

# Dynamic Modeling of a Methanization Plant

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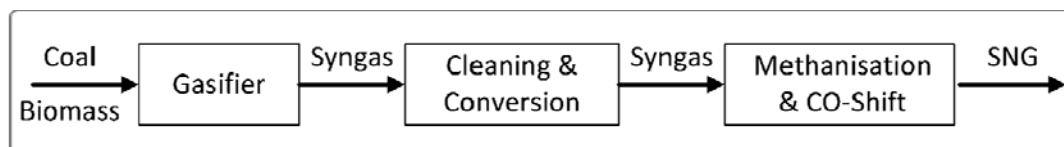
## Abstract

The chemical and physical modeling and transient simulation of a methanization plant with chemical reactors is useful for dimensioning, optimization, operation and analyzing of critical processes. The paper introduces the results of the development of a dynamic model for a commercial methanization process. The discussed models base on the free Modelica language and Dymola as user interface. The methanization plant consists of 3 adiabatic fixed bed reactors and steam generation units for heat recovery. Calculation results are shown for the dynamic behavior of the methanization plant at a load change.

*Keywords: chemical reactor, thermodynamic equilibrium, dynamic simulation, part load, heat recovery, CH<sub>4</sub>*

## 1 Introduction

It is well known that the oil and natural gas reserves are limited. The production of fuels is based almost completely on oil and natural gas. Hence there is the wish to extend availability of a secure energy supply. One solution is the conversion of coal or biomass to synthetic or substitute natural gas (SNG) by gasification and methanization to substitute the rising natural gas need. The SNG can be used in electricity generation in combined-cycle power plant stations. Both coal and biomass are suitable as the reserves of coal will subsist more than 150 years and biomass is a renewable energy source. The SNG synthesis consists of the three main steps gasification, gas cleaning & conversion and the methanization. The Gasifier was modeled already by Fahlke in [1] and the cleaning and conversion step of the synthesized gas (Syngas) was modeled by Heil in [2]. This paper focuses on the methanization step where the Syngas composition is changed to the SNG composition in order to substitute natural gas which is shown in Table 1. The simulation of a methanization plant is in interest for plant manufactures and operators to optimize the construction and the operation. Further interests are studies of critical processes for understanding of complex physical and chemical processes during part load and plant faults in order to increase the reliability and availability of the plant.



**Figure 1: SNG synthesis concept****Table 1: Gas composition of Syngas, SNG and natural gas**

Gas species	Syngas Vol.-%	SNG Vol.-%	Natural Gas Vol.-%
Ref.	[3]	[4]	[5]
CH <sub>4</sub>	0...20	94...98	85...98
H <sub>2</sub>	12...45	0...2	0
CO	6...58	0	0
CO <sub>2</sub>	5...33	0...2	0...2

## 2 Process description

The raw gas for the SNG synthesis contains mainly H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, N<sub>2</sub>. This composition of the raw gas depends on the gasification technology [3]. The SNG synthesis is a heterogeneously catalyzed process. During the methanization, the following chemical reactions occur. The hydrogenation of carbon oxides to methane are the so called CO methanization reaction in equation (R-1) and the CO<sub>2</sub> methanization reaction in equation (R-2) [3].

