



# Investigation of various catalysts for partial oxidation of tar from biomass gasification



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## ABSTRACT

The formation of tar during biomass gasification limits the use of the product gas in small scale CHP units like gas engines. Catalytic partial oxidation can be applied to remove tar and convert it into fuel gas by using a catalyst under sub-stoichiometric addition of oxygen. In the present study, different catalyst materials, i.e. several perovskite-type materials and one Ni-based catalyst, which shall be used in combination with an oxygen carrier material, were investigated in lab-scale experiments regarding their catalytic activity in partial oxidation of naphthalene as model tar compound. Furthermore, the influence of the trace substances HCl, KCl, and H<sub>2</sub>S on the performance of the Ni-based catalyst being the best performing catalyst was tested. Since the Ni-based catalyst is significantly poisoned by H<sub>2</sub>S, it was also tested in combination with a CuO-based sorbent. In addition to H<sub>2</sub>S reduction, the sorbent increased the catalytic activity of the entire system significantly, so that naphthalene was almost completely converted at temperatures above 450 °C despite the presence of 140 ppm H<sub>2</sub>S.

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## 1. Introduction

Gasification in small decentralized plants with regional energy-supply structure is an efficient way to generate heat and power from biomass. However, the formation of unwanted high boiling hydrocarbons and tars [1–3] during biomass gasification limits the use of the product gas in a CHP unit (combined heat and power), e.g. a gas engine. Therefore, such small CHP systems are not well established in the market by now. Current tar removal processes are still not sufficient to guarantee a safe and/or economical operation. By way of example, gas engines require a very high quality of the produced fuel gas related to the maximum amount of tars, dust, and corrosive gaseous impurities in order to be used. In case of tars, these requirements are currently either not reached or can only be reached with a very high expense on apparatus and operational techniques. Gas scrubbing is often used to remove several impurities from the gas [4]. However, PAH-containing (polyaromatic hydrocarbons) sludge and phenol-containing wastewater are produced by scrubbing, which need to be further processed, and thus cause either high technical effort or high disposal costs.

Catalytic partial oxidation as a catalytically active thermochemical process provides an effective way for tar removal and

conversion [5,6]. The partial oxidation is operated with a sub-stoichiometric addition of oxygen, so that the tars, i.e. CH- and CHO-compounds, will mainly be partially oxidized to CO and H<sub>2</sub> preventing complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O. Different catalysts for (partial) oxidation of tars derived during biomass conversion have been investigated in the past. Carnö et al. investigated the oxidation of hydrocarbons from wood combustion with Pt and CuO<sub>x</sub>/MnO<sub>x</sub> supported on alumina [7]. The Pt-catalyst had with 85–95% conversion at >400 °C a higher activity for naphthalene than the metal oxide catalyst, and deactivation was also less pronounced. In a comparative investigation by Miyazawa et al. on catalytic partial oxidation of tar from biomass pyrolysis Rh/CeO<sub>2</sub>/SiO<sub>2</sub> and Ni catalysts exhibited much higher performance than other materials like active clay, USY zeolite, MS-13X, dolomite, alumina, silica sand and fluorite [5]. However, Rh/CeO<sub>2</sub>/SiO<sub>2</sub> exhibited higher and more stable activity under the presence of high concentration (280 ppm) H<sub>2</sub>S than the Ni catalyst [8]. Ni/CeO<sub>2</sub> showed smaller amount of coke and thus less deactivation than Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/ZrO<sub>2</sub>, Ni/TiO<sub>2</sub>, and Ni/MgO [6]. Wang et al. found 99% conversion of naphthalene using a monolithic Ni-catalyst [9]. Herrmann found complete conversion of naphthalene above 500 °C using a Mo<sub>8</sub>V<sub>2</sub>W<sub>1</sub>O<sub>x</sub>-catalyst [10]. Ammendola et al. found high catalytic activity of Al<sub>2</sub>O<sub>3</sub> supported Rh, LaCoO<sub>3</sub> and Rh-LaCoO<sub>3</sub> catalysts for conversion of tars from maple wood pyrolysis [11]. Böhning found almost complete conversion of tar from fixed-bed wood gasification above 700 °C using Pd- and Ni-based catalysts [12].

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**Table 1**  
Composition and BET surface ( $\text{m}^2/\text{g}$ ) of the catalyst materials.

Catalysts	Composition	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )
B21	$\text{LaCoO}_{3-\delta}$	18
B22	$\text{LaFeO}_{3-\delta}$	15
B23	$\text{LaMnO}_{3-\delta}$	22
B24	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$	35
B25	NiO	500

The supply of oxygen is very often realised by simply injecting air rather than pure oxygen to the producer gas. However, the producer gas is significantly diluted when using air resulting in a heating value insufficient for proper use in a gas engine [12]. Therefore, a combination of an oxygen carrier material (OCM) with a catalyst for partial oxidation has been proposed recently [13]. OCMs, well known from application in chemical looping combustion [14], are capable to take up oxygen at high oxygen partial pressure in air and release oxygen at low oxygen partial pressure in producer gas, thus providing oxygen without dilution by nitrogen. In afore mentioned investigations [13] mainly perovskite type materials are used as OCM due to their relatively high oxygen storage capacity.

During the gasification of biomass also inorganic trace gases such as HCl, alkali salts, and  $\text{H}_2\text{S}$  are released which could influence the performance of the catalyst. By way of example,  $\text{H}_2\text{S}$  would deactivate Ni-catalysts [15]. Cu-based sorbents were reported to be used for sorption of  $\text{H}_2\text{S}$  decreasing the  $\text{H}_2\text{S}$  concentration in the synthesis gas to less than 100 ppm at temperatures below  $810^\circ\text{C}$  [16,17]. Regeneration of these sorbents can be performed with air, fortunately together with the OCM in the planned system.

