Thermodynamic Analysis of Methanol Steam Reforming Conditions for HT-PEMFC Feeding: An Aspen Plus® Study

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Abstract

Methanol is a promising hydrogen carrier for compact and low-carbon power generation systems, owing to its liquid state, high volumetric energy density, and potential production from renewable hydrogen and captured CO_2. In this context, high-temperature proton exchange membrane fuel cells (HT-PEMFCs) can be effectively integrated with methanol steam reforming, due to their tolerance to moderate CO concentrations in the reformate. However, the operating conditions of the reformer strongly affect both reformate quality and thermal integration of the overall system.

This study presents an Aspen Plus® thermodynamic analysis of a methanol steam reformer integrated with an HT-PEMFC system. The model includes the methanol/water feed evaporation section, the reformer, the fuel cell stack, the catalytic burner, and heat recovery units. A sensitivity analysis was carried out by varying the methanol content in the MeOH/H_2O feed mixture and the reformer temperature, while keeping the main fuel cell operating parameters fixed. The analysis focused on dry reformate composition, reformer heat duty, catalytic burner heat release, and the Thermal Self-Sustainability Index.

The results show that the H_2 content in the reformate remains high and relatively stable over the investigated range, whereas CO formation is strongly affected by both reformer temperature and methanol content. Methanol-rich mixtures improve the thermal contribution of the catalytic burner and increase the Thermal Self-Sustainability Index, but also lead to higher CO concentrations. A favourable operating window, combining CO_dry≤3mol% and TSI≥1, was identified only under high heat recovery efficiency conditions. Intermediate methanol contents, particularly 65 vol%, provided the best compromise between reformate quality and thermal self-sustainability.

1 Introduction

The transition to low-carbon energy systems requires the development of efficient technologies and energy carriers derived from renewable sources. In this context, hydrogen is widely recognized as a key energy carrier for decarbonization. However, the storage and distribution of hydrogen still present significant challenges due to its low volumetric energy density. For this reason, attention has shifted toward energy carriers capable of simplifying storage, handling, and distribution. Among the available alternatives, methanol (MeOH) represents one of the most promising solutions due to its liquid state, compatibility with existing infrastructure, and higher volumetric energy density compared to compressed hydrogen [1][2]. Moreover, MeOH can be synthesized from captured carbon dioxide (CO_2) and renewable hydrogen, supporting sustainable Power-to-X pathways and circular carbon utilization strategies [3].

High-temperature proton exchange membrane fuel cells (HT-PEMFCs) are of great interest for MeOH-based energy systems. Unlike low-temperature proton exchange membrane fuel cells (LT-PEMFCs), HT-PEMFCs operate at temperatures between 160°C and 220°C and can tolerate carbon monoxide (CO) concentrations up to approximately 3 %mol without significant loss of performance [4][5]. This feature greatly simplifies system configuration, as there is no need for extensive gas purification processes. As a result, the integration of methanol reforming technology and HT-PEMFC fuel cells has emerged as a promising solution for compact and efficient power generation systems [6].

Within these integrated systems, methanol steam reforming (MSR) is a key process unit, as it directly affects hydrogen production, reformate composition, CO concentration, and overall thermal management. MSR is typically carried out at temperatures between 240 and 300°C through highly endothermic reactions that require a continuous supply of heat [7]. Therefore, the reformer's operating conditions strongly influence both the electrochemical performance of the fuel cell

and the thermal integration of the entire system. Parameters such as the reforming temperature and the steam-to-carbon ratio determine hydrogen yield, CO formation, methanol conversion, and the reformer's heat demand, creating significant trade-offs between the quality of the reforming product and thermal self-sufficiency [8].

Despite growing interest in MeOH-fuelled HT-PEMFC systems, the literature still lacks a thermodynamic evaluation of the operating range of the reformer suitable for powering HT-PEMFCs. Little attention has been paid to evaluating the combined effect of operating temperature and the steam-to-carbon ratio on the composition of the reformate and on the reformer's heat demand under conditions compatible with thermal self-sufficiency. For this reason, this study investigates the thermodynamic behavior of methanol steam reforming for HT-PEMFC applications through process simulation with Aspen Plus®. The study focuses on the effect of the main operating parameters on hydrogen production, CO concentration, MeOH conversion, and the reformer's heat load. The objective is to identify operating conditions suitable for efficient powering of HT-PEMFCs and favorable thermal integration.

2 Materials and Methods

This study analyzes an integrated methanol steam reformer/HT-PEMFC configuration developed in the Aspen Plus® environment with the aim of investigating the influence of the reformer's operating conditions on the system's thermal self-sufficiency. The simulation model was implemented based on a recent configuration described in the literature for HT-PEMFC systems fuelled by methanol reformate, while the simplified process flow diagram is shown in **Fig.1** [9].

The Peng–Robinson method was adopted for the thermodynamic description of the system, chosen for its reliability in modeling the gas mixtures involved in steam reforming, combustion, and electrochemical conversion processes [10]. The model was developed using a modular approach, in which the various process units were represented by specific Aspen Plus® blocks to reproduce the behavior of the entire integrated system.

2.1 System Description

The system under analysis consists of a methanol/water feed line, a fuel evaporator, a steam reformer for methanol, an HT-PEMFC stack, a catalytic burner, and a heat recovery section. The process layout is designed to integrate hydrogen production, electrochemical conversion, and heat recovery to reduce the system's external heat demand.