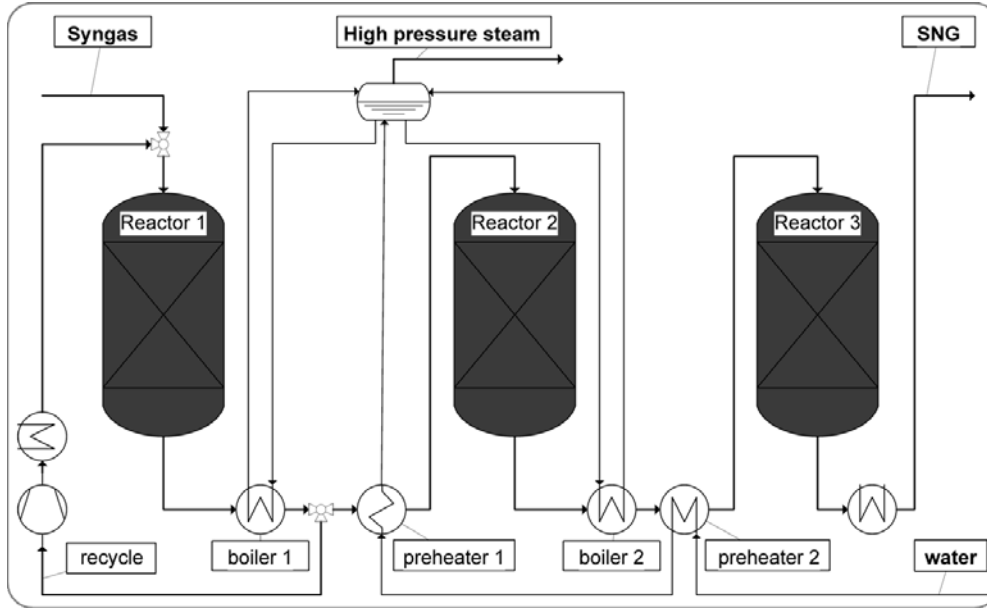


Two further independent reactions are important: the homogenous water gas reaction in equation (R-3) and the Boudouard reaction in equation (R-4).



All the reactions of the methanization are exothermic. Hence, the methanization is favored at low temperatures. Furthermore the methanization is benefited at high pressure, as the reactions (R-1) and (R-2) execute with volume decreasing. The major criterion is to achieve efficient removal of heat for the catalytic methanization reactor system. The first reason is to minimize catalyst deactivation due to thermal stress. The second reason is to avoid a limitation in the methane yield due to approaching the chemical equilibrium. The Topsøe recycle energy-efficient methanization process (TREMP) from Haldor Topsøe is a suitable reactor concept for the production of SNG [4], which is used for the modeling.

The TREMP consists of 3 adiabatic fixed bed reactors with gas recycle cooling and interstage gas cooling. Efficient recovery of the reaction heat is essential for the industrial methanization technology. That's why a counter current water cycle stream is used for the interstage cooling. The water cycle is simultaneously used for high pressure steam generation. A gas-recycle back to the inlet of at the first reactor limits the yield and the temperature increase in the reactor [6]. This is necessary to avoid catalysts sintering.



**Figure 2:** Flow sheet of the Topsøe recycle energy efficient methanization process

### 3 Model description

The aim of the modeling is to implement a TREMP methanization plant library with physical based models of components in the Siemens Modelica/Dymola library. The implemented library is based on the Modelica Fluid library, which offers a modeling environment with respect to the implementation of the three balance equations and the interaction through the fluid ports. The created library enables investigations of a reactor, a heat exchanger, a simple pump, a flash, and a gas and water splitter. The used model components base on the Modelica library, whereas the thermodynamic equilibrium model is a new development.

#### The reactor model

The methanization reactor yield depends on the thermodynamic equilibrium, which will be achieved both in the full and the part load of the methanization plant, Harms in [6]. The thermodynamic equilibrium constant  $K_a$  is used along the law of mass action to determine the molar fractions of the components and the yield of the reactions at the thermodynamic equilibrium.  $K_p$  is the equilibrium constant of the partial pressures,  $p_i$ , of the species, which is connected to the  $K_a$  with the fugacity coefficients,  $K_\alpha$ , in equation 1.

$$K_p = K_a / K_\alpha \quad (1)$$

The law of mass action for the  $K_p$  is described in equation 2 for a chemical reaction like in equation 3.

$$K_p = \frac{p_C^{v_C} \cdot p_D^{v_D}}{p_A^{v_A} \cdot p_B^{v_B}} \quad (2)$$



The equilibrium constant of the molar fractions ( $K_X$ ) is necessary to calculate the chemical equilibrium.  $K_X$  can be computed with  $K_p$ , the total pressure,  $p$ , and the sum of stoichiometric coefficients,  $\nu_i$ , of the chemical reaction, as it is shown in equation 4. The molar fraction of the species,  $X_i$ , can be determined with equation 5.

$$K_X = K_p \cdot p^{-\sum \nu_i} \quad (4)$$

$$K_X = \frac{X_C^{\nu_C} \cdot X_D^{\nu_D}}{X_A^{\nu_A} \cdot X_B^{\nu_B}} \quad (5)$$

