



## Experimental and modeling study of catalytic steam reforming of methane mixture with propylene in a packed bed reactor



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### ABSTRACT

Producer gas from biomass gasification contains mainly hydrogen, carbon dioxide, carbon monoxide, methane and some other low molecular hydrocarbons like propylene. This paper reports mathematical simulation and experimental study of steam reforming of methane mixture with propylene in a packed bed reactor filled with nickel based catalysts. Due to the high heat input through the reformer tube wall and the endothermic reforming reactions, a two-dimensional pseudo-heterogeneous model that takes into account the diffusion reaction phenomena in gas phase as well as inside the catalyst particles has been used to represent temperature distribution and species concentration within the reactor. Steam reforming of propylene is faster and more selective than methane and it is shown that addition of propylene to the methane steam mixture reduces the conversion of methane. The obtained results play a key role in optimization and design of a commercial reactor.

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### 1. Introduction

Climate change and global warming are the most important challenges facing the world today; therefore research and developments have focused on the use of renewable energy as an alternative to fossil fuels, [1]. Amongst the renewable energies, one of the most important energy sources in near future is biomass. Because of its wide spread availability, renewable in nature and potential in neutral in relation to global warming, biomass has proved to help to meet the world energy demands and supply much larger amounts of useful energy with fewer environmental impacts than fossil fuels, [2]. Biomass can be converted into commercial products via either biological or thermochemical processes, [3,4]. Gasification is a well established technique to convert biomass fuels into liquid and gaseous products, [5,6]. The gaseous products are mainly hydrogen, carbon monoxide, carbon dioxide, methane, and other low-molecular hydrocarbons like propylene. Steam reforming of hydrocarbons produced by biomass gasification is regarded as one of the most important and economic processes for the industrial production of hydrogen and synthesis gas, which can subsequently be converted to numerous valuable basic chemicals for refinery industry, ammonia production or as feedstock to

the Fischer–Tropsch process for liquid hydrocarbons production, [7–11].

Although steam methane reforming process is widely investigated, [12–17], no data is available in the literature on steam reforming of methane mixture with propylene. The present work investigates a heterogeneous model to present steam reforming of methane mixture with propylene in a fixed bed reactor filled with catalyst particles. The reaction system was mathematically modeled in steady-state and model solutions by Finite Element Method software, COMSOL Multiphysics were carried out. Due to the strongly endothermic nature of the reforming process, a large amount of heat is supplied by means of electrical heating which keep the outer surface of the reactor at certain temperature. Therefore reformer tube wall and the catalyst tubes are exposed to significant axial and radial temperature gradients, [12]. In developing of these kinds of reactors the knowledge of the temperature profiles and gas compositions within the reactor play an important role and are important for designing and optimizing the catalysts structure and the reactor geometry to achieve the best performance.

### 2. Mathematical model

Several chemical reactions can take place during steam methane reforming process, [12,18–21]. The most important and thermodynamically probable reaction of steam reforming of methane

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## Nomenclature

$C_{pi}$	heat capacity of component $i$ (J/kg · K)
$d_p$	catalyst pellet diameter (m)
$d_o$	outside diameter of the reactor tube (m)
$d_i$	inside diameter of the reactor tube (m)
$D_{er}$	effective radial diffusivity ( $m^2/s$ )
$D_{ei}$	effective diffusivity of component $i$ ( $m^2/s$ )
$E$	activation energy (kJ/kmol)
$f$	friction factor
$F_i$	molar flow rate of component $i$ (mol/s)
$F_t$	total molar flow rate (mol/s)
$G$	mass flow velocity ( $kg/m^2s$ )
$\Delta H_i$	enthalpy of the reaction $i$ (kJ/kmol)
$M_i$	molar weight of the component $i$ (kg/kmol)
$P_i$	partial pressure of the component $i$ (bar)
$p_{s,i}$	partial pressure inside catalyst (bar)
$p$	total pressure (bar)
$r_i$	inside radius (m)
$r_{CH_4}$	methane reaction rate ( $kmol/kg_{cat}s$ )
$r_{CO_2}$	carbon dioxide reaction rate ( $kmol/kg_{cat}s$ )
$R_i$	reaction rate of the reaction $i$ ( $kmol/kg_{cat}s$ )
$R$	universal gas constant (kJ/kg K)
$T$	gas temperature (K)
$T_w$	outside reactor surface temperature (K)
$u_s$	gas velocity (m/s)
$U$	overall heat transfer coefficient ( $Kw/m^2 K$ )

$V$	volume of the catalyst particle ( $m^3$ )
$y_i$	molar fraction of component $i$
$z$	axial coordinate (m)

### Greek letters

$\alpha_w$	convective heat transfer coefficient ( $Kw/m^2 K$ )
$\eta_i$	effectiveness factor for reaction $i$
$\lambda_{er}$	effective radial thermal conductivity ( $Kw/m K$ )
$\lambda_w$	thermal conductivity of the tube ( $kw/m K$ )
$\xi$	radial coordinates of the catalyst particle (m)
$\rho_b$	bulk density of the catalyst ( $kg_{cat}/m^3$ )
$\rho_g$	gas density ( $kg/m^3$ )
$\nu$	void fraction of the packed bed