The liquid mixture of methanol and water is first sent to the fuel evaporator, where it is vaporized before entering the reformer. This step allows the reformer to be fed with a gaseous mixture of methanol and steam suitable for the steam reforming process. The vaporized feed is then converted into a hydrogen-rich stream, called reformate, which consists mainly of H_2, CO_2, CO, and residual H_2O. The composition of the reformate depends on the reformer's operating conditions, particularly the reforming temperature and the feed concentration in methanol.

The hydrogen-rich reformate is subsequently fed to the anode side of the HT-PEMFC stack, which operates at a fixed temperature of 160 °C. In the fuel cell, part of the hydrogen is converted into electrical energy, while the unreacted fraction leaves the anode as exhaust gas. At the same time, air is fed to the cathode side to provide the oxygen necessary for the electrochemical reaction.

The anode and cathode exhaust gases are finally directed to the catalytic burner. In this unit, the remaining combustible species are oxidized, allowing the chemical energy still contained in the exhaust gases to be recovered as thermal energy. The hot exhaust gases leaving the catalytic burner are then sent to the heat recovery section. In this section, the available thermal energy is used to preheat the cathode air stream and to support the evaporation of the methanol–water feed. This heat recovery strategy reduces the external thermal demand of the process and improves the integration between the reformer, the HT-PEMFC stack, and the burner.

2.2 Reformer

The reformer converts a mixture of methanol and water into a hydrogen-rich gas (reformed gas) used to power HT-PEMFC fuel cells. Inside the reactor, the following processes primarily take place [9]:

$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	Reforming Reaction	(1)
$CH_3OH \rightarrow CO + 2H_2$	Decomposition Reaction	(2)
$CO + H_2O \rightarrow CO_2 + H_2$	WGS	(3)

From a modeling perspective, the reformer was simulated in the Aspen Plus® environment using the *RGibbs* module. This approach is based on minimizing the Gibbs free energy and allows for the automatic determination of the equilibrium chemical composition of the reformate without having to explicitly specify the stoichiometry of the individual reactions.

The use of the RGibbs model is particularly well-suited for representing complex reforming systems, in which multiple chemical reactions occur simultaneously under conditions of thermodynamic equilibrium. The total Gibbs free energy of the reaction system is [11][9]:

$$E_{Gibbs}^{tot} = \sum_{i=1}^{N} n_i \cdot \mu_i \tag{4}$$

where n_i is the number of moles of species i, and μ_i is their chemical potential.

Finding the values of n_i that minimize the objective function E_{Gibbs}^{tot} is the constraint in this equation. Lagrange multipliers are the appropriate technique that is typically used to minimize the Gibbs free energy problem. The elemental balance, which can be stated as follows, is the problem's constraint.

$$\sum_{i=1}^{N} n_i \cdot a_{i,j} = A_j \quad j = 1, 2, \ldots, k \tag{5}$$

where $a_{i,j}$ denotes how many atoms of the j element there are in a mole of the i species. The total number of atoms of the element j in the reaction mixture is denoted by A_j. The Lagrange function (L) is:

$$L = E_{Gibbs}^{t} - \sum_{j=1}^{k} \lambda_j \cdot \left(\sum_{i=1}^{N} n_i \cdot a_{i,j} - A_j \right) \tag{6}$$

where the Lagrange multiplier is denoted by λ_j. The partial derivatives of Equation (6) are set to zero to determine the extremum point, as follows:

$$\frac{\partial L}{\partial n_i} = 0 \tag{7}$$

This results in a collection of non-linear equations that can be resolved using an iterative method [9].

The reformer was initially simulated using an operating temperature of 270 °C, in accordance with the reference configuration reported in the literature [9].

2.3 HT-PEMFC Stack

In Aspen Plus®, the HT-PEMFC was modelled using two separate blocks designed to simulate the anode and cathode behaviour of the cell. The anode was modelled using a *Splitter*, which was used to separate the fraction of hydrogen consumed during the electrochemical process from the unconverted portion of the syngas. The cathode, on the other hand, was represented by a stoichiometric *RStoic* reactor, within which the following hydrogen conversion reaction was implemented [9]:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \tag{8}$$

This approach makes it possible to approximate the operation of the fuel cell within the Aspen Plus® environment, which does not allow for a direct description of the electron transfer associated with electrochemical phenomena.

The electrical performance of the HT-PEMFC was calculated by means of a Fortran subroutine implementing the empirical voltage model adopted in the reference study. The subroutine was used to estimate cell voltage, current, and electrical power as a function of the hydrogen consumed in the stack. The fuel cell was simulated assuming a constant operating temperature of 160 °C, which was kept constant under all conditions investigated during the analysis. The main nominal operating parameters of the HT-PEMFC system are reported in **Table 1**.

Table 1 Nominal operating parameters of the HT-PEMFC system.

Parameters	Data
Anode feeding stream	Hydrogen rich gas
Cathode feeding stream	Air
Nominal Power	5 kW
Number of cells	120
Number of stacks	1
Maximum utilization H_2	0,74
Stack temperature	160 °C
Active area	165 cm^2
Exhaust temperature	160 °C

These values define the base-case configuration adopted in the simulation, while the reformer temperature and the water-to-methanol molar ratio were subsequently varied in the sensitivity analysis.

2.4 Catalytic Burner

In Aspen Plus®, the catalytic burner was modeled using an *RStoic* stoichiometric reactor, assuming complete combustion of the combustible species present in the inlet stream. The oxidation reactions of hydrogen, carbon monoxide, and any unconverted methanol were implemented within the block.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (9)$$

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O \quad (10)$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad (11)$$

This model allows for the calculation of the heat released by the combustion of the off-gases and for the evaluation of their contribution to the system's overall energy balance.

The heat produced by the burner is used to supply the thermal duty required by the reformer, where endothermic reactions take place. Furthermore, the flue gases exiting the burner are used in the heat recovery section to preheat the air stream supplied to the fuel cell cathode. In this way, the burner plays a central role in the plant's energy integration, as it reduces the need for external heat and enables the assessment of the possibility of achieving thermal self-sufficiency.

In this study, the exhaust gases from the Catalytic Burner are maintained at a constant temperature of 270 °C.

3 Sensitivity Analysis

To evaluate the effect of key operating conditions on the performance of the methanol-fuelled HT-PEMFC, a sensitivity analysis was conducted on the composition of the MeOH/H_2O mixture and the reformer temperature. The analysis focused on the quality of the reformate, the thermal duty of the reformer, and the heat released by the catalytic burner.

The volume fraction of methanol in the MeOH/H_2O mixture was varied between 50 and 70 vol%, while the reformer temperature was varied between 240 and 300 °C.

The 50 vol% case was included in the analysis of reformate quality but excluded from the discussion of burner duty and TSI when the model indicated the need for external heat input.

The quality of the reformate was evaluated based on the dry-basis molar fractions of CO and H_2. CO was taken as a critical parameter for compatibility with the HT-PEMFC, while the H_2 content was used as an indicator of anode fuel availability [12].

To evaluate the heat balance of the reforming section, the Thermal Self-Sustainability Index was introduced:

$$TSI = \frac{\eta_{rec}\, Q_{CB,available}}{Q_{REF}} \quad (12)$$

where $Q_{CB,available}$ is the heat available from the catalytic burner, Q_{REF} is the thermal duty of the reformer, and η_{rec} is the heat recovery efficiency. Three values of η_{rec} were considered: 50%, 70%, and 85%. Values of $TSI \geq 1$ indicate that the heat recoverable from the burner is theoretically sufficient to cover the reformer's thermal demand.

The operating window was defined by simultaneously setting $CO_{dry} \leq 3mol\%$ and $TSI \geq 1$.

4 Results and Discussion

4.1 Effect on Reformate Quality

Fig.2 shows the combined effect of reformer temperature and the composition of the MeOH/H_2O mixture on the CO content in the reformate, expressed on a dry basis. The results show an increase in CO with both reformer temperature and the volumetric fraction of methanol in the feed. The CO content ranges from values below 1 mol% dry under conditions with higher methanol dilution and lower temperature, up to values exceeding 6 mol% dry for mixtures with higher methanol content and at higher temperatures.

Fig.3 shows that the H_2 content remains high and relatively stable over the investigated range, with values ranging approximately from 73 to 75 mol% dry. This indicates that all simulated conditions produce a hydrogen-rich reformate. However, the quality of the gas fed to the HT-PEMFC is primarily limited by CO formation.

4.2 Effect on Thermal Balance

Fig.4 shows the thermal duty of the reformer as a function of operating temperature and the volume fraction of methanol in the MeOH/H_2O mixture. This thermal duty represents the heat demand of the reforming section and was used as a reference for calculating the TSI.

Fig.5, on the other hand, shows the thermal duty of the catalytic burner. The results for the mixture containing 50 vol% methanol are not shown, since under those conditions the concentration of combustible species in the anode off-gas does not allow the burner to reach the target temperature of 270 °C without external heat input. For the remaining compositions, the heat released by the burner increases significantly with the methanol content, while the effect of the reformer temperature is more limited.

This trend shows that mixtures with a higher methanol content improve the burner's thermal efficiency, but this benefit must be weighed against the increase in CO content observed in the reformate.

The comparison between the reformer's heat input and the heat available from the burner was then summarized using the TSI.

Fig.6 shows the trend of the TSI calculated assuming a heat recovery efficiency of 70%. The TSI increases primarily with the volumetric fraction of methanol, confirming that the methanol content is the parameter that most influences the burner's thermal availability. However, cases characterized by higher TSI values also coincide with conditions that favour CO formation, confirming the existence of a trade-off between thermal self-sustainability and reformate quality.

4.3 Trade-off Between CO content and TSI

Fig.7 shows the trade-off between the CO content in the reformate and the Thermal Self-Sustainability Index, calculated assuming a heat recovery efficiency of 85%. This value was selected because, among the efficiencies considered, it represents the first condition under which certain operating points fall within the defined operating window; for lower efficiencies, no simulation simultaneously satisfies the adopted criteria. The dashed lines identify these criteria, namely $CO_{dry} \leq 3mol\%$ and $TSI \geq 1$. The region highlighted in green, therefore represents the conditions that simultaneously satisfy the constraint on reformate quality and that on the reformer's thermal self-sustainability.

The results show that mixtures with lower methanol content have lower CO levels but insufficient TSI values. Conversely, mixtures with higher methanol content provide greater thermal availability but exceed the specified CO limit. Intermediate conditions, particularly those associated with the mixture containing 65% methanol by volume, therefore represent the most favourable compromise.

Overall, the analysis shows that selecting operating conditions requires a trade-off between the quality of the reformate and the thermal self-sustainability of the reforming section, which is heavily dependent on the efficiency of heat recovery from the catalytic burner.

5 Conclusions

In this study, a thermodynamic analysis of an integrated methanol steam reformer/HT-PEMFC system was conducted using Aspen Plus®. The objective of the study is to evaluate the effect of the reformer's operating conditions on the quality of the reformate and on the system's thermal integration. The sensitivity analysis showed that the H_2 content in the reformate remains high and relatively stable within the investigated range. The CO concentration, on the other hand, is strongly influenced by both the reformer temperature and the methanol concentration in the feed. Conditions richer in methanol and higher temperatures favour an increase in CO, thus representing a limitation for compatibility with the HT-PEMFC.

