



Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: <http://www.elsevier.com/locate/biombioe>

## Research paper

# Influence of bed material coatings on the water-gas-shift reaction and steam reforming of toluene as tar model compound of biomass gasification

Matthias Kuba <sup>a,\*</sup>, Fabian Havlik <sup>b</sup>, Friedrich Kirnbauer <sup>a</sup>, Hermann Hofbauer <sup>b</sup>

<sup>a</sup> Bioenergy 2020+ GmbH, Wiener Straße 49, 7540 Güssing, Austria

<sup>b</sup> Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9, 1060 Vienna, Austria

## ARTICLE INFO

## Article history:

Received 7 August 2015

Received in revised form

26 November 2015

Accepted 27 November 2015

Available online xxx

## Keywords:

Biomass gasification

Bed material coating

Catalytic conversion

Water-gas-shift reaction

Steam reforming

## ABSTRACT

A promising technology replacing fossil energy carriers for the production of electricity, heat, fuels for transportation and synthetic chemicals is steam gasification of biomass in a dual fluid bed (DFB). The principle of this technology is the separation into a gasification and a combustion reactor. Bed material, nowadays olivine, circulates between them, and has two functions. It acts as a heat carrier from the combustion to the gasification zone and as catalyst regarding gasification reactions. Today, an alternative to olivine does yet not exist.

In this work, experiments in a lab-scale test rig were performed investigating the catalytic activity of different fresh and used bed materials, such as olivine and quartz. The enhancement of the catalytic activity due to particle coatings was tested regarding the water-gas-shift reaction and steam reforming of toluene. Calcite is known as an active material in this respect and is therefore used as a benchmark substance.

Experiments revealed a correlation between the catalytic activity of bed particle coatings towards both the water-gas-shift reaction and the reduction of toluene by steam reforming. Results showed bed material particles with a calcium (Ca)-rich layer achieve satisfactory conversion of carbon monoxide and reduction of toluene. Furthermore, a qualitative comparison regarding hydrogen production relative to the benchmark material CaO is given for the water-gas-shift and steam reforming of toluene and ethene - used as model substance for lighter hydrocarbons. These results are the basis for further research on the catalytic properties of potential bed materials for DFB gasification of biomass.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Research on energy from renewable sources has risen considerably since the early 2000s. Substitution of fossil energy carriers by renewable sources plays an ever-increasing role in energy technology. The awareness of global warming caused by combustion of fossil fuels has increased the development of technologies using biomass since it is considered as a major source of renewable energy. Biomass is suitable for use in pyrolysis, combustion and gasification as CO<sub>2</sub>-neutral feedstock [1]. Gasification transforms the solid feedstock into a gaseous secondary energy carrier, which is referred to as product gas. Chemical properties of biomass differ

from those of fossil fuels, triggering new challenges in the operation of such systems. Compared with fossil fuels biomass contains higher amounts of low melting ashes and it also produces a higher yield of heavier hydrocarbons, which are also referred to as tars, during gasification owed to higher volatile matter. The Tar Guideline (a standard for tar sampling and measuring) defines tar as follows: Generic (unspecific) term of entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 to C6). Benzene is not included in tar [2].

During gasification of a biomass feedstock tars are primarily produced in the pyrolysis stage. The three main constituents of biomass, namely cellulose, hemicellulose and lignin, break down into primary tars. Typical primary tars include phenol and cresol. Above temperatures of 500 C these primary tars start to recombine into non-condensable gases and heavier molecules. These compounds are referred to as secondary tars. At further increased

\* Corresponding author.

E-mail address: [matthias.kuba@bioenergy2020.eu](mailto:matthias.kuba@bioenergy2020.eu) (M. Kuba).

temperatures primary and secondary tars may be destroyed and tertiary tars produced. Tertiary tars can either be alkyl tertiary products or condensable tertiary aromatics. Alkyl tertiary products include, for example, methylacenaphthalene, methylnaphthalene, toluene and 1H-indene. Condensed tertiary aromatics are mainly poly-aromatic hydrocarbons (PAHs), such as naphthalene or pyrene. These undesirable by-products cause operational problems in downstream equipment by forming depositions [3].

