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Process simulation for solar steam and dry reforming

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Abstract

In co-operation with the German Aerospace Center, the Solar-Institut Jülich has been analyzing the different technologies that are available for methanol production from CO_2 using solar energy. The aim of the project is to extract CO_2 from industrial exhaust gases or directly from the atmosphere to recycle it by use of solar energy. Part of the study was the modeling and simulating of a methane reformer for the production of synthesis gas, which can be operated by solar or hybrid heat sources. The reformer has been simplified in such a way that the model is accurate and enables fast calculations. The developed pseudo-homogeneous one-dimensional model can be regarded as a kind of counter-current heat exchanger and is able to incorporate a steam reforming reaction as well as a dry reforming reaction.

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1. Introduction

In today's industry, there are essentially three reforming processes which are well established to produce hydrogen-rich syngas:

- (Heated) steam reforming (SR)

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- Partial oxidation (POX)
- autothermal reforming (ATR)

These methods aim at high efficiencies to ensure low costs and high conversion rates. Heterogeneous catalysis is used to reduce reaction temperatures while maintaining sufficiently high reaction rates. Often fixed bed catalyst pellets are used.

Nomenclature

ε	porosity
λ	thermal conductivity [W/(m K)]
μ	dynamic viscosity [Pa s]
ϕ	interaction parameter used for thermal conductivity and dynamic viscosity to estimate the corresponding value for a gas mixture
ρ	density [kg/m³]
ξ	conversion
A	Arrhenius constant
E	activation energy [kJ/kmol]
F	correction factor
H	enthalpy [J/kg]
K	equilibrium constant
K_{ad}	adsorption coefficient
L	length of reformer tube [m]
M	molar mass [kg/kmol]
Nu	Nusselt number
Pr	Prandtl number
Re	Reynolds number
T	temperature [K]
T^0	initial temperature [K]
U	overall heat transfer coefficient [W/m²]
$\dot{Q}$	heat [W]
c_p	specific heat capacity at constant pressure [kJ/(kg K)]
d	diameter [m]
f	friction factor
h	convective heat transfer coefficient [W/(m² K)]
p	partial pressure [bar]
r	reaction rate [kmol/(kg_{cat} s)]
v	velocity [m/s]

SR terms the conversion of hydrocarbons ($H_nC_mO_l$) and water into syngas. Subsequently, the four main reactions for the SR process are given:

SR_a: $$C_nH_mO_l + (n-1)H_2O \rightarrow nCO + (\frac{m}{2} + n - 1)H_2 \quad (1)$$

SR_b: $$C_nH_m + nH_2O \rightarrow nCO + (\frac{m}{2} + n)H_2 \quad (2)$$

WGS: $$CO + H_2O \Leftrightarrow CO + H_2 \quad (3)$$

Methanation: $$CO + 3H_2 \Leftrightarrow CH_4 + H_2O \quad (4)$$

In total, the reforming process is highly endothermic. Catalysts used for SR are nickel and noble metals. Reforming temperatures are generally between 300°C and 650°C at the inlet and 700°C to 950°C at the outlet. Reactions (1) and (2) are irreversible except for CH_4 and CH_3OH. The most common applications are fired steam reformers, where the reactor tubes are placed inside of a furnace. Typical sizes of such fired steam reformers are 40 to 400 reactor tubes with a length of 10 to 12 m and a diameter of 10 to 12 cm.

Another concept is the gas heated reforming (GHR). Here, additional tubes are placed over the reactor tubes. The so-called annulus is flushed by a heating gas, which transfers the heat to the reactor tube mainly through convection. The GHR is of special interest for solar reforming, because, if combined with a solar tower equipped with an open volumetric receiver (including storage), the heated gas can directly be supplied from the receiver to the GHR.
POX describes the exothermic reaction, in which a substoichiometric composition of hydrocarbons and oxygen (O_2) reacts and produces heat (5).

POX: $$C_nH_mO_l + \frac{n-1}{2}O_2 \rightarrow nCO + mH_2 \quad (5)$$

If a surplus of O_2 is given to the reaction, total oxidation reaction takes place as competing reaction producing extra heat, which results in an accumulation of H_2O and CO_2. The corresponding total oxidation reaction is

TOX: $$C_nH_mO_l + (n + \frac{m-2l}{4})O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O \quad (6)$$

ATR is a combination of SR and POX. If the reforming process is carefully managed and if the correct reactant gas composition is applied, no external heat supply is needed. The process utilizes reaction (5) to generate heat, so that reforming reactions (1) and (2) can start. Then reactions (3) and (4) are continued until the equilibrium condition is reached.

