Equilibrium analysis for methanation focusing on CO_2 derived substitute natural gas

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Abstract: In this study the methanation of synthesis gas (syngas) is investigated with a focus on achieving maximum methane and minimum CO by full methanation of CO_2. For this study, we have considered a comprehensive thermodynamics analysis of CO_2 hydrogenation. This will help us to understand the thermodynamic behaviour of the reactions involved in the methanation process. We have discussed the behavior of the species, CO_2, H_2, CH_4, and H_2O at the equilibrium with temperature, pressure, and fuel ratio variation in order to get the desired output. The preliminary study will focus on selecting the optimum conditions (temperature, pressure, and H_2/CO_2 ratio) for performing the experiments and for catalyst development.

Keywords: Equilibrium calculations, Thermodynamic analysis, CO_2 methanation, Gibbs free energy minimization

1. INTRODUCTION

It is assumed that the main element for the increase in atmospheric temperature is the increase of the CO_2 concentration. The greenhouse gas CO_2, therefore, needs to be reduced in the scope of the energy transition from fossil to renewable sources. This needs new concepts for the sustainable energy supply and also for energy storage. Hence, it is essential to reintegrate the secondary products like H_2 and CO_2 into the energy supply in order to reduce the direct CO_2 emission discussed by Kopyscinski et al. (2010); Seemann et al. (2010).
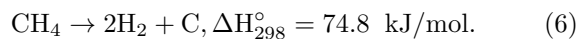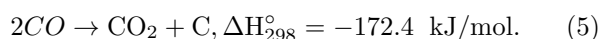
The conversion of CO_2 into methane is a promising approach for a CO_2 neutral production circle and this process is commonly known as methanation. The excess energy produced in methanation by renewable energies is converted into chemical energy. There is a possibility to feed the produced CH_4 into the existing network of natural gas referred as 'power-to-gas' approach (PtG) (Müller et al. (2013, 2019)).

The sufficient supply of H_2 required for the hydrogenation of CO_2 is generated by some kind of renewable energy. This ensures a CO_2 neutral process (Ursua et al. (2012); Razzaq. et al. (2013); Müller et al. (2019)). The exhaust CO_2 can be used as a CO_2 source to fully convert the hydrogen/CO_2 to methane by the Sabatier reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H^\circ_{298} = -165.0 \ \text{kJ/mol.} \quad (1)$$

This reaction is thermodynamically favoured and catalysts can be useful to achieve acceptable conversion from CO_2 into CH_4 (Du et al. (2007); Ma et al. (2009); Müller et al. (2017); Rachow (2017)). In this study, we want to comprehend the thermodynamics involved in the methanation processes.

Other than the Sabatier reaction, the following main competitive reactions depending on the fuel composition also needs to be considered:

$$CO + 3H_2 \rightarrow CH_4 + H_2O, \Delta H^\circ_{298} = -206.1 \ \text{kJ/mol.} \quad (2)$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2, \Delta H^\circ_{298} = -247.3 \ \text{kJ/mol.} \quad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H^\circ_{298} = -41.2 \ \text{kJ/mol.} \quad (4)$$

$$2CO \rightarrow CO_2 + C, \Delta H^\circ_{298} = -172.4 \ \text{kJ/mol.} \quad (5)$$

$$CH_4 \rightarrow 2H_2 + C, \Delta H^\circ_{298} = 74.8 \ \text{kJ/mol.} \quad (6)$$

The above listed reactions are some of the important reactions expected to happen in a methanation process. However, in this study our focus is only to consider the thermodynamic point of view by using the thermochemistry of all the species which are used in the system. Some of the thermodynamic investigations of methanation reactions are discussed by Greyson et al. (1955); Anderson (1986); Gao et al. (2012); Jia et al. (2016) and catalytic studies are conducted by Beuls et al. (2012); Ocampo et al. (2009); Hu et al. (2012).

Although there are some thermodynamic investigations available in literature, we still need a further comprehension of the complex methanation reactions. Hence, in this work, we discuss the thermodynamic impact of CO_2 methanation on formation of products. The main species considered for the study are CH_4, CO_2, H_2 CO, and H_2O with a focus to maximize the methane formation and

minimize the CO formation for the considered conditions for investigation.

2. METHODOLOGY

Apart from the LOGEcat model for catalyst investigations used by Rakhi et al. (2022b,a, 2023); Rakhi and Mauss (2024) from the LOGEsoft software suite (LOGEsoft (2008)), there is also an Equilibrium Reactor model in the software package. We have used the equilibrium reactor model to perform the simulations discussed in this paper. We only need the thermodynamic data for all the species involved in the methanation process in each phase for the equilibrium reactor model and this allows to determine the chemical state of a mixture under equilibrium conditions including any number of gas-phase or bulk species for the thermodynamic equilibrium calculations.

The equilibrium composition of a reactive system is calculated using the Gibbs free energy minimization method which is based on the principle that the total Gibbs energy of the system has its minimum value at chemical equilibrium without considering the individual equilibrium constants (Adhikari et al. (2007); Ozkara-Aydinoglu (2010); Rossi et al. (2009)). The distribution of the products under a minimum free energy is achieved by utilizing a general mathematical technique which does not require the knowledge of the chemistry of the reactions. However, all the species in a reaction system including reactants as well as the products needs to be given. Then the Gibbs energy is calculated using the Gibbs energy under standard conditions and the law of the mass action:

$$\Delta_r G = \Delta_r G^\theta + RT \ln \prod_i a_i^{\nu_i} \quad (7)$$

The meaning of the symbols, $\Delta_r G$, $\Delta_r G^\theta$, R, T, $\prod$, a, and ν are the change in the Gibbs free energy, standard Gibbs free energy for the reaction r, universal gas constant, temperature, product across all i-indexed variables, activity coefficient, and stoichiometric coefficient of species i, respectively. Since the change in the free energy at equilibrium is zero, the equilibrium constant (K_{eq}) is given as:

$$K_{eq} = \exp\left(\frac{-\Delta_r G^\theta}{RT}\right) \quad (8)$$

This equations determines the direction of the reaction. The change in the standard free energy, $\Delta_r G^\theta$ can be calculated using the Gibbs-Helmholtz equation given as:

$$\Delta_r G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (9)$$

The symbols, ΔH^θ and ΔS^θ represent the change in the reaction enthalpy and the change in the reaction entropy, respectively. The polynomial functions of temperature are used to determine the state functions and heat capacity in the equilibrium reactor model. The polynomial coefficients for all the species available in the methanation process can then be provided in the state function input file using a standard format for NASA coefficients. These polynomials can be used to drive all the other thermodynamic properties needed for the thermodynamic equilibrium calculations. The Gibbs free energy for the Sabatier reaction (Equation 1) can be calculated using the equations ($t = T[K]/1000$):

$$\Delta H^\theta(t) = \Delta H^0_{298.15K} + dH_{CH_4} + 2 * dH_{H_2O} \\ - dH_{CO_2} - 4 * dH_{H_2} \quad (10)$$

$$\Delta S^\theta(t) = S^0_{CH_4} + 2 * S^0_{H_2O} - S^0_{CO_2} - 4 * S^0_{H_2} \quad (11)$$

$$\Delta_r G^\theta(T) = \Delta H^\theta(t) - T * \frac{\Delta S^\theta(t)}{1000} \quad (12)$$

The equilibrium constant, K_{eq}, is expected to be reduced with increasing temperature for the Sabatier reaction (Equation 1) due to its exothermic nature. While solving all the above equations, a system of linear simultaneous equations is achieved containing many unknowns and it yields a new composition representing new approximation of the composition giving minimum free energy. The information achieved with these thermodynamic equilibrium calculations can be useful to develop a catalyst for the methanation process by providing a background in selecting the most favourable conditions for the experiments and catalytic simulations.

A detailed summary of the possible reactions involved in the methanation of carbon oxides is given by Mills and Steffgen (1974); Nahar and Madhani (2010). We have used the gaseous compounds, CO, H_2O, CO_2, H_2, O_2, and CH_4 for the equilibrium calculations. The high hydrocarbons, solid carbon, and oxygen-containing compounds (methanol, methanoic acid, acetic acid etc.) are ignored because they are available in very small amount in the equilibrium gas mixture.

3. VALIDATION

The validation of the equilibrium solver is done against the literature results from Gao et al. (2012). The validation is done for one inlet condition, i.e., $H_2/CO_2 = 4$ at 1 atm in a temperature range of 200-800°C. Note that the equilibrium calculations provided in literature are also simulations and these simulations are performed using the CHEMCAD solver. Therefore, we have taken the reference data simulated with CHEMCAD and compared with the calculations from our equilibrium reactor model from LOGEsoft software package.

For the considered inlet condition for validation, we have compared the product fraction of CO_2 methanation at equilibrium for all the species, CO_2, H_2, CH_4, H_2O, and CO before exploring the new conditions. The equilibrium calculations with our solver matched with the reference very well (not shown here). After a successful validation, the solver is further used for equilibrium calculations at various unexplored conditions to select the optimum parameters for the methanation process and the the inlet conditions considered for the simulations are given in Table 1.

Table 1. Summary of the inlet fuel composition on which the investigation is performed.

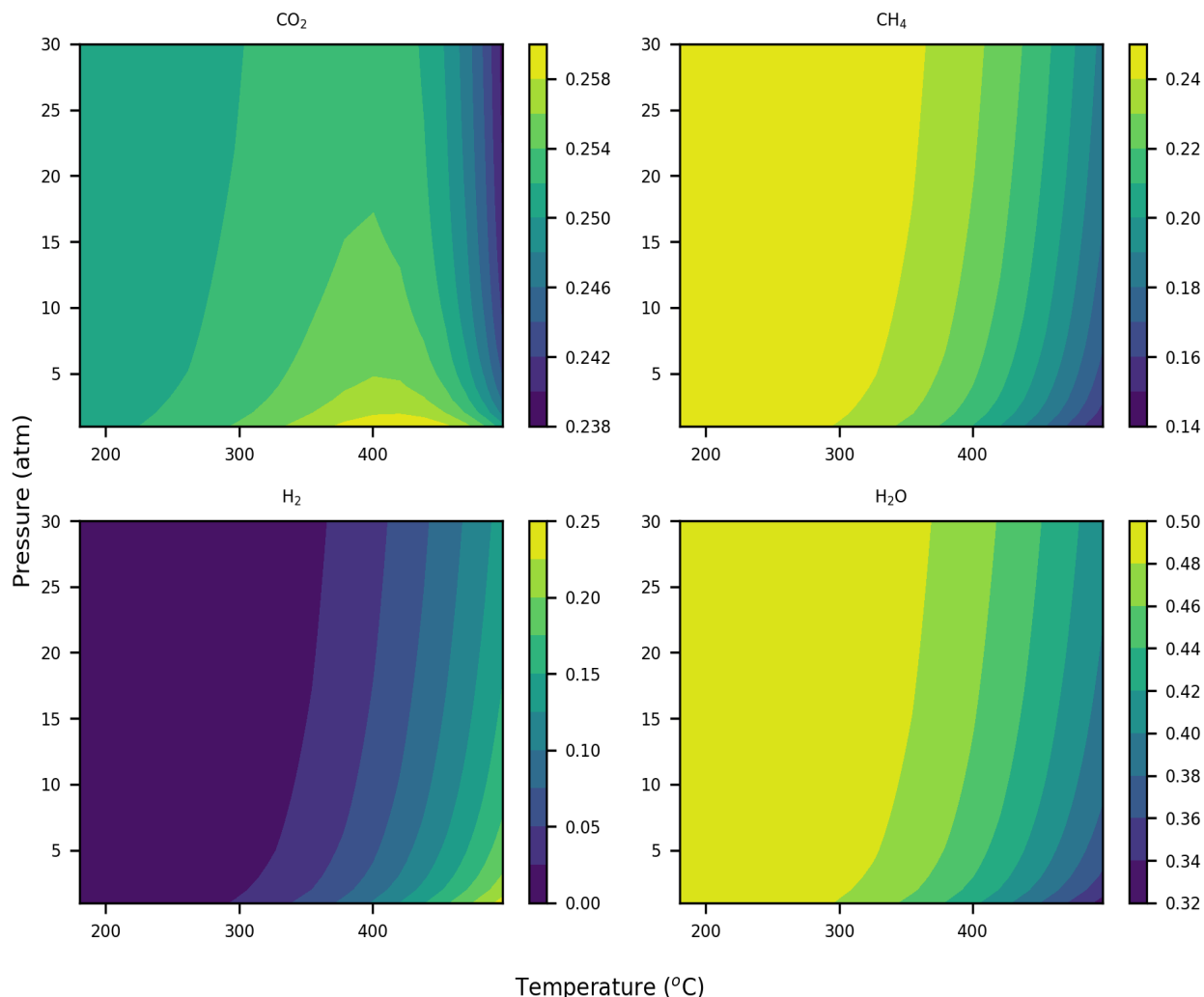| Simulation Run	H_2/CO_2 (vol. %)	H_2 (vol. %)	CO_2
R1	2	66.6	33.4
R2	4	80.0	20.0
R3	6	85.7	14.3

Fig. 1. Products fractions at the reactor outlet for species, CO_2, H_2, CH_4, and H_2O varying with the pressure and temperature for $H_2/CO_2=2$.

4. RESULTS

After validating the equilibrium reactor model using the methodology explained in the previous sections, the model is further applied to investigate the effect of CO_2 methanation. The simulations performed with the inlet conditions given in Table 1 are discussed in this section to select the H_2/CO_2 fuel composition for catalytic simulations. Note that the temperature used to perform the simulations is varied in the range 200-500°C and pressure from 1 atm to 30 atm for all the inlet conditions given in the table.

Starting with the low fuel ratio, i.e., $H_2/CO_2=2$, where the amount of hydrogen is double the amount of CO_2 at the inlet, the measurement of the species, CO_2, H_2, CH_4, and H_2O varying with the pressure and temperature is presented in Fig. 1. With this inlet composition, the CO_2 is mostly unused in the entire temperature and pressure range considered for the study.

However, hydrogen is fully used as indicated in the lower panel of Fig. 1. The H_2 mole fraction at the reactor outlet is zero or close to zero up to 400 °C in the entire pressure range, i.e., up to 30 atm shown in the figure with blue colour. The figure also depicts that with increasing temperature and pressure, more unreacted hydrogen is expected at the reactor outlet for the methanation process.

Hence, low temperatures and low pressures are recommended for better conversion of hydrogen for this fuel composition. However, for $H_2/CO_2=2$, the low temperatures and low pressures are not favourable for CO_2 conversion. The CO_2 conversion is expected to be good for high temperatures.
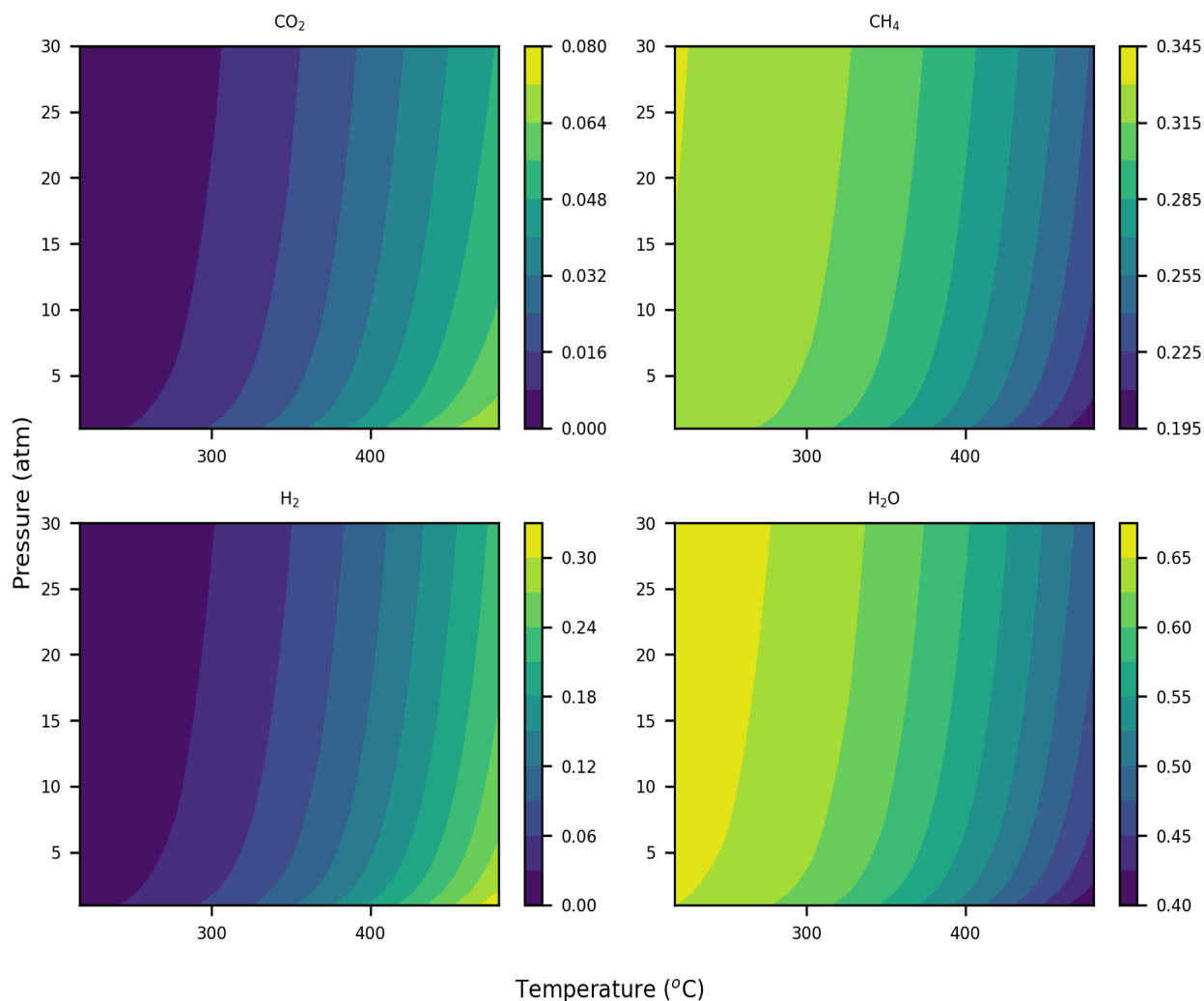
Fig. 2. Products fractions at the reactor outlet for species, CO_2, H_2, CH_4, and H_2O varying with the pressure and temperature for $H_2/CO_2{=}4$.

CH_4 and H_2O product fractions shown in the right side of Fig. 1 indicates that methane as well as water formation at low temperature in the entire pressure range considered for the investigation is very high shown with the yellow colour in the figure. So, in order to maximise the methane formation, it may be useful to operate the reactor at the condition with fuel ratio, $H_2/CO_2{=}2$ at low temperature. However, this fuel ratio is not favourable considering the conversion of CO_2. Therefore, we considered also the other fuel compositions for the investigation.

Next, we computed the thermodynamic equilibrium by increasing the hydrogen mole fraction and reducing the CO_2 mole fraction at the inlet condition, i.e, $H_2/CO_2{=}4$ and the product fraction of all the species at the considered temperature and pressure range is shown in Fig. 2. The species CO_2 and H_2 mole fractions are on the left side and for CH_4 and H_2O on the right side of the figure.

Note that by reducing the CO_2 mole fraction in the fuel composition leads to almost 100% conversion of CO_2. This is indicated in the figure by the blue colour showing zero unreacted CO_2 at low temperatures. For operation at high temperatures, high pressures are recommended. From the

H_2 mole fraction scale, we note that the conversion for this species is very good even after increasing hydrogen for this fuel composition, i.e., $H_2/CO_2{=}4$.

From right side of the figure, we note the the formation of methane and water is good for this fuel ratio as well, however, both the species mole fraction at the reactor outlet in equilibrium for $H_2/CO_2{=}4$ are slightly reduced.

The hydrogen is further increased and CO_2 is reduced to analyse the influence for another fuel ratio, i.e., $H_2/CO_2{=}6$ on all the species at thermodynamic equilibrium. The results for this fuel ratio are shown in Fig. 3 for CO_2 and H_2 mole fractions on the left side and for CH_4 and H_2O on the right side of the figure.

By comparing the scales for CO_2 in Fig. 2 and 3, the CO_2 consumption is improved more by further reducing the CO_2 mole fraction in the initial fuel composition. This behaviour is seen in the complete range of temperature and pressure considered for the calculation. However, with the increase in the hydrogen for $H_2/CO_2{=}6$, a lot of unreacted hydrogen is noted at the equilibrium. For improving the hydrogen conversion for this fuel composition,

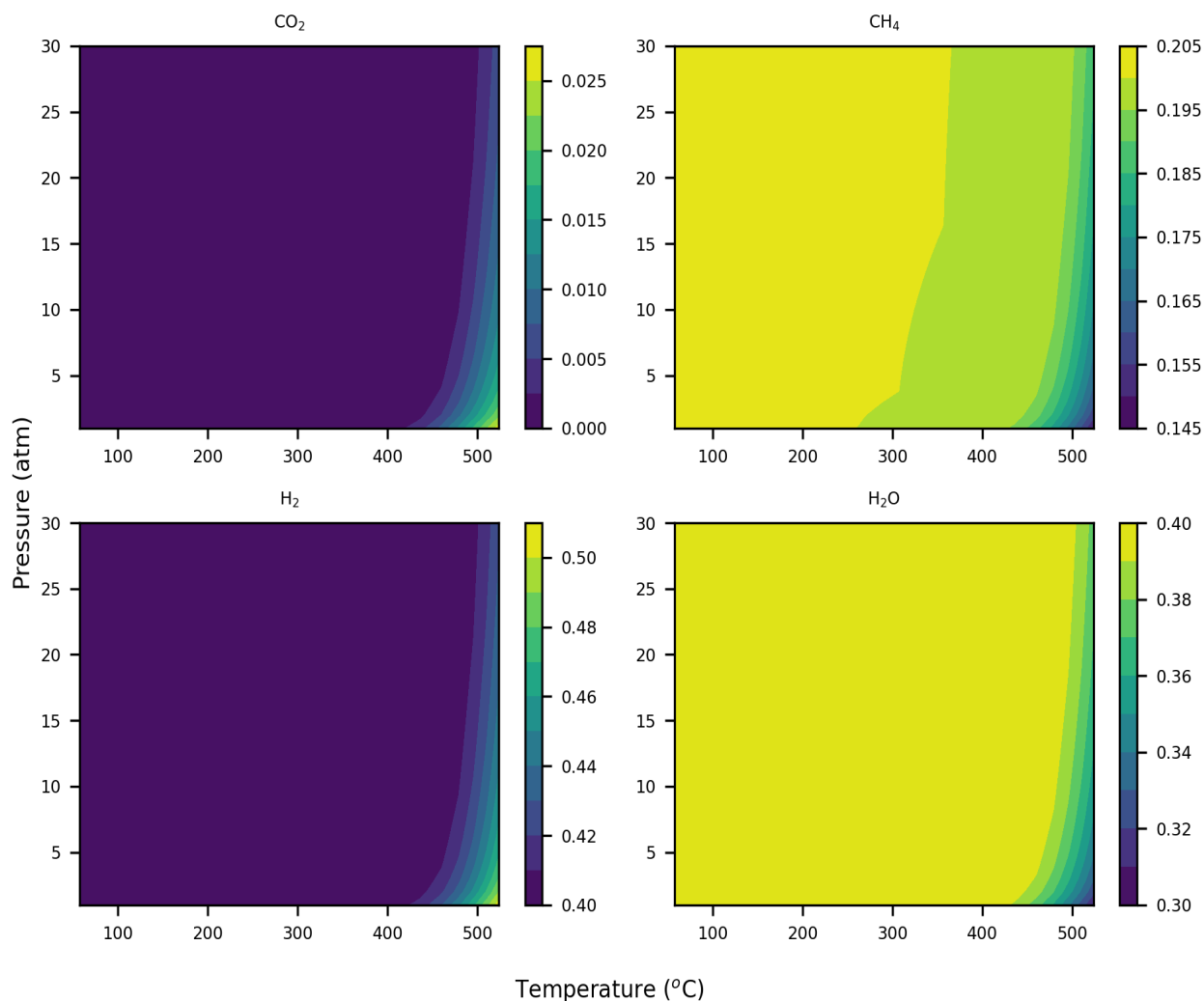Fig. 3. Products fractions at the reactor outlet for species, CO_2, H_2, CH_4, and H_2O varying with the pressure and temperature for $H_2/CO_2=6$.

high temperatures and pressures can be investigated. This indicated that this fuel composition is not favourable for hydrogen conversion.

Not only hydrogen is unreacted but also the formation of methane at equilibrium for this fuel composition is reduced. This can be seen by comparing the scales for methane from Fig. 2 and 3. Similar to methane, water formation is also reduced for this fuel composition.

Considering the conversion of CO_2, $H_2/CO_2=2$ is not favourable and for conversion of H_2, $H_2/CO_2=6$ is not favourable. $H_2/CO_2=4$ is the most favourable fuel composition for conversion of H_2 as well as CO_2 along with maximum formation of methane for this ratio.

5. CONCLUSIONS

The thermodynamic equilibrium composition for CO_2 methanation of the species, CO_2, H_2, CH_4, and H_2O are shown at the reactor outlet for the Sabatier temperature range, i.e., approximately 250-450°C in the pressure range from 1 atm to 30 atm.

For the equilibrium calculations for the methanation process, fuel composition plays very important role in the entire pressure and temperature range considered for the investigation. For the low range of temperature, H_2/CO_2 should be more than 2 to achieve good conversion of CO_2, however, this ratio should be less than 6 for good conversion of H_2. For maximum methane formation, $H_2/CO_2=4$ is the most favourable fuel composition.

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