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# Steam reforming of tars at low temperature and elevated pressure for model tar component naphthalene

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## ABSTRACT

A process of pressurized gasification and power generation in a hybrid system of Solid Oxide Fuel Cell (SOFC) and gas turbine enables an efficient use of biomass. This process requires tar reforming in order to protect the SOFC from plugging. Tars must be converted at 5 bar absolute pressure (bara) while avoiding secondary steam reforming of methane in order to reduce the required heat input for the tar reformer. This can be realized at low reforming temperatures (<700 °C) where methane conversion is reduced due to chemical equilibrium. A laboratory-scale test rig is introduced, which enables an investigation of the steam reforming of the model tar component naphthalene at up to 5 bara. Deactivation of the nickel catalyst caused by coke formation was detected. Despite the reduced amount of free active centers on the catalyst surface, stationary naphthalene conversions are possible at temperatures between 600 °C and 700 °C. The lower the temperature, the more active centers are covered. For stationary conditions a hyperbolic approach for the reaction rate of steam reforming of naphthalene is developed and parameters for 650 °C and 700 °C are determined.

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## Introduction

In biomass gasification, renewable raw materials or residues can be used to produce electrical energy or fuels. The predominantly hydrogen-rich product gas of the absorption enhanced reforming (AER-) process [1–5] can be converted into electricity in gas engines, gas turbines or fuel cells. A further possibility is to convert the product gas catalytically into gaseous fuels like pure hydrogen or synthetic natural gas

(SNG) as well as liquid fuels using such methods as the Fischer–Tropsch process. Advantages of using a pressurized gasifier are its smaller volume, as well as its compatibility with pressurized downstream applications like methanation or conversion in a gas turbine without the need to cool the gas for compression. Product gases of any gasifier contain impurities such as particles, chlorine, sulfur and tars [6], which must be removed before the power generation or fuel synthesis. The present work focuses on tar removal, for which tars are defined as all undesired higher hydrocarbons of the

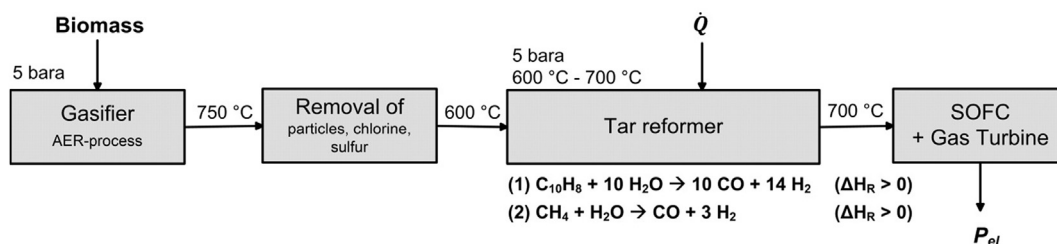
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<sup>1</sup> I did this work at German Aerospace Center, but now I do not work there any more. Yet my former colleague Holger Fischer still works there.

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**Fig. 1 – Concept of pressurized gasification of biomass for power generation in a hybrid solid oxide fuel cell (SOFC) and gas turbine system.**

gasification gas [7]. More specifically, the catalytic steam reforming of tars is investigated [8,9]. Since the use of catalytic additives in the gasifier bed material [10,11] or in ceramic filters [12] is not sufficient to achieve the required tar conversions of over 99% for power generation in fuel cells, tar reforming in a fixed bed downstream from the gasifier is considered.

As can be seen in Fig. 1, the pressurized product gas of the AER-process is cleaned and then converted in a hybrid power generation system consisting of a Solid Oxide Fuel Cell (SOFC) and a gas turbine [13–19]. The AER-process consists of two reactors. In the first one biomass is gasified with steam and in the second one, combustion of residual coke takes place, which provides the necessary heat for the gasification. CO<sub>2</sub> is bound at the bed material CaO and therefore the AER-product gas contains small concentrations of CO<sub>2</sub> and high concentrations of H<sub>2</sub>. The product gas composition can be seen in Table 1.

**Table 1 – Simulated AER product gas composition at 5 bara in mole fraction and typical tar yield of AER product gas referred to dry gas [20].**

$Y_{H_2O}$	$Y_{H_2}$	$Y_{CO}$	$Y_{CH_4}$	$Y_{C_2H_4}$	$Y_{C_2H_6}$	$Y_{C_3H_8}$	$Y_{CO_2}$	Tar
60%	26%	2.4%	5.6%	1.2%	0.6%	1.2%	3.0%	1–5 g/m <sup>3</sup> <sub>N</sub>

Particles, chlorine and sulfur impurities can be removed at temperatures greater than 600 °C [6] (see Fig. 1). Afterwards tars are reformed catalytically by using the steam contained in the gas (see Eq. (1) in Fig. 1).

The reaction takes place in a temperature range of 600 °C–700 °C and at a pressure of 5 bar absolute pressure (bara). The advantage of a low reformer temperature (<700 °C) is a reduction in the secondary steam reforming of methane (see Eq. (2) in Fig. 1) due to chemical equilibrium and therefore less heat demand for that endothermic reaction. In the case of the pressurized AER product gas shown in Table 1, at approximately 650 °C no methane will be converted in the tar reformer at 5 bara. The challenges of lower temperatures, however, are the slower reaction kinetics of tar reforming and the risk of coke formation at the nickel catalyst, especially at pressures higher than atmospheric. Therefore a detailed understanding of tar reforming reaction kinetics is required for the design of that process unit.

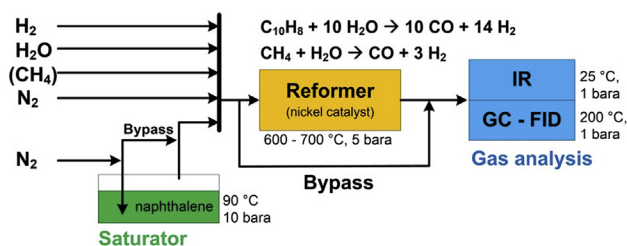
A laboratory-scale test rig with a fixed catalytic bed was built to investigate the reaction kinetics experimentally. Naphthalene (C<sub>10</sub>H<sub>8</sub>) is used as the model tar component because it is the main component of tars in AER product gas (mass fraction of 31.5% of tars heavier than toluene [2]), it is often an intermediate product at the tar reforming process and its reaction rate is low in comparison to other tars.

Jess [21] found that naphthalene as a model tar is strongly adsorbed on the surface of a nickel catalyst and inhibits the simultaneous conversion of methane and benzene. Due to this inhibition at higher concentrations the reaction order of steam reforming of naphthalene itself is, at 0.2, much lower than 1. Therefore Depner [22] uses a hyperbolic Eley–Rideal approach for steam reforming of naphthalene on a nickel catalyst. This approach is based on adsorption of naphthalene and includes inhibition of the reaction due to active centers on the catalyst surface being covered by naphthalene. While Jess [21], Depner [22] and current works of Hamel et al. [23], Kaisalo et al. [24] and Kurkela et al. [25] investigate tar reforming at temperatures higher than 700 °C, Fraubaum et al. [26] and Kienberger et al. [27] focus on temperatures even lower than 500 °C with combined methanation.

The aims of this work are to demonstrate stable steam reforming of naphthalene in a temperature range of 600 °C–700 °C, to derive an approach for the conversion rate of naphthalene, and to determine the kinetic parameters for this approach.

## Experimental

An average molar gas composition of the technical tar reformer in Fig. 1 of 45%–55% hydrogen and 35%–37% steam is synthesized as feed for the reformer at the test rig (see Fig. 2). Further gas components such as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and other



**Fig. 2 – Schematic draft of the test rig.**

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