It has to be noted that the thermodynamic equilibrium constant depends on the temperature. The temperature dependency can be approximated with equation 6. The parameters A and B of equation 6 are given in Table 2. Two simplifications were assumed for the calculation of the thermodynamic equilibrium. The first is the assumption of the ideal gas law for the species. Therewith the fugacity coefficients can be neglected in equation 1,  $K_a = 1$ . The second simplification is the neglect of the Boudouard reaction, equation (R-4), which will occur if the stoichiometric ratio of equation 7 is lower than 3. In that case, carbon is produced as a product of reaction (R-4). Carbon leads to catalyst deactivation by deposition on the catalyst surface.

$$\ln(K_A) = A + B/T \quad (6)$$

**Table 2: Parameters A and B of equation 6 for reaction (R-1) and (R-3) [7]**

reaction	A	B
(R-1)	-29.3014	26248.4
(R-3)	-4.3537	4593.2

$$\frac{H_2 - CO}{CO + CO_2} \geq 3 \quad (7)$$

If the stoichiometric ratio of the reactants of equation 7 is at least three or more, CO reacts with  $H_2$  completely to  $CH_4$  and  $H_2O$  according to reaction (R-1). The stoichiometric ratio of equation 7 can be adjusted by converting CO with  $H_2O$  to  $CO_2$  and  $H_2$  as long as the  $H_2O$  content is high enough, see Anderlohr in [8]. Hence the ratio of equation 7 has to be higher than three in technical processes. Finally the system of methanization reactions can be reduced to reaction (R-1) and (R-3), as the stoichiometric ratio of equation 7 for all the gas streams in the TREMP is higher than three, as well. Therewith the molar fraction of the species can be determined with the equations 8 to 13, in which 0 stands for the initial state and 1 for the equilibrium state. The conversion  $U_1$  and  $U_2$  is the conversion of the reactions (R-1) and (R-3), with their sum being equal to the total conversion of CO, see equation 14.

$$X_{H_2,1} = \frac{C_{H_2,0} - 3C_{CO,0} \cdot U_1 + C_{CO,0} \cdot U_2}{1 - 2 \cdot C_{CO,0} \cdot U_1} \quad (8)$$

$$X_{CH_4,1} = \frac{C_{CH_4,0} + C_{CO,0} \cdot U_1}{1 - 2 \cdot C_{CO,0} \cdot U_1} \quad (9)$$

$$X_{H_2O,1} = \frac{C_{H_2O,0} + C_{CO,0} \cdot U_1 - C_{CO,0} \cdot U_2}{1 - 2 \cdot C_{CO,0} \cdot U_1} \quad (10)$$

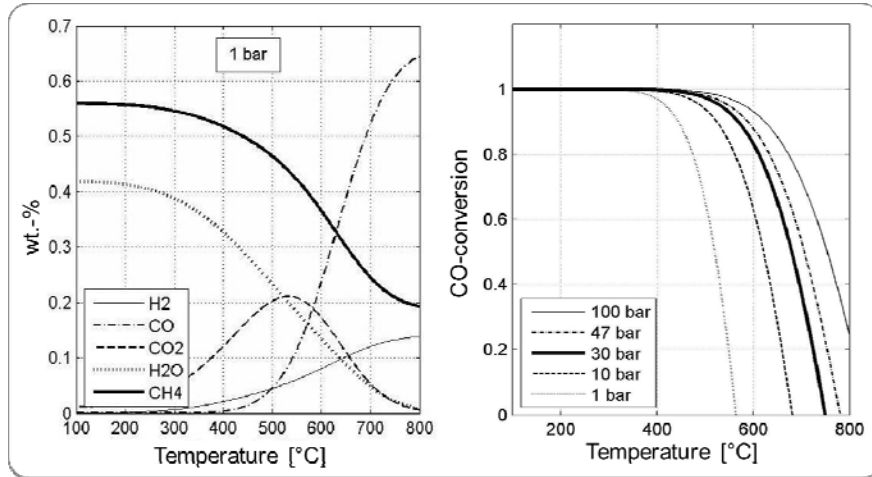
$$X_{CO,1} = \frac{C_{CO,0} - C_{CO,0} \cdot U_1 - C_{CO,0} \cdot U_2}{1 - 2 \cdot C_{CO,0} \cdot U_1} \quad (11)$$

$$X_{CO_2,1} = \frac{C_{CO_2,0} + C_{CO,0} \cdot U_2}{1 - 2 \cdot C_{CO,0} \cdot U_1} \quad (12)$$

$$X_{N_2,1} = \frac{C_{N_2,0}}{1 - 2 \cdot C_{CO,0} \cdot U_1} \quad (13)$$

$$U_{Ges} = U_1 + U_2 = \frac{C_{CO,0} - C_{CO,1}}{C_{CO,0}} \quad (14)$$

In order to determine the chemical equilibrium at known temperature and pressure, a non-linear equation system of the above mentioned equations need to be solved. The results of an example calculation are given in Figure 3.



**Figure 3: Chemical composition and CO-conversion at equilibrium state (initial composition in wt.-%: 33,5 H<sub>2</sub>; 6,7 CO; 3,7 CO<sub>2</sub>; 18,2 H<sub>2</sub>O; 37,4 CH<sub>4</sub>; 0,5 N<sub>2</sub>)**

The energy balance needs to be completed by the produced reaction heat which influences the equilibrium temperature. The amount of the produced reaction heat increases the conversion of the reactions is. A high reaction heat value leads to high temperatures. However, a high temperature leads to a low yield. The reaction heat flow,  $\dot{Q}_R$ , can be determined by equation 15, in which  $\Delta h$  is the specific reaction enthalpy of the reaction and  $M_{Gas}$  the mean molar mass of the gas. The temperature dependency of the specific reaction enthalpy is approximated with equation 16. The parameters of equation 16 for reaction (R-1) and (R-3) are given in Table 3.

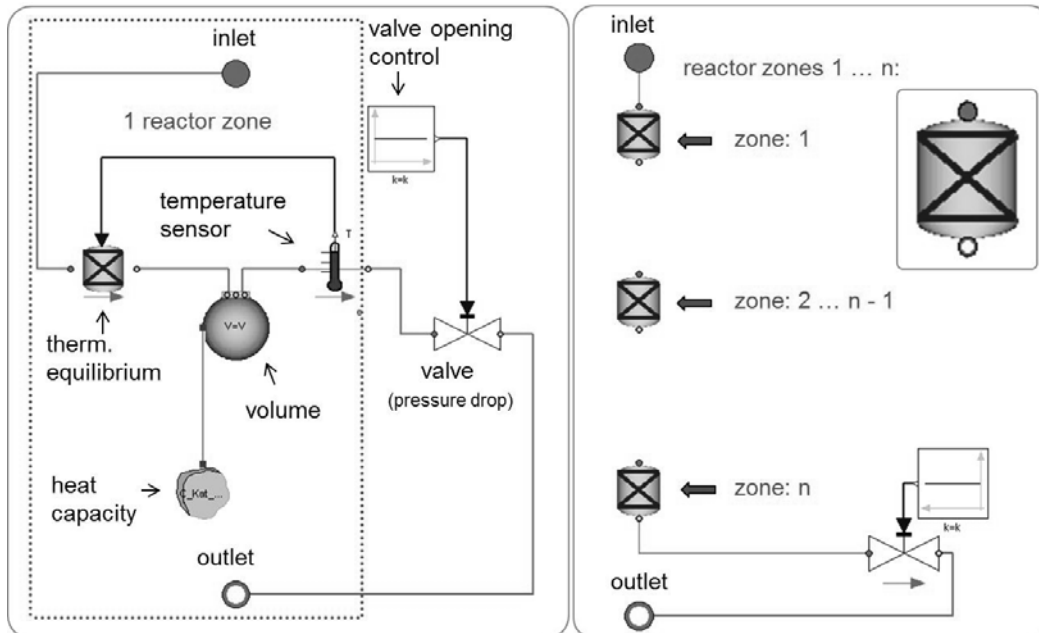
$$\dot{Q}_R = (\Delta h_{(R-1)} \cdot U_1 + \Delta h_{(R-3)} \cdot U_2) \cdot \dot{m}_{Gas} \cdot (X_{CO,1}/M_{Gas,1} - X_{CO,0}/M_{Gas,0}) \quad (15)$$

$$\Delta h = A \cdot T^2 + B \cdot T + C \quad (16)$$

**Table 3: Parameters A, B and C of equation 16 for reaction (R-1) and (R-3), [7]**

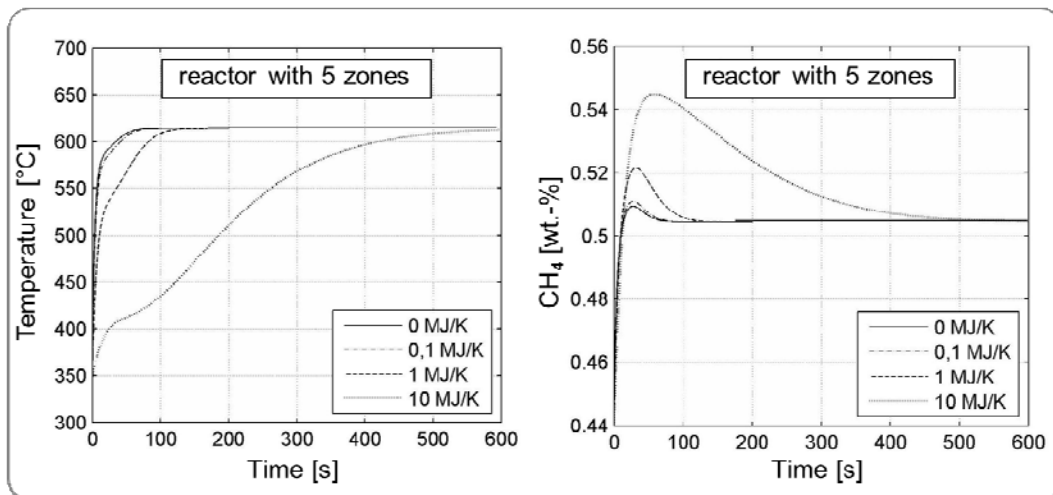
reaction	A	B	C
(R-1)	0.0266	-47.7331	-205094.5788
(R-3)	0.0026	-7.4437	-41557.3842

The configuration of the reactor model is shown in Figure 4. The model components include a SNG\_reaction model, a volume, a heat capacity, a temperature sensor and a linear valve with a constant block. The calculation of the thermodynamic equilibrium occurs in the SNG\_reaction model. The volume component represents the volume of the reactor. The heat capacity model is the heat capacity of the catalyst bed and the reactor wall. The valve model is used to simulate the pressure drop of the gas flow through the catalyst bed.



**Figure 4: Reactor configuration (Left: 1 zone reactor; Right: multiple zone reactor)**

The reactor model has three main parameters: volume, pressure drop and heat capacity. The parameters have different impact on the reactor performance. The greater the reactor volume, the later the steady state will be achieved. The pressure drop changes the pressure and therewith the reactor yield. The pressure drop is predefined by the user. The impact on the heat capacity is more difficult. In the case of a high heat capacity, the reactor model needs to be split into a series of identical reactor zones, which are duplicates of the reactor model configuration as shown in Figure 4. The higher the heat capacity, the more zones are needed to reach the steady state for temperature and methane at the same time, (which is physically necessary). If the number of zones was to low, the temperature change would not be in accordance with the thermodynamic equilibrium. An example of the transient temperature and methane concentration for a 5 zone reactor model at heat capacities in the range of 0 to 10 MJ/K is given in Figure 5. The cold reactor ignition or extinction can not be simulated, because no attention is paid to kinetic effects of the chemical reactions.



**Figure 5: Temperature and methane concentration for a reactor model with 5 zones at heat capacities in the range of 0 to 10 MJ/K**

The steady state results of the simulation calculation are validated with a single reactor model of the TREMP methanization plant. The results are compared to two references. The first one is the experimental result of the TREMP which are published by Harms in [6]. The second reference is the steady state simulation result which is generated with the software ChemCAD by assuming the chemical equilibrium. The results of the reactor model are compared with the data of these two references in Table 4. The error of the species is always lower than 4 % except for hydrogen at low concentrations, where the error can reach up to 10 % (under certain conditions).