A gasification process using a dual fluid bed (DFB) system was developed at the Vienna University of Technology. Syngas gained from biomass feedstock can be further used to produce electricity, heat, fuels for transportation or synthetic chemicals. Thanks to the flexibility of the technology it can quickly react to changes in the energy market [4]. The technology is successfully demonstrated in Güssing, Austria. Industrial power plants using the same technology are in operation in Oberwart, Austria, Ulm, Germany, and Gothenburg, Sweden. New-generation DFB gasification of biomass using an improved reactor design where the contact of bed material and product gas is drastically increased is currently being investigated at the Vienna University of Technology [5–7]. Therefore, catalytic properties of bed materials will become more and more important for DFB gasification of biomass in the future.

Separating endothermic gasification from exothermic combustion into two different reactor zones is the main principle of the DFB process. Between those zones a bed material circulates, which has two major roles. First, it acts as a heat carrier to transport the energy released in combustion to the gasifier, where it is needed for the reactions. Second, it is catalytically active regarding the water-gas-shift reaction and decomposition of biomass tars. Olivine, a magnesium iron silicate, is currently used as bed material because of its catalytic activity, resistance to abrasion and satisfactory behavior in terms of agglomeration processes [4].

Catalytic activity of potential bed materials has been investigated in relation to different tar model compounds. Benzene, toluene and naphthalene are often used as model substances for either monocyclic or polycyclic aromatic hydrocarbons in steam reforming experiments. Usually, synthetically created or altered naturally occurring minerals have been investigated in lab-scale experiments regarding their activity for steam reforming reactions [8–15]. Furthermore, different natural minerals, e.g. ilmenite, have been investigated as potential alternative bed materials regarding their catalytic activity [16,17]. An extensive review of the literature on naturally occurring and synthetically created catalysts has been performed previously [18,19].

Biomass ash contains critical components which might lead to operational difficulties. One major issue is the interaction between ash and bed material in fluidized bed systems [20]. Through interaction between biomass ash and bed materials the development of layers can be observed for quartz particles in biomass combustion plants. These layers are initiated by potassium (K) attacking the particle surface. Over time calcium (Ca) diffuses into the first K-dominated layer and a second outer layer starts to grow outwards [21]. Since these layers on quartz particles originate from interaction with biomass ash they are critical in terms of agglomeration and slagging. Partly molten layers in zones of elevated temperatures act as glue and cause particles to stick together. Therefore, formation of particle layers is seen as critical in biomass combustion [22–24].

A similar layer build-up can be observed for olivine in biomass gasification. During long-term operation of the DFB biomass plant in Güssing two calcium-rich layers were formed on olivine particles. The inner layer mainly consisted of calcium silicates, whereas the outer layer had a more heterogeneous composition similar to fine ash [25–28]. Layer formation is caused by notable amounts of calcium in the feedstock and addition of calcium-rich additives to

the gasifier. These Ca-rich layers led to enhanced catalytic activity regarding tar decomposition in the gasifier. This observation showed that layers positively influence gasification processes and are therefore desirable [27]. Further investigations of olivine used in a pilot-scale plant showed an increase of the catalytic activity regarding the water-gas-shift reaction owed to layer formation [27], which was confirmed by lab-scale tests [29]. Calcium has been identified as playing an important role in terms of catalytic activity if present as CaO. Consequently, it is clear that layer formation has both negative (agglomeration, slagging) and positive (catalytic activity) effects regarding biomass gasification.

Knowledge of increasing catalytic activity through layer build-up on olivine raises the question of whether specific materials are necessary because of their catalytic characteristics. If the layer itself were catalytically active, all material could be used as a bed catalyst for decomposition of tars as long as a Ca-rich layer was built around it. Therefore, this paper focuses on the investigation of fresh and layered olivine and quartz particles and compares their catalytic activity. Calcite, which is known to be an excellent natural catalyst [29], is used as reference material. Furthermore, both the water-gas shift reaction and steam reforming of the tar model compound toluene are examined to see if the catalytic activity of bed particle coatings is increased in a similar manner for those different reactions. In addition, a qualitative comparison of the catalytic activity towards hydrogen production is given for the different materials. The comparison includes the water-gas-shift reaction and steam reforming of toluene and ethene - which is used as model compound for lighter hydrocarbons.

## 2. