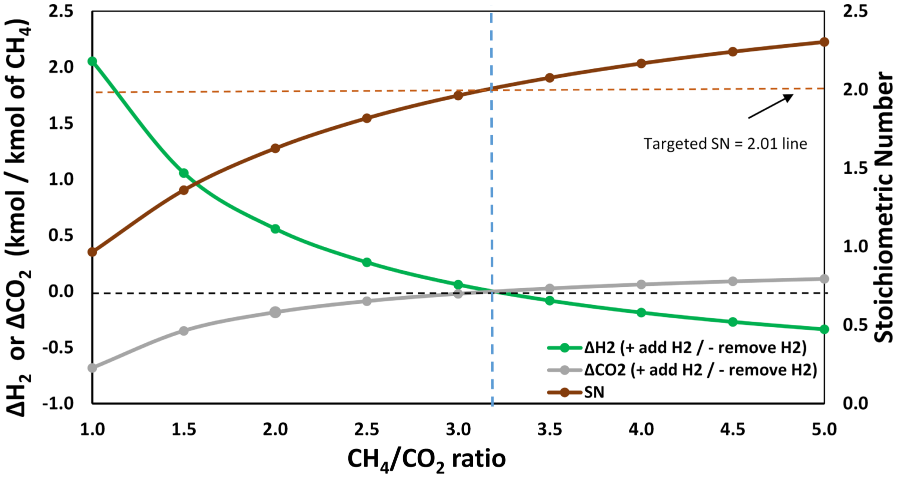

Figure 6. H_2 and CO_2 adjustment required to reach SN = 2.01 as a function of biogas CH_4/CO_2 ratio (950 °C, 25 bar, S/C = 3).

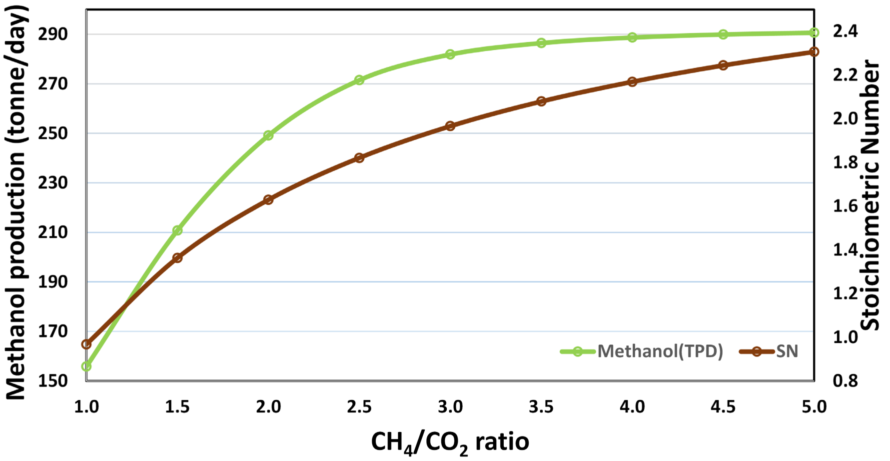

Figure 7. Methanol production rate and SN as functions of biogas CH_4/CO_2 ratio.

S/C ratio. SN increases steadily with increasing CH_4/CO_2 ratio for all S/C values, reflecting improved hydrogen availability as the methane fraction increases. Increasing S/C shifts SN upward across the studied composition range, but the effect reduces at higher S/C, indicating limited additional stoichiometric leverage once sufficient steam is supplied. Importantly, CO_2-rich feeds remain H_2-deficient (SN < 2.01) even at elevated S/C, demonstrating that steam adjustment alone cannot ensure methanol-grade stoichiometry over the full range of biogas compositions studied.