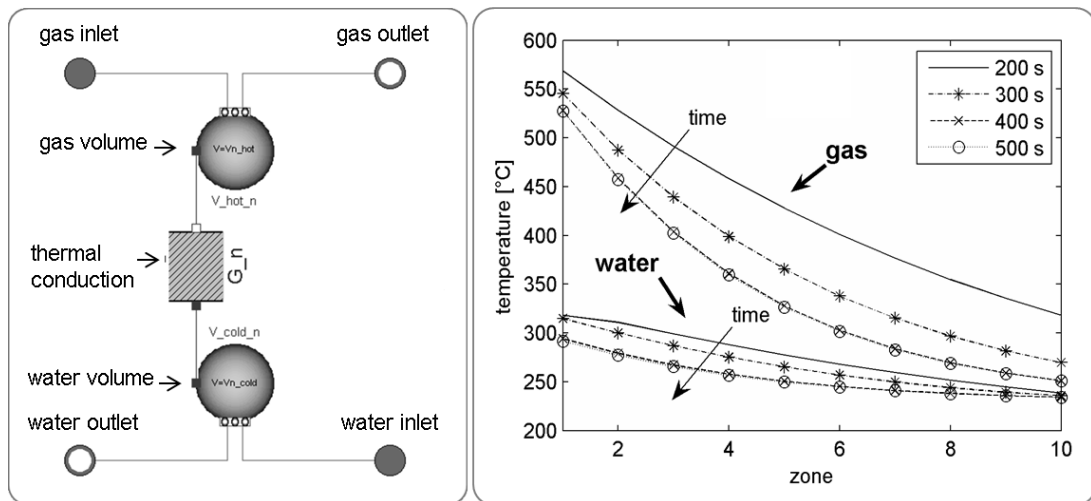
### **The heat exchanger model**

The second important model for the modeling of the methanization plant is the heat exchanger, which is assumed by a simple design to enhance the numerical stability and the calculation speed. The heat exchanger design comprises an outside tube, filled with hot

SNG gas, which has an inside tube filled with water. The configuration of a heat exchanger zone is given in the left image of Figure 6. The zone consists of two volume models. One volume model contains SNG gas and the other water/steam. The volume model is connected by a thermal conduction model. The heat exchanger consists of series such zones. The water and the gas are in counter current flow as the fluid ports are set up in this way. A minimum number of zones are needed to reflect the phenomena that the outflow of the cold side can be hotter than the outflow of hot side, in certain cases. Consequently, a temperature profile can be generated along the heat exchanger as it is shown in the right image of Figure 6.

**Table 4: Comparison of the outlet gas composition of the first reactor of the TREMP with the reactor model in Modelica and in ChemCAD**

	Unit	Inlet TREMP	Outlet TREMP	Outlet Modelica	Outlet ChemCAD
Temperature	°C	300	600	600	599
Pressure	bar	30	30	30	30
H <sub>2</sub>	wt.-%	4,97	2,47	2,40	2,41
CO	wt.-%	13,80	2,01	2,04	1,97
CO <sub>2</sub>	wt.-%	11,97	12,13	11,79	11,92
H <sub>2</sub> O	wt.-%	24,11	31,48	31,82	31,76
CH <sub>4</sub>	wt.-%	44,12	50,81	50,92	50,91
N <sub>2</sub>	wt.-%	1,03	1,10	1,03	1,03

