



## Full Length Article

# Thermodynamic modelling of the methanation process with affinity constraints



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## HIGHLIGHTS

- New thermodynamic methodology for modelling CO<sub>2</sub> and CO methanation processes.
- Constrained thermodynamic equilibria is defined based on the reaction affinities.
- Only key limiting reactions need to be defined for the chemical system.
- Methodology applicable to other high temperature and fuel conversion processes.

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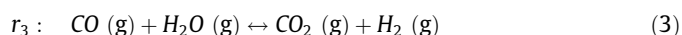
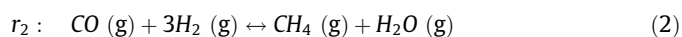
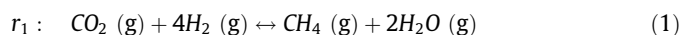
## ABSTRACT

A constrained thermodynamic model was developed in order to describe the product gas composition of a methanation process. The non-equilibrium affinities of CO<sub>2</sub> and CO methanation reactions were applied as additional constraints to the chemical system while solving the local thermodynamic equilibrium. The affinities of these reactions were modelled as a linear temperature dependent function based on published and experimental data. The applicability of modelling methodology was validated against two independent literature datasets and against our own experiments. In all cases, the model predicted the product gas composition of main species CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub>. In two cases, it was sufficient to add only a single constraint describing the affinity of CO<sub>2</sub> methanation reaction and in one case, two constraints describing the affinities of CO and CO<sub>2</sub> reactions were needed. Results suggest that the modelling methodology presented can be utilised to describe different kinds of methanation process conditions, but the affinity models need to be defined based on the experimental reaction kinetic data. This methodology and the developed OD-reactor model is applicable, for example, as part of a larger process simulation where additional details of methanation process are needed.

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## 1. Introduction

The methanation process has attracted interest in recent years, as this technique could provide a possible solution for storing renewal electricity produced by solar and wind energy. According to the Sabatier reaction [1], Eq. (1), the carbon dioxide from power plants and hydrogen produced by excess electricity reacts to form methane and water. The respective reaction can be written for carbon monoxide, Eq. (2). The third important reaction to be considered during the methanation process is the water-gas shift reactions written in Eq. (3).



The reaction rates of these three reactions are slow at lower temperatures, <500 °C [2] and thus catalysts are applied for increasing the reaction rates. For example, nickel-based catalysts are often applied [3,4]. Studies of reaction kinetics [5–10] comprise a large share of the models of methanation processes as the reaction rate has been the major issue to be improved. Often Langmuir–Hinshelwood kinetics is applied in these studies. Different modelling approaches of the methanation process are reviewed by [11]. While kinetic studies provide additional information about the reaction mechanism related to particular catalyst and reaction conditions, the applicability of these models is often limited.

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Kinetic models include several parameters to be fitted and thus additional uncertainty is introduced into the models. Furthermore, care should be taken in identifying whether a particular publication deals with CO or CO<sub>2</sub> methanation.

Another approach to modelling the high temperature conversion processes is the thermodynamic equilibrium approach. The reaction kinetics as well as heat and mass transfer are often rapid in these conditions, and thus the ideal equilibrium approach is feasible. Yet, in real industrial processes, there are often constraining factors, and thus the global thermodynamic equilibrium is not reached. The reason might be insufficient mixing, incomplete heat and mass transfer or slow reaction kinetics due to lower temperatures. To overcome these limitations of pure equilibrium models, a constrained thermodynamic equilibrium method has been developed.

Thermodynamic equilibrium calculation constrained by selected reaction rates was first utilised for modelling the nitric oxide and carbon monoxide emissions from the internal combustion engines [12], and later applied to a variety of different problems related to oxidation of different fuels during internal combustion [13–16]. A parallel approach was developed and utilised for modelling multiphase high temperature industrial processes [17–19], for metallurgical processes [20–23], for aqueous suspensions in pulp and paper industry [24–27] and for biochemical processes [28–30]. In addition, the constrained thermodynamic equilibria are successfully applied to modelling several phenomena during the thermal conversion of biomass [31–34]. The reviews and introductions of the calculation of constrained thermodynamic equilibrium are available by several authors found in the literature [13,20,21,35,36].

As the constrained thermodynamic equilibrium is successfully applied to several industrial problems, many of them related to high temperature applications in the field of energy production such as biomass gasification [31], this approach was chosen to be used in this study. The aim is to develop a practical OD-reactor model that describes the product gas composition as a function of feed gas composition and reaction temperature for a certain catalyst and reactor type. Simultaneously, a methodology for utilising the affinities of constraining reactions as part of the constrained thermodynamic model is illustrated.