Figure 5 further illustrates this behaviour by showing the pressure sensitivity at constant temperature (950 °C) for S/C = 3. Across the 10-35 bar range studied, pressure has very little effect on SN compared to CH_4/CO_2 ratio. Together, the results in Figures 4 and 5 indicate that while S/C and pressure shift the absolute SN level, the dominant factor governing the transition between H_2-deficiency and H_2-excess regimes is the feed CH_4/CO_2 ratio. This observation motivates the introduction of an explicit stoichiometric correction step when feed composition varies, rather than relying solely on reformer operating adjustments.

In Figure 6, the required stoichiometric correction to reach SN = 2.01 is expressed as a function of the biogas CH_4/CO_2 ratio for a fixed reformer operating point (950 °C, 25 bar, S/C = 3). The maroon curve represents the reformer-outlet SN before any adjustment. The green curve gives the hydrogen adjustment, ΔH_2 (kmol H_2 per kmol CH_4 in the feed) required to reach SN = 2.01, and the grey curve gives the corresponding required CO_2 adjustment, ΔCO_2(kmol CO_2 per kmol CH_4 in the feed). Positive values indicate addition of the respective component, while negative values indicate removal. The blue dashed vertical line marks the feed composition at which the reformer outlet already meets SN = 2.01, so no correction is required. For CO_2-rich feeds (left of the blue dashed line), the syngas is hydrogen-deficient, and the target can be reached by adding H_2 (or alternatively removing CO_2). For CH_4-rich feeds (right of the blue dashed line), the syngas becomes hydrogen-rich, and the correction reverses, requiring CO_2 addition (or alternatively H_2 removal). Overall, the figure links feed composition directly to the magnitude and direction of the adjustment required, while leaving the practical choice of correction route open, without prescribing a specific implementation route.

Finally, Figure 7 shows how changes in the CH_4/CO_2 ratio affect methanol production when the eSMR is operated at 950 °C, 25 bar, and S/C = 3, and no SN adjustment is applied upstream of the methanol reactor. Biogas flow was fixed at 500 kmol/h (to isolate the composition effect) while varying only the CH_4/CO_2 ratio. As the SN value increases with increasing CH_4/CO_2 ratio, the methanol production also increases quickly until the SN reaches the target for methanol production.

Once SN exceeds the target, the increase in methanol production becomes progressively smaller and eventually levels off. This indicates that further increase in SN provide limited additional benefit and can be interpreted as excess hydrogen relative to methanol demand. Together with Figure 6, this result highlights why maintaining SN close to the design value is important: it maximises methanol production while avoiding regimes where additional high-cost H_2 delivers diminishing returns.

CONCLUSION

This work quantified how biogas composition and reformer operating parameters can influence synthesis-gas stoichiometry and methanol production in an integrated biogas-to-methanol process under steady-state conditions. The results show that biogas composition, expressed through the CH_4/CO_2 ratio, is the dominant factor controlling the reformer-outlet stoichiometric number (SN).

Reformer temperature and pressure influence methane conversion and shift SN, but their impact on stoichiometry remains moderate compared with CH_4/CO_2 and becomes less significant as operation approaches high-temperature, equilibrium-limited conditions. When assessed over a bounding design range intended to bracket CO_2-rich to CH_4-rich cases across different sources and possible CO_2 upgrading levels, the process transitions between H_2-deficiency and H_2-excess regimes. Expressing the resulting SN deviation as a correction requirement provides a practical basis for design screening and reveals a crossover near $CH_4/CO_2 \approx 3.21$, where the reformer outlet meets the required SN without adjustment.

Propagating the same composition into the methanol section shows that methanol output improves as SN increases, but the gains diminish once SN exceeds the target value required for methanol production. This indicates that very high SN values mainly create surplus H_2 that is not converted to methanol, rather than delivering proportional increases in methanol production. Overall, the findings emphasise that robust biogas-to-methanol design should be centred on maintaining SN near the synthesis target and sizing conditioning capacity to accommodate plausible feed-composition differences, rather than relying on reformer operating adjustments alone.

Control, energy efficiency, heat integration, hydrogen supply cost, or economic trade-offs were not part of this work. These aspects depend strongly on feed composition and reformer conditions and should be addressed in future work.

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