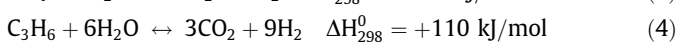
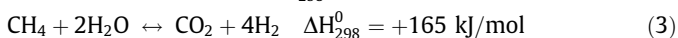
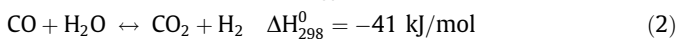
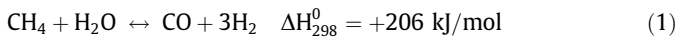
### Superscripts

0	inlet conditions
s	catalyst surface conditions
Stag	stagnant

### Subscripts

cat	catalyst
i	initial
p	particle
w	wall

mixture with propylene consists of four reversible reactions: the strongly endothermic reforming reactions (1), (3), (4) and the moderately exothermic water–gas shift reaction (2), [22–24]:



The mathematical model is based on the Langmuir–Hinshelwood mechanism where the reaction rates are investigated and given by Xu and Froment [23]:

$$R_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}} \left[ P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_1} \right]}{DEN^2} \quad (4a)$$

$$R_2 = \frac{\frac{k_2}{P_{H_2}} \left[ P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_2} \right]}{DEN^2} \quad (4b)$$

$$R_3 = \frac{\frac{k_3}{P_{H_2}^{3.5}} \left[ P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_3} \right]}{DEN^2} \quad (4c)$$

where

$$DEN = 1 + K_{CH_4} P_{CH_4} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + \frac{K_{H_2O} P_{H_2O}}{P_{H_2}} \quad (4d)$$

where  $R_1$  and  $R_3$  are the reaction rates of reactions (1) and (3) producing carbon monoxide and carbon dioxide, and the water gas shift reaction (WGS) with reaction rate  $R_2$  as independent reaction. The rate constants and adsorption constants are Arrhenius function type and are function of temperature, [23]:

$$k_j = A_j \times e^{-E_j/RT} \quad j = 1, 2, 3 \quad (5a)$$

$$K_i = B_i \times e^{-\Delta H_i/RT} \quad i = CH_4, H_2, H_2O, CO, CO_2 \quad (5b)$$

Regarding propylene reforming reaction, (4), intrinsic kinetic expressions reported by Figueiredo and Trimm are adopted, [24]:

$$R_4 = 2.81 \times 10^{-2} \frac{P_{C_3H_6}}{1 + 0.09P_{C_3H_6}} \times \exp(-8000/T) \text{ mol}/(s \cdot g) \quad (5c)$$

The formation rate of each component was then calculated by using Eqs. (1)–(4) and (4a)–(5c); for example for methane propylene and carbon dioxide components:

$$R_{CH_4} = -R_1 - R_3 \quad (5d)$$

$$R_{C_3H_6} = -R_4 \quad (6e)$$

$$R_{CO_2} = R_2 - R_3 + 3R_4 \quad (6f)$$

Partial pressures of gases were correlated to their own concentrations by using the ideal gas law. The values of pre-exponential factors and activation energies, with the correspondent dimensions, used in the Arrhenius expression, are listed in Table 1, [23].

Considering Reynolds number in steam reformers, it is assumed that axial diffusion effects are negligible compared to the axial convection. There is no radial convection compare to axial convection and external heat and mass transfer resistance are negligible;

**Table 1**

Kinetics parameters for the reactions involved in methane steam reforming.

Rate coefficients		
$k_1 = 9.49 \cdot 10^{16} \cdot e^{-28879/T}$	$kmol \cdot kPa^{0.5}/(kg \cdot hr)$	
$k_2 = 4.39 \cdot 10^4 \cdot e^{-8074.3/T}$	$kmol \cdot kPa^{-1}/(kg \cdot hr)$	
$k_3 = 2.29 \cdot 10^{16} \cdot e^{-29336/T}$	$kmol \cdot kPa^{0.5}/(kg \cdot hr)$	
Adsorption coefficient constants		
$K_{CH_4} = 6.65 \cdot 10^{-6} \cdot e^{4604.28/T}$	$kPa^{-1}$	
$K_{H_2O} = 1.77 \cdot 10^3 \cdot e^{-10666.35/T}$	$kPa^{-1}$	
$K_{H_2} = 6.12 \cdot 10^{-11} \cdot e^{9971.13/T}$	$kPa^{-1}$	
$K_{CO} = 8.23 \cdot 10^{-7} \cdot e^{8497.71/T}$	$kPa^{-1}$	
Equilibrium constants		
$K_1 = 10266.76 \cdot e^{(-2630/T+30.11)}$	$kPa^2$	
$K_2 = e^{(4400/T-4.063)}$		
$K_3 = K_1 \cdot K_2$	$kPa^2$	

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