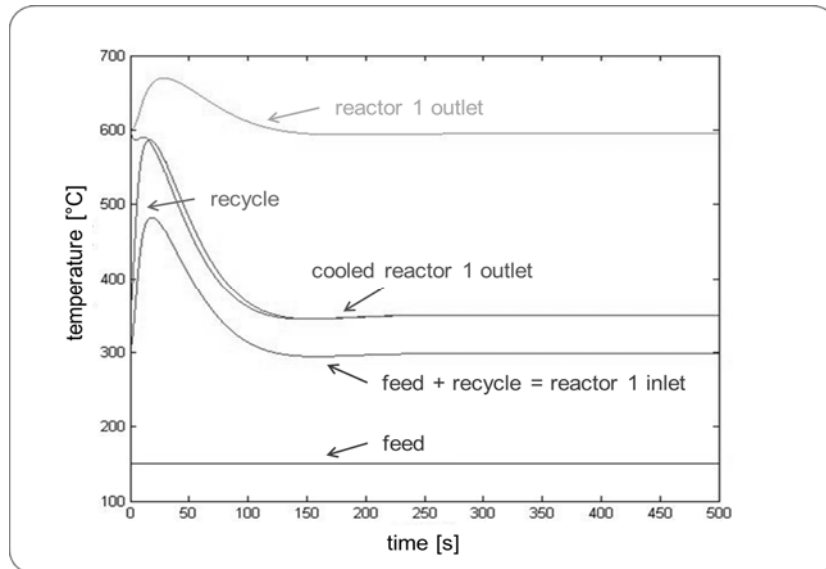


**Figure 6: Left: Heat exchanger configuration for one zone; Right: Transient temperature profile of a heat exchanger model with 10 zones during a part load simulation**



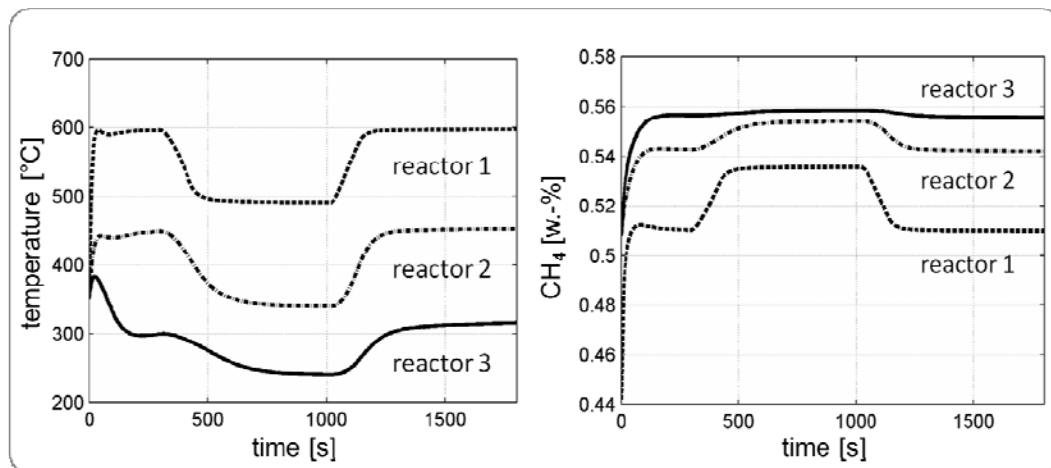
## 4 Transient part load behavior

The reactor and the heat exchanger model are used to build up the model of the methanization plant, as shown in Figure 2. The model of the methanization plant is utilized for transient simulation studies. All the simulations start with a transient oscillation as it is shown in the simulation example of the 1<sup>st</sup> reactor with recycle in Figure 7.



**Figure 7: Transient oscillation of the gas temperatures during the start up**

In the following, results of a part load simulation are presented. The simulation of the load change is faster than real time. In order to realize the part load, the feed mass stream was reduced to 50 % after reaching steady state (which is after 300 s simulation time) see Figure 8.



**Figure 8: Transient gas temperatures and methane concentration at the outlet of reactor 1, 2 and 3 during at part load**

The steady state in part load is achieved after a simulation time of 1000 s. The results indicate lower gas temperatures in the reactors at part load leading to higher methane concentrations in the gas, see in Figure 9. After 1000 s simulation time the feed mass stream was re-increased back to 100 % (full load). The steady state is reached after a simulation time of 2000 s. The temperature and the methane concentration achieve the same level as before the part load. Finally, the gas product quality at part load is almost equal to the qualities at full load. Furthermore, it is still possible to produce steam, but the pressure of the steam needs to be adjusted.

## 5 Conclusion

The paper shows that the dynamic modeling of a methanization plant is possible. Therefore simplifications are necessary which are implemented in the methanization plant model. The steady state results could be validated successfully by both a steady state flow sheet simulation with ChemCAD and technical process data from Harms [6]. Despite the simplifications in the model a good agreement with the technical process could be achieved. However, the dynamic behavior could be only validated by a plausibility check. The methanization plant model is finally useful for the development and check of control concepts, and furthermore for the analysis of fault scenarios and load changes.

## 6 Literature

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