In contrast to POX, SR and ATR, dry reforming is not yet a broadly established reforming method in industry, even if some commercial plants are in operation. Generally, more heat is required for dry reforming (DR) and less H_2 is produced. However, one big advantage of DR is the fact that the CO_2 emission could be reduced significantly compared to conventional reforming processes. Furthermore, both processes DR and SR are similar in aspect of endothermicity, operating pressures and temperatures [1]. The basic reaction of DR is as follows:

$$CH_4 + CO_2 \Leftrightarrow CO + 2H_2 \quad (7)$$

However, due to the lack of steam, there is a high coking potential in DR which leads to catalyst deactivation. Regarding the solar powered DR process, four advantages can be mentioned compared to traditional DR and SR:

- the calorific value of methane can be increased up to 28%
- there is no contamination of flue gas from combustion
- no pure oxygen sources are required
- a fully supported solar reforming process does not produce emissions during operation

This study aims at modeling and simulating a methane reformer which can be operated by fossil, solar or hybrid heat source. Additionally, the concept of dry reforming of methane with carbon dioxide will be implemented. The developed model will be integrated into a simulation scenario which describes the production of methanol from sunlight and carbon dioxide. The introduction of solar energy will be modeled on the basis of an open volumetric receiver.

2. Models

For the development of simulation models for steam and dry reforming processes the reformer has been simplified in such a way that the model is accurate and fast to solve. The model is a pseudo-homogenous one-

dimensional model, which means that there is no change in radial direction in the reactant gas or the annulus gas in terms of pressure, velocity or reaction rate. Pseudo-homogeneous means that the catalyst and the reactant gas are seen as one homogeneous mixture, which has the same properties as the real heterogeneous mixture.
The model describing the energy conservation of the annulus gas has been developed based on [2]. The change in energy is occurring due to the heat exchange only:

$$\rho_g c_{p,g} v_z = -4U / d_t (T - T_{an}) \cdot \frac{A}{A_{an}} \tag{8}$$

The fraction on the right describes the ration of the reformer tube cross-sectional area and the annulus cross-sectional area. The described ratio is equal to the ratio of the corresponding volumes as the tube lengths are the same for the reformer and the annulus tube. The conservation of energy equation is the only ordinary differential equation (ODE) in the annulus model. The velocity v is calculated with the ideal gas law:

$$v = \frac{R \cdot \dot{n} \cdot T}{p \cdot A} \tag{9}$$

The pressure loss is calculated by the algebraic expression:

$$\Delta P_{an} = f \frac{(L - z) \cdot v_{an}^2}{2 \cdot d_{an}} \tag{10}$$

Here, the friction factor f is valid in the range 1e4<Re<5e6

$$f = (0.790 \cdot \ln(\mathrm{Re}_{an}) - 1.64)^{-2} \tag{11}$$

The physical properties of the reformer are mostly dependent on pressure and temperature. Various models have been used to calculate density, specific heat capacity, dynamic viscosity and thermal conductivity. All described estimation methods can be applied to the seven gases considered in the reformer model.

The simplest calculation for the estimation of the density of a gas mixture is to use the ideal gas law. Real gases behave like ideal gases at high temperatures and low pressures. The high reforming temperatures and low to moderate pressures still allow the use of the ideal gas law. Rearranged for the density ρ the following equation is derived

$$\rho = \frac{P}{R \cdot T} \cdot \sum x_i \cdot M_i \tag{12}$$

Here, R is the specific gas constant, x the molar fraction and M the molar mass of species i.

The dynamic viscosity is calculated from [3] with the method of Wilke for low pressure gas mixtures. First, the individual viscosity has to be calculated for the pure components. The reduced temperatures T_r and the reduced viscosities μ_r are calculated from the critical temperature T_c, critical pressure P_c, critical compressibility factors Z_c and dipole moment μ_{dp} of each species. Finally Wilke's method gives the viscosity of the gas mixture:

$$\mu_g = \sum_{i=1}^{7} \frac{x_i \cdot \mu_i}{\sum_{j=1}^{7} x_j \cdot \phi_{ij}} \tag{13}$$

with

$$\phi_{ij} = \frac{(1+(\mu_i/\mu_j)^{0,5} \cdot (M_j/M_i)^{0,25})^2}{(8 \cdot (1+M_i/M_j))^{0,25}} \tag{14}$$

The thermal conductivity λ_g for multi-component gas mixtures at low pressures can be estimated according to [4] with the method of Miller & Chah for gases at 1 bar.

$$\lambda_i = A_i + B_i T + C_i T^2 + D_i T^3 \tag{15}$$

The coefficients can be found in table 1. The numbers 1 to 7 indicate the species according to following key: 1 = CH_4, 2 = H_2O, 3 = CO, 4 = H_2, 5 = CO_2, 6 = N_2, 7 = O_2. Interaction between the species can be estimated in the following way [5]:

$$\lambda_g = \sum_{i=1}^{7} \frac{x_i \cdot \lambda_i}{\sum_{j=1}^{7} x_j \cdot \phi_{ij}} \tag{16}$$

Table 1: Coefficients for thermal conductivities

	1	2	3	4
A	-1.869E-03	7.341E-03	5.067E-04	8.099E-03
B	8.727E-05	-1.013E-05	9.125E-05	6.689E-04
C	1.179E-07	1.801E-07	-3.524E-08	-4.158E-07
D	-3.614E-11	-9.100E-11	8.199E-11	1.562E-10
	5	6	7	
A	-7.215E-03	3.919E-04	-3.273E-04	---- ----
B	8.015E-05	9.816E-05	9.966E-05	---- ----
C	5.477E-09	-5.067E-08	-3.743E-08	---- ----
D	-1.053E-11	1.504E-11	9.732E-12	---- ----

Heat transfer for the simulation model has been calculated by two different approaches. On the one hand, heat transfer has been modeled according to a calculation by Wesenberg from 2006 [5]. Here, the effective radial conductivity of the catalyst bulk within the reformer tube is:

$$\lambda_{er} = \lambda_{er,s} + \lambda_g \frac{\mathrm{Re}_p \cdot \mathrm{Pr}}{3.2 + 49.4 d_p / d_t} \tag{17}$$

In the above equation, $\lambda_{er,s}$ is required to have a thermal conductivity when the velocity υ is zero.

$$\lambda_{er,s} = \lambda_{g\varepsilon} + \lambda_g \frac{0.895 \cdot (1-\varepsilon) \cdot \left(\ln\left(\frac{\lambda_p}{\lambda_g} - 0.5439 \left(\frac{\lambda_p}{\lambda_g} - 1 \right) \right) - 0.4561 \frac{\lambda_p - \lambda_g}{\lambda_p} \right)}{\frac{1}{2} \cdot 0.7042 \left(\frac{\lambda_p - \lambda_g}{\lambda_p} \right)^2} \tag{18}$$

The left hand side of equation (16) gives the pure gas contribution and the right hand side gives the catalyst bulk contribution. This can be seen from how the catalyst porosity ε is used. The Nusselt numbers for the inner wall at r = r_1, r = r_2 and r = r_3 are calculated as follows:

$$Nu_1 = 4.9 \cdot \left(\frac{d_p}{d_t} \right)^{0.26} \cdot \mathrm{Re}_p^{0.45} \cdot \mathrm{Pr}^{1/3} \tag{19}$$

$$Nu_2 = \frac{F_{c2}(f/8)/(\mathrm{Re}_{an} - 1000) \cdot \mathrm{Pr}}{1 + 12.7 \cdot \sqrt{f/8} \cdot (\mathrm{Pr}^{2/3} - 1)} \tag{20}$$

$$Nu_3 = \frac{F_{c3}(f/8) \cdot (\mathrm{Re}_{an} - 1000) \cdot \mathrm{Pr}}{1 + 12.7 \cdot \sqrt{f/8} \cdot (\mathrm{Pr}^{2/3} - 1)} \tag{21}$$

The correction factors for annular ducts are:

$$F_{c2} = 0.86 \cdot (r_2 / r_3)^{-0.16} \tag{22}$$

$$F_{c3} = 1 - 0.14 \cdot (r_2 / r_3)^{0.6} \tag{23}$$

The friction factor f is described in equation (11). Finally, as a result, the following heat transfer coefficients can be calculated:

$$h_1 = \frac{Nu_1 \cdot \lambda_{er}}{d_p} \tag{24}$$

$$h_2 = \frac{Nu_2 \cdot \lambda_{an}}{d_{an}} \tag{25}$$

$$h_3 = \frac{Nu_2 \cdot \lambda_{an}}{d_{an}} \tag{26}$$

Another possibility to calculate the convective heat transfer coefficients h_1 is developed by Froment [2]:

$$Nu_1 = Nu_s + 0.033 \cdot \mathrm{Re}_p \cdot \mathrm{Pr} \tag{27}$$

By applying the equations for Nusselt number, Reynolds number and Prandtl number, h_1 can be calculated.

$$h_1 = h_s + 0.033 \cdot c_{p,g} \rho_g v \text{, with} \tag{28}$$

$$h_s = 10.21 \cdot \frac{\lambda_{er,s}}{d_t^{4/3}} \tag{29}$$

The version of Froment or the version of Wesenberg can be chosen in the simulation for the calculation of the heat transfer coefficient.

3. Reactions

The SR reaction model is based on the Langmuir-Hinshelwood approach. Three reactions are taken into account: the reverse water gas shift (rWGS), the reverse methanation (rMeth) and the actual SR reaction.

rWGS: $CO_2 + H_2 \Leftrightarrow CO + H_2O$ $\Delta H_r = 41$ MJ/kmol (30)

rMeth: $CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2$ $\Delta H_r = 164$ MJ/kmol (31)

SR: $CH_4 + H_2O \Leftrightarrow CO + 3H_2$ $\Delta H_r = 206$ MJ/kmol (32)

The reforming reactions are based on [1], [6] and [7]. The temperature dependence of the reactions is described by the Arrhenius relation (33):

$$k_i = A_i \cdot e^{(-1000\frac{E_i}{R \cdot T})} \tag{33}$$

Here, k is the rate coefficient, E is the activation energy in kJ/kmol and A is the Arrhenius constant. Furthermore, the absorption coefficient K_{ad} depends on the temperature and is given similarly to the Arrhenius relation (34):

$$K_{ad,i} = A_{ad,i} \cdot e^{(1000\frac{-\Delta H_{ad,i}}{R \cdot T})} \tag{34}$$

In equation (16) K_i and ΔH_{ad} resemble the adsorption coefficient and the adsorption enthalpies, respectively.

The corresponding reaction rates for the used catalyst $Ni/MgAl_2O_4$ are:

$$r_1 = \frac{k_1}{p_{H_2}^{2.5}} \cdot \frac{p_{CH_4} \cdot p_{H_2O} - \frac{p_{H_2}^3 \cdot p_{CO}}{k_1}}{3600 \cdot DEN^2} \tag{35}$$

$$r_2 = \frac{k_2}{p_{H_2}} \cdot \frac{p_{CO} \cdot p_{H_2O} - \frac{p_{H_2} \cdot p_{CO_2}}{k_2}}{3600 \cdot DEN^2} \tag{36}$$

$$r_3 = \frac{k_3}{p_{H_2}^{3,5}} \cdot \frac{p_{CH_4} \cdot p_{H_2O} - \frac{p_{H_2}^4 \cdot p_{CO_2}}{k_3}}{3600 \cdot DEN^2}, \text{ with} \tag{37}$$

$$DEN = 1 + K_{CO} \cdot p_{CO} + K_{H_2} \cdot p_{H_2} + K_{CH_4} \cdot p_{CH_4} + \frac{K_{H_2O} \cdot p_{H_2O}}{p_{H_2}} \tag{38}$$

The rates correspond to the SR reaction, the water gas shift (WGS) reaction and the rMeth reaction, respectively.

Several models for the dry reforming reactions on an Ir/Al_2O_3-catalyst have been described in [1]. It was found that the rWGS is the most important side reaction. The reaction rate r for the SR reaction and the rWGS are as follows:

$$r_1 = \frac{k_1}{3600} \cdot \frac{p_{CH_4} \cdot P_{CO_2} - p_{CO}^2 \cdot p_{H_2}^2}{K_1} \tag{39}$$

$$r_2 = \frac{k_2}{3600} \cdot \frac{p_{CH_4} \cdot P_{CO_2} - p_{CO}^2 \cdot p_{H_2O}^2}{K_2} \tag{40}$$

In the model the catalyst reaction mechanism is neglected. Thus, there are no adsorption coefficients required. This model has been chosen, because all relevant data could be supplied by [1]. The equilibrium constant K_j is determined by the law of mass action. The corresponding values for the temperatures of 873 K and 923 K are 0.19 and 1.31 for the SR reaction and 0.37 and 0.48 for the WGS reaction [8]. These values are linearly extrapolated and the pressure dependence due to Le Chatelier's Principle is neglected in this very simple approach.

4. Results

Two heat transfer models have been implemented to calculate the convective heat transfer coefficient h1 on the inner reformer tube wall. If using the Wesenberg's approach the heat transfer resistance is very low. This reduces the influence of h1 on the heat transfer process significantly. Thus, the velocity in the reformer tube does hardly effect the heat exchange. When using the approach of Froment, a physically more meaningful result is found. However, there are still differences.

In the following tables the effects on several output values of the options chosen are presented. Table 2 shows the results of SR with and without radiation for the convective heat transfer coefficient h1 with the approaches of Wesenberg and Froment.

In Table 3 the results for DR are shown. The values cannot be validated since no reasonable source could be found with all parameters given as required for the simulation. Thus, the values are checked for plausibility when compared with SR. Furthermore, the reaction model chosen here had to be expanded by a linear extrapolation for the equilibrium constants. This might not be adequate for very high or very low temperatures.

Table 2: Simulation results for steam and dry reforming

	Steam Reforming				Dry Reforming			
	Radiation		No Radiation		Radiation		No Radiation	
	WES	FROM	WES	FROM	WES	FROM	WES	FROM
Temp. reformer tube T^1[K]	1010.4	995.8	952.82	942.56	853.48	850.14	844.52	843.68
Conversion ξ	51.10 %	47.75%	38.29%	36.19%	68.09%	63.88%	49.76%	46.29%
Heat transfer $\dot{Q}$	-97.77	-91.29	-73.44	-69.45	-90.44	-85.46	-69.6	-65.71
Temp. annulus T_{an}^0 [K]	746.09	779.95	872.32	892.7	784.3	810.21	891.93	911.71
P^1 [bar]	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1

High temperatures promote endothermic reactions. Consequently, the conversion strongly depends on the reformer temperature. Figure 1 reveals an almost linear dependence between the temperature in the annulus and conversion in the reformer in the temperature range between 1000 K and 1600 K.

By extrapolatiion of this dependency towards lower temperatures one can estimate that the reaction will not proceed at temperatures below 700K. On the other side, temperatures above 1600 K will not enhance conversion linearly. The CH_4 conversion levels off in close proximity to 100%.

In Table 3 the simulation results of different reactant gas composition are shown. The most relevant parameter is the methane conversion. The conversion increases by a factor of about 2 from 17.59% to 37.42% when the gas composition is changed from a 1:1 CH_4 to H_2O ratio to 1:3. As the molar fraction of CH_4 is halved the conversion should double. However, the absolute methane yield is about 2 percentage points higher. This is in agreement with the common procedure to run steam reformers with an over-stoichiometric composition. Additionally, the coking potential is reduced, which enhances the lifetime of the catalyst. When looking at reactant gas compositions with CO_2 one finds that conversion reduces. All in all, it can be said that an optimisation can be achieved, if the reactor is operated with steam excess.

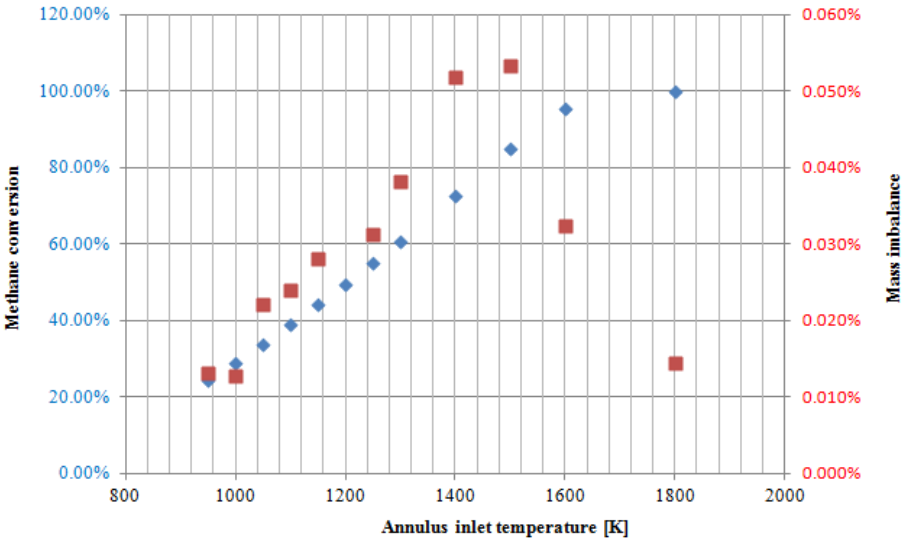

Figure 1: The effect of the inlet annulus temperature in the reformer tube on conversion and accuracy

Table 3: Effect of reactant gas compostion

	Steam reforming					
	Radiation					
x_{CH4}	0.5	0.25	0.25	0.33	0.5	0.5
x_{H2O}	0.5	0.75	0.5	0.33	0	0.25
x_{CO2}	0	0	0.25	0.33	0.5	0.25
P_{end} [bar]	37.5	37.3	36.5	36.3	36.0	36.7
Conversion ξ	17.59%	37.42%	29.69%	20.74%	12.06%	13.55%

As mentioned before, the reaction performance depend mainly on the temperature distribution, when the initial reactant gas composition is set. In Figure 2 the dry gas composition, i.e. without H_2O, is shown on the left of Wesenbergs approach [5] and on the right from the results of the simulation described in this paper. At a first glance, there is a very high congruency between both diagrams. The curves of the individual molar fractions have equal trends. Only when looking closely at the intersection points, it can be seen that the intersection point of the mole fractions is shifted slightly to the left. This means there is a higher convergence and a higher temperature present. The reason for this can be found in very small thermal resistances on the reformer tube side of the model. Furthermore, in this study a one-dimensional pseudo-homogenous reformer model has been used. Wesenberg used a two-dimensional heterogeneous model. This can explain the observed differences between both models. Nevertheless, the general behaviour of the reformer is predicted to be the same with both models.

5. Conclusion

In this study a new model of a gas heated reformer has been developed, which aims at being comprehensive and easily extendable. Next to SR the possibility of DR has been implemented to use the model as a kind of counter-current heat exchanger. Another main feature is that there are extensive diagnostic possibilities which allow insight into the reformer and return graphical as well as code line outputs. The model has been validated and it could be proven that the range of dimensionless numbers is acceptable, the reaction model for steam reforming has been implemented correctly. The dry reforming model still needs further validation as further data base is required. Furthermore, the model has been expanded by the annulus model which allows the heating gas to influence the reaction. Further a window mask has been introduced to allow easy access to important parameters, like radiation, unit selection and choice of reaction type.

In a next step, the model will be implemented into a simulation environment to evaluate the solar production of methanol from CO_2. Therefore, the model will be expanded with the possibility to introduce concentrated solar energy as heat source for the reforming reaction.

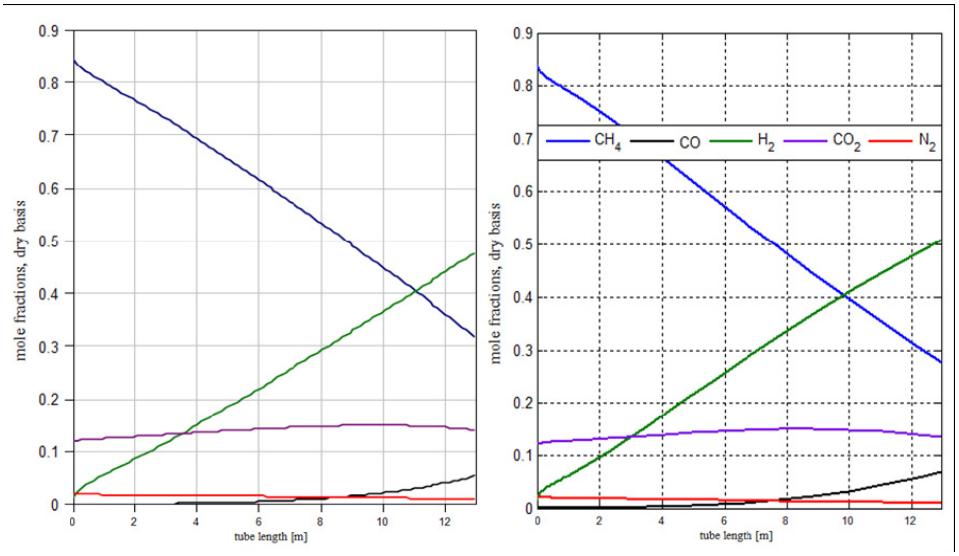

Figure 2: left: Dry molar fractions in the reformer tube for the Wesenberg [5]-model. right: Dry molar fractions simulated in this study

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