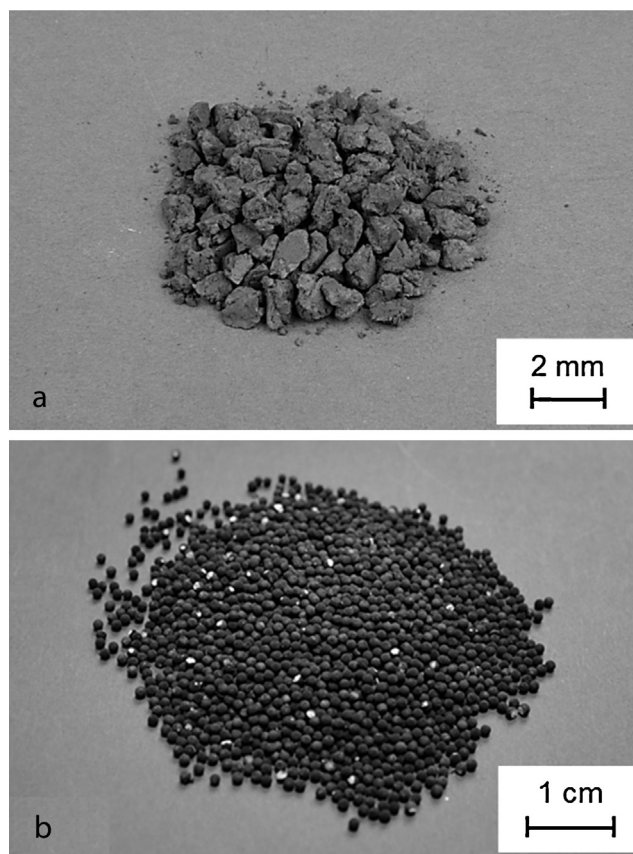
In this work, different catalyst materials for subsequent combination with afore mentioned OCMs were investigated regarding their catalytic activity in partial oxidation of naphthalene, which was used as a model compound for tar from fixed-bed biomass gasification. Furthermore, the influence of trace impurities such as HCl, KCl and  $\text{H}_2\text{S}$  on the catalytic activity of the materials was investigated. Finally, the benefit of a CuO-based  $\text{H}_2\text{S}$  sorbent material for the performance of the catalysts was tested.

## 2. Experimental

### 2.1. Materials selection, preparation, and characterisation

Several materials were investigated in this work as candidates for catalysts as listed in Table 1. These materials were selected based on long-term research experience as well as literature findings. B21, B22, B23, and B24 are standard perovskite-type catalysts for oxidation processes which differ from each other mainly in composition and their activation temperatures. They were chosen due to their compatibility to the perovskite-type OCM materials. B25 (NiO) is a cheap, well-known catalyst material used for example in SOFC (solid oxide fuel cell) as a catalytic ingredient of the anode material catalysing the oxidation of the fuel [18,19]. All materials were prepared and delivered as pure single-phase powders ( $<10\ \mu\text{m}$ ) by Fraunhofer-IKTS, Hermsdorf, Germany.

The catalytic activity of the catalysts was examined in a flow channel reactor. Since a high pressure drop would be induced when using powdered catalyst materials as filling, coarser particles are required. For this purpose, the respective catalyst powders were sprayed into a stainless steel container with 1 wt.% of carboxymethylcellulose as binder solution. By rotating the container, the powders agglomerated to form large spherical particles which were then sintered at  $1150^\circ\text{C}$  for 6 h. During sintering, the binder was burned to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Thus, there is no contamination of the catalyst material. In this way, the catalysts were agglomerated



**Fig. 1.** Agglomerated catalyst (a) and CuO-sorbent (b).

to a granule size of 1–2 mm (Fig. 1a). Remaining smaller particles were removed by sieving. After sintering, an X-ray examination was done to determine the phase composition of the sintered catalysts. The mineral phases of the materials remained the same after sintering and were regarded as a pure phase (Fig. 2). Furthermore, the BET surface of the sintered materials was determined by low-temperature  $\text{N}_2$  adsorption (Table 1).

The preparation of the CuO-based sorbent was carried out by immersing the support material, i.e. corundum spheres with 1 mm in diameter, in a saturated copper nitrate solution. After short stirring, this solution was heated in a vacuum oven at  $180^\circ\text{C}$  for 5 h so that the copper nitrate completely decomposed into CuO,  $\text{NO}_2$ , and  $\text{O}_2$ . Thus, a CuO-coated sorbent with a weight proportion of 21.4% CuO was obtained. Fig. 1b shows the CuO-coated sorbent.

The materials were characterised by X-ray diffraction (XRD) and chemical analysis, i.e. inductively coupled plasma optical emission spectroscopy (ICP-OES) and Cl-Ion chromatography (IC) after soda extraction, before and after the experiments. Furthermore, catalyst B25 was characterised by thermogravimetric analyses (TGA).

### 2.2. Experimental set-up

Naphthalene ( $\text{C}_{10}\text{H}_8$ ), an aromatic 2-ring molecule, was used as a model tar compound because it is relatively stable in comparison to other commonly used tar model compounds such as benzene and toluene. Furthermore, naphthalene is in fact the major fraction of the two ringed aromatics in tar [20] and it is often used as tar model compound in Refs. [20–25].

The naphthalene conversion capability of the catalysts was examined by molecular beam mass spectrometry (MBMS). MBMS can provide effective real-time, on-line quantification of high-temperature condensable and non-condensable gases [26,27]. A

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