From a thermal standpoint, increasing the methanol content improves the heat released by the catalytic burner and, consequently, the Thermal Self-Sustainability Index. However, this benefit comes at the expense of reformate quality. There is therefore a trade-off between the reformer's thermal self-sustainability and CO reduction. The results show that, among the conditions analysed, the intermediate compositions of the MeOH/H_2O mixture, particularly the case with 65 vol% methanol, represent the most favourable compromise. Furthermore, the emergence of an operating window that

simultaneously satisfies the CO constraint and the TSI ≥ 1 criterion is only possible by assuming high thermal recovery efficiencies from the burner.

Overall, the study highlights that the selection of operating conditions for a MeOH reformer/HT-PEMFC system cannot be based solely on maximizing hydrogen production, but must also consider the quality of the reformate, the heat available from the burner, and the efficiency of heat recovery. The results obtained therefore provide useful guidance for the preliminary design and optimization of HT-PEMFC systems fuelled by reformed methanol, also in view of future experimental analyses and more comprehensive technical-economic or environmental assessments.

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Figure Captions

Fig.1 Process flow diagram

Fig.2 Dry CO content in the reformate as a function of reformer temperature and MeOH content in the feed

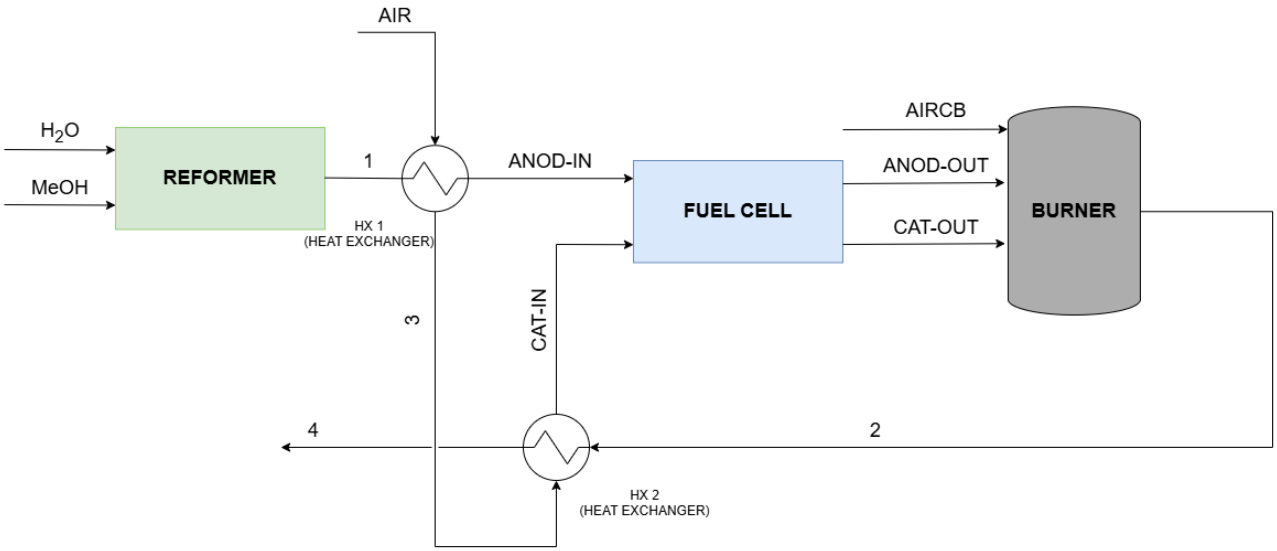
Fig.3 Dry H_2 content in the reformate as a function of reformer temperature and MeOH content in the feed

Fig.4 Reformer heat duty as a function of reformer temperature and MeOH content in the feed

Fig.5 Catalytic burner heat release as a function of reformer temperature and MeOH content in the feed

Fig.6 Thermal Self-Sustainability Index calculated for a burner heat recovery efficiency of 70%

Fig.7 CO–TSI trade-off plot calculated for a burner heat recovery efficiency of 85%, with the favourable operating region defined by CO



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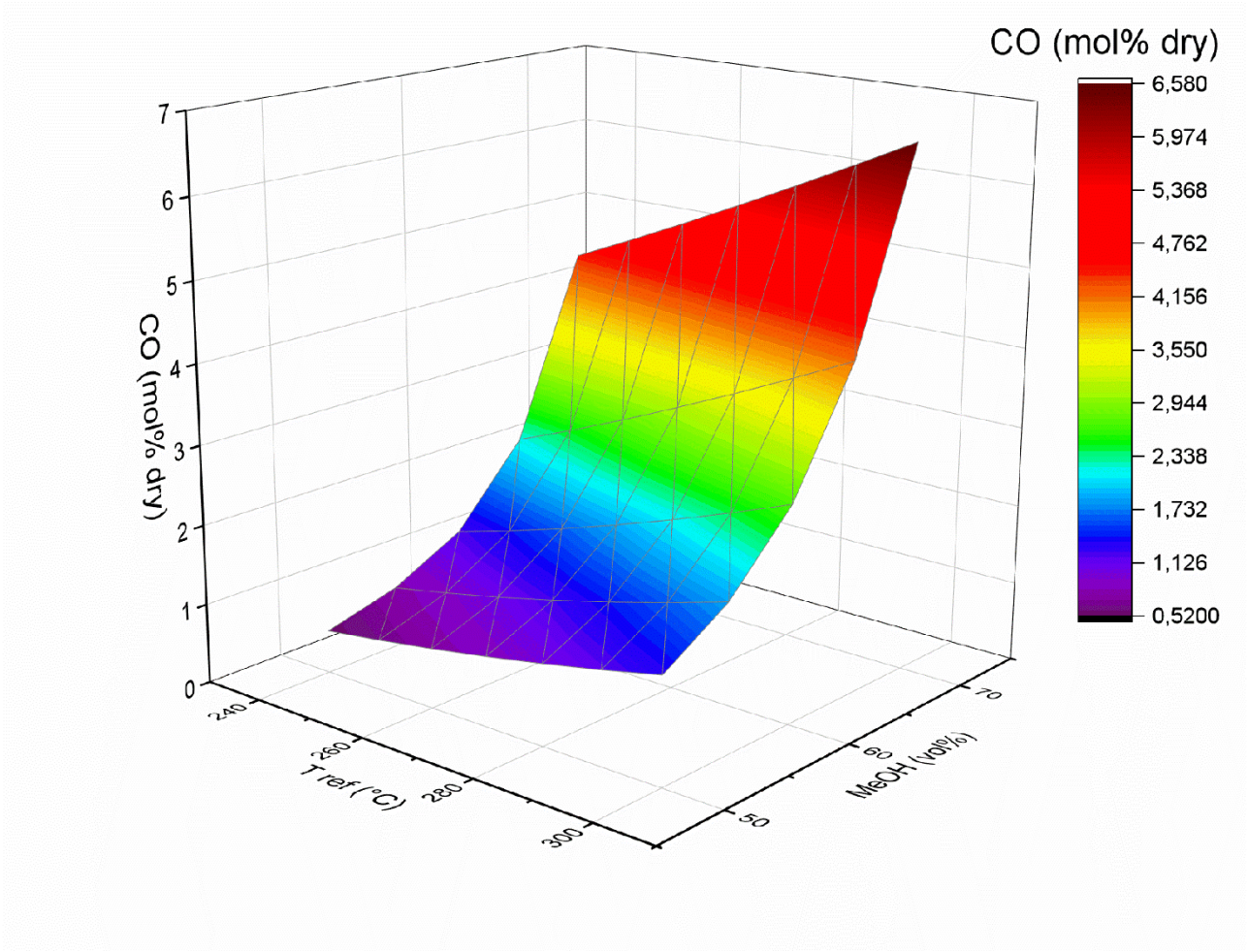


Fig.2 Dry CO content in the reformate as a function of reformer temperature and MeOH content in the feed

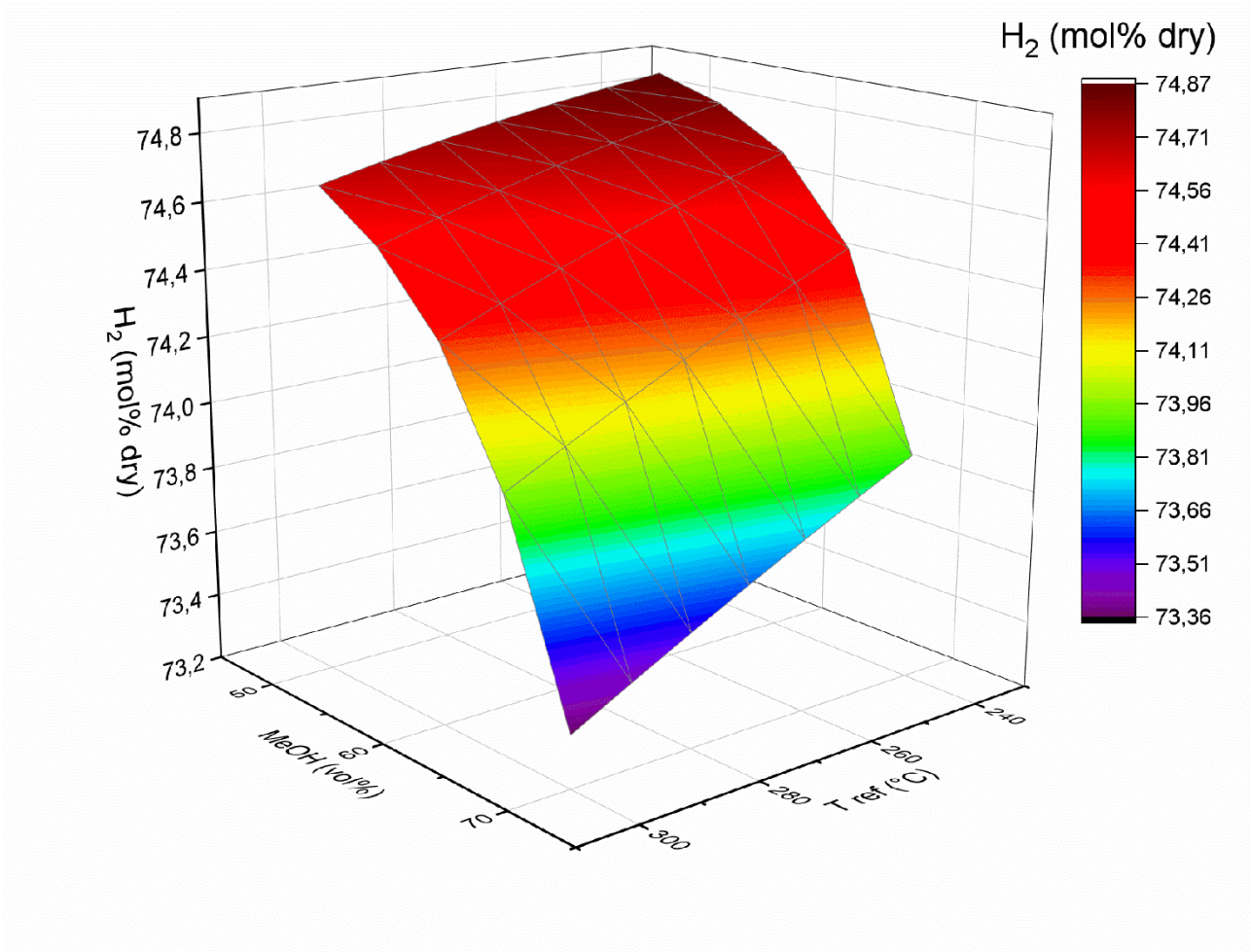


Fig.3 Dry H_2 content in the reformate as a function of reformer temperature and MeOH content in the feed

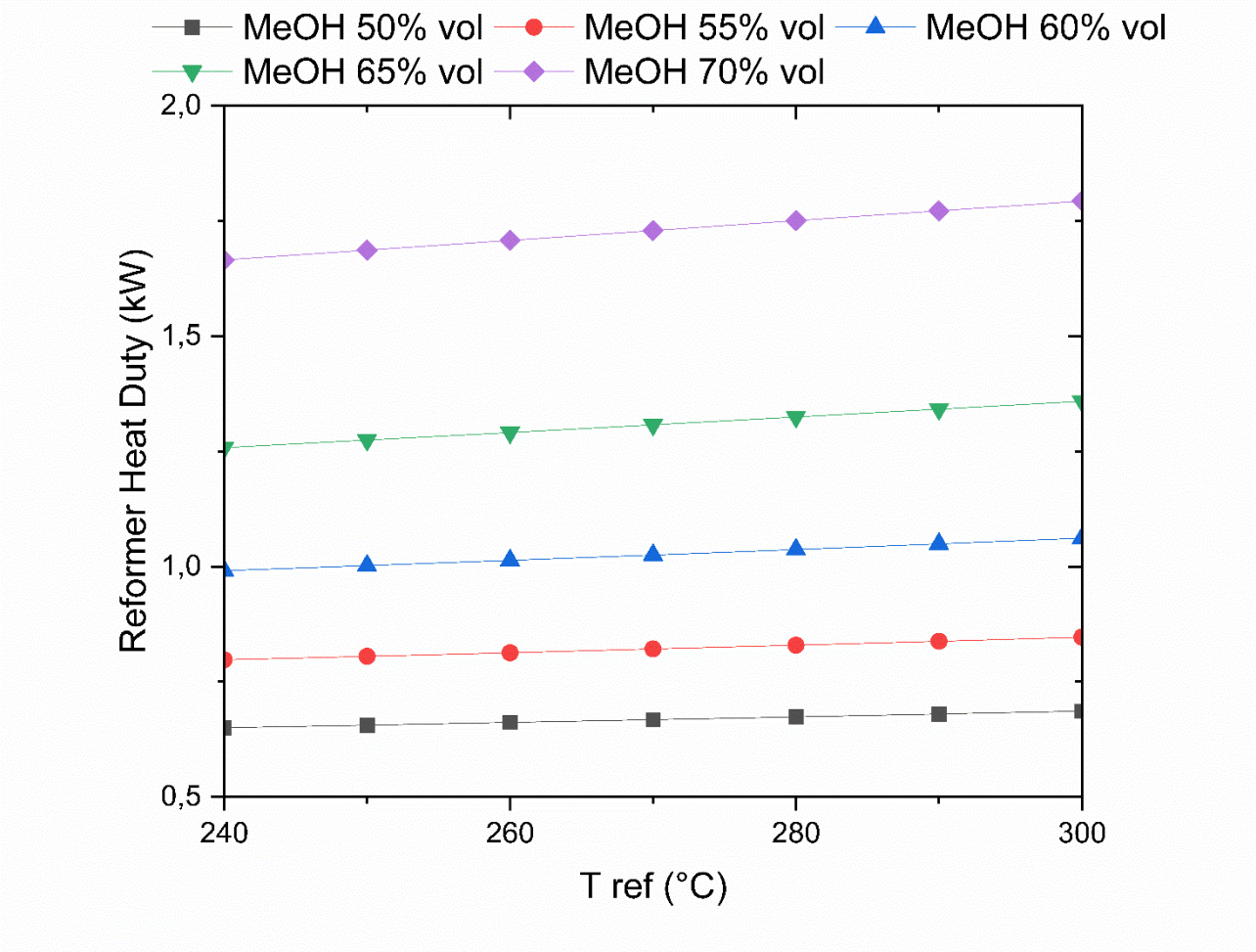


Fig.4 Reformer heat duty as a function of reformer temperature and MeOH content in the feed

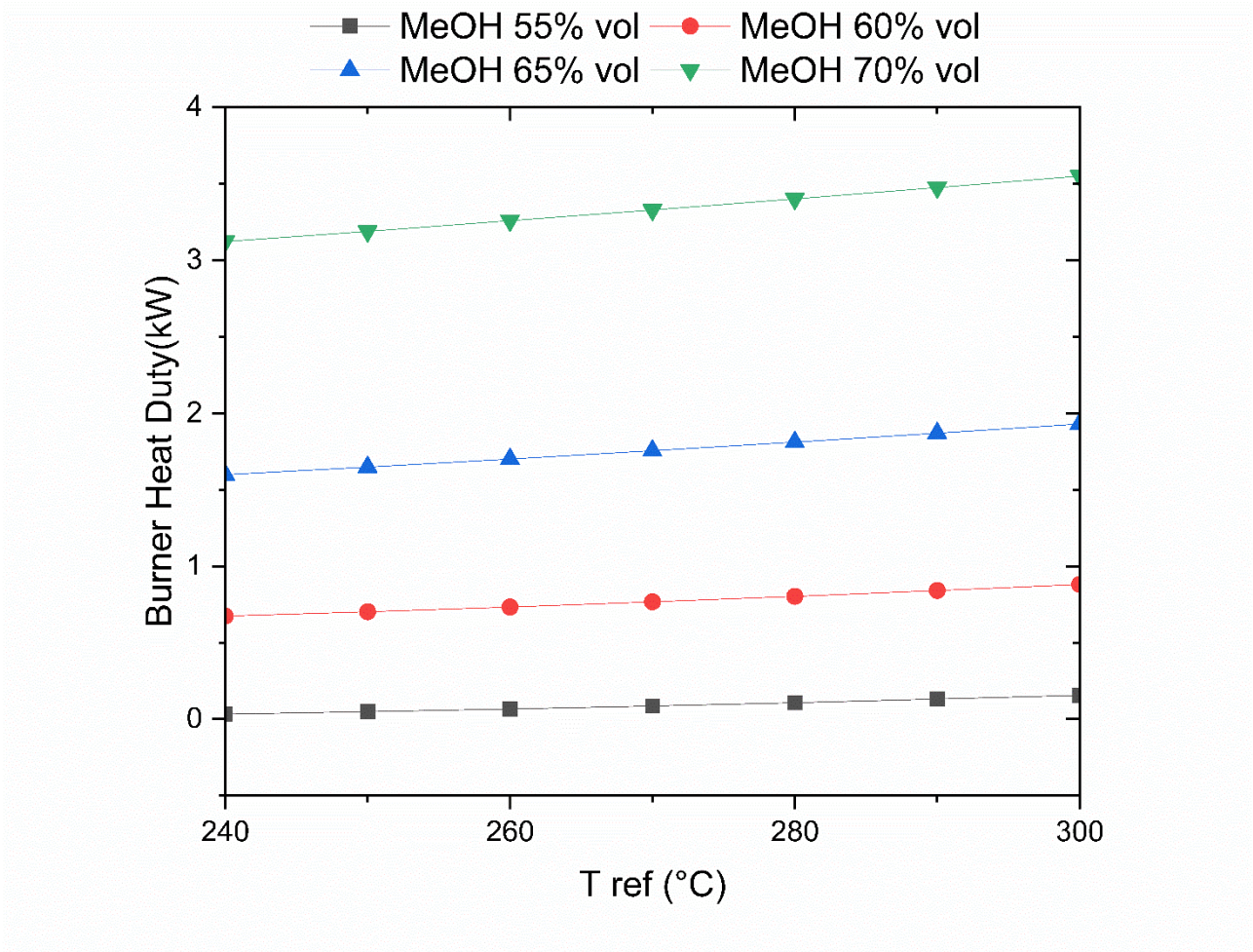


Fig.5 Catalytic burner heat release as a function of reformer temperature and MeOH content in the feed

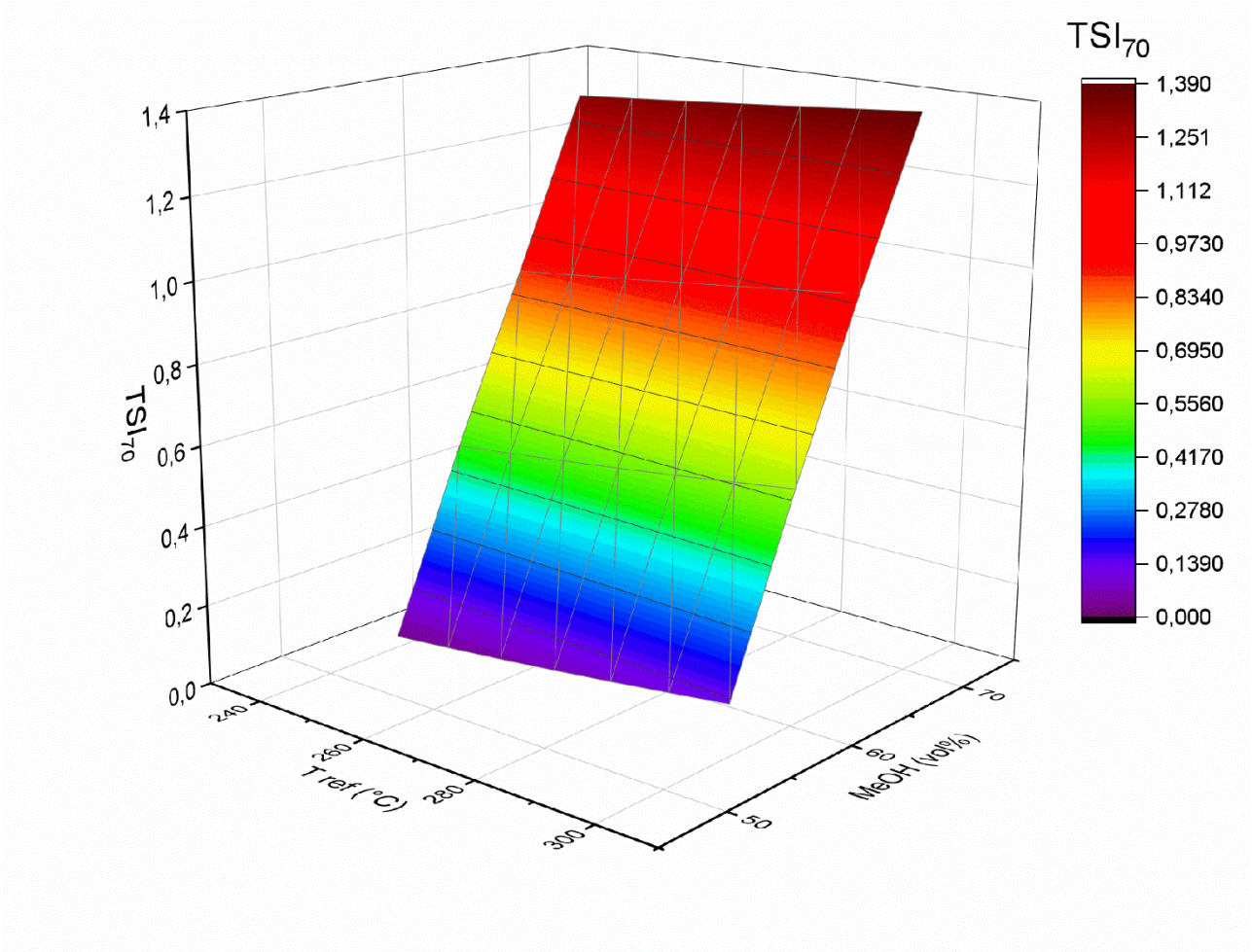
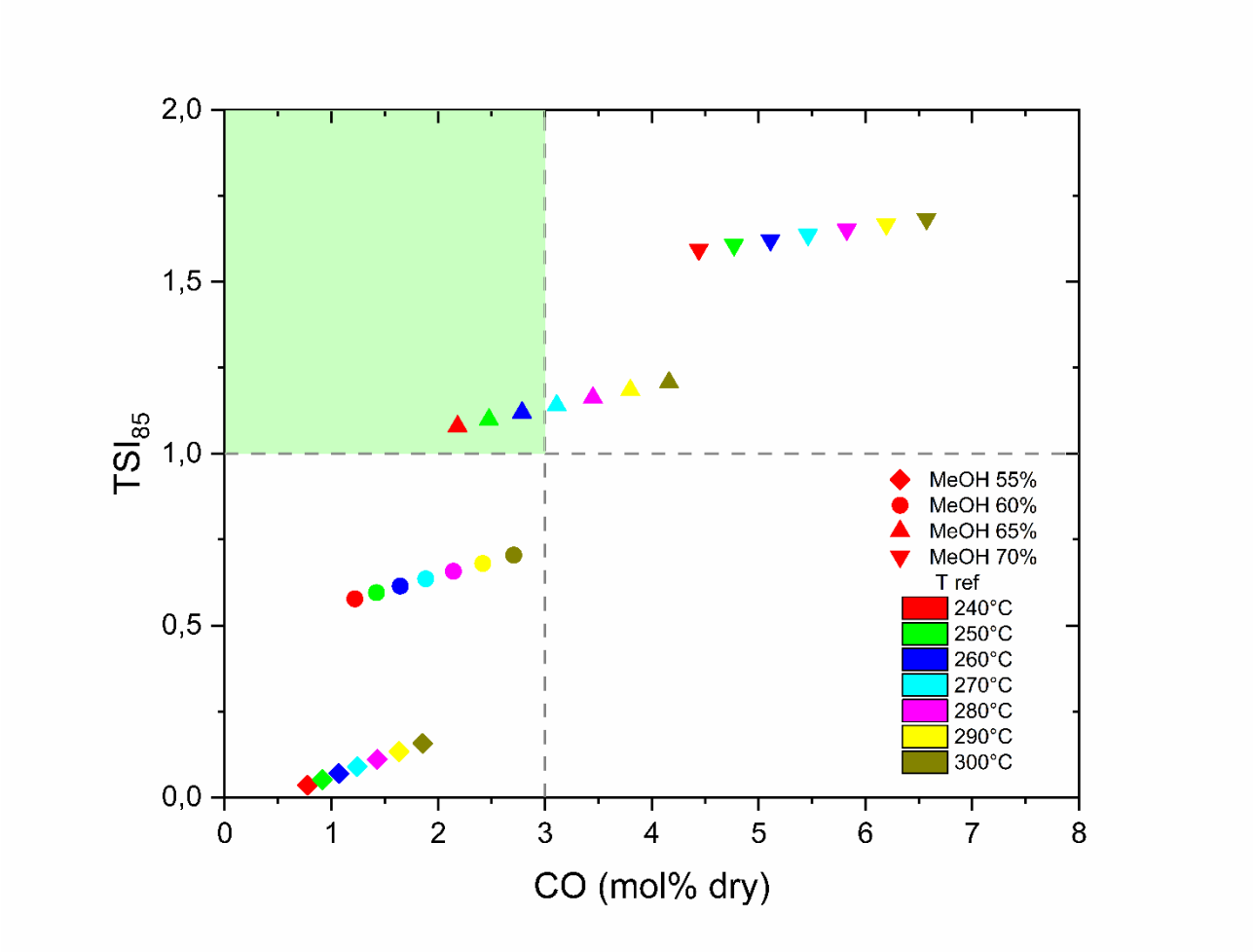


Fig.6 Thermal Self-Sustainability Index calculated for a burner heat recovery efficiency of 70%



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