## 2. Methodology

### 2.1. Modelling approach

The modelling approach is based on the constrained free energy technique (CFE) [21,36,37]. This methodology is extending the calculation of thermodynamic equilibria by introducing additional immaterial constraints to the chemical system. Based on these constraints, the local equilibrium state is determined. The methodology presented for modelling the methanation process is first evaluated against the literature data [3,4]. ChemSheet [38] is applied as modelling tool, and thermodynamic data of gaseous species is obtained from HSC [39].

### 2.2. Experimental setup

The proposed constrained thermodynamic model of the methanation process will first be validated against two datasets from the literature. Subsequently, the modelling methodology is evaluated with a small set of our own experiments of the methanation process in order to ensure that the methodology presented is feasible.

The experimental setup is described in Fig. 1. The reactor system has two lines, one passing through the heat exchanger (HEX) tube/shell reactor, and another bypassing the reactor. Therefore,

the reaction mixture can be analysed before and after the reaction. The reactor is heated by a heating jacket to be able to reach the desired reaction temperatures. However, the tube/shell reactor has a constant steam flow in the shell side and reacting gases flowing in a counter-current in the tube side. The reactor is equipped with seven thermocouples, of which five are located along the catalyst bed and two in the inlet and outlet of the steam loop. The reactor design is given in Figs. 2a and 2b.

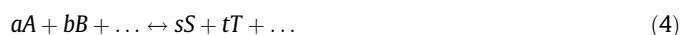
The catalyst used in the experiments is a commercial Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with ca. 15 w-% of nickel with a particle of 200–300 μm. The catalyst is reduced in-situ before the experiments at atmospheric pressure, 600 °C and a gas composition of H<sub>2</sub>/N<sub>2</sub> of 50/50 vol-% with a total volume flowrate of 1 l/min.

After the reactor, the gas mixture is cooled down and the condensable compounds are collected in a cold trap. A side stream of the dried gas is by a micro gas chromatograph (GC). The gas composition was analysed in the GC using a thermal conductivity detector (TCD) and a flame ionization detector (FID). See below the configuration of the system.

The temperature inside the catalyst bed varied between 310 and 360 °C. The applied pressure is 5.0 bar absolute. The amount of CO<sub>2</sub> in the feed gas was between 9 and 17 v-%. Respectively the amount of H<sub>2</sub> in the feed gas was between 47 and 64 v-% and for CH<sub>4</sub> 6–26 v-%. The amount of CO in the feed gas was 0 v-% in all the experiments except one and a constant amount of 13 v-% of H<sub>2</sub>O was fed to the reactor. The details of feed conditions are given in Table 3.

### 2.3. Theory

Thermodynamic equilibrium of the stoichiometric chemical system can be defined based on the equilibrium constants,  $K_r$ . For a particular reaction,  $r$  in Eq. (4), the equilibrium constant is given based on the equilibrium concentrations, partial pressures or fugacities in gaseous phases, Eq. (5).



$$K_r = \frac{[S_{eq}]^s [T_{eq}]^t \dots}{[A_{eq}]^a [B_{eq}]^b \dots} \quad (5)$$

Respectively, the reaction quotient,  $Q_r$ , can be defining for those reactions, which are not in equilibrium (for example, the methanation reactions in this study). Here the concentrations of reacting constituents during non-equilibrium state are used for the calculation of the reaction quotient, Eq. (6).

$$Q_r = \frac{[S]^s [T]^t \dots}{[A]^a [B]^b \dots} \quad (6)$$

If the chemical system is of limited extent, the state of the system can be solved based on the equilibrium constant and reaction quotients as given above. However, for the larger chemical systems it is often unfeasible to define the equilibrium constants or the reaction quotients to all possible reactions. A non-stoichiometric approach based on the minimization of Gibbs Energy of the chemical system is often used in these cases. A distinct benefit of this approach is that the Gibbs'ian technique allows for the calculation of all chemical reactions, reaction enthalpy and state variables simultaneously and interdependently. This is often practical when solving industrial problems [13,17,25]. The Gibbs free energy of a chemical system,  $G$ , is defined in Eq. (7) subject to Eqs. (8) and (9).

$$G = \sum_{\alpha} \sum_k n_k^{\alpha} \mu_k^{\alpha} \quad (7)$$

$$n_k^{\alpha} \geq 0 \forall k \quad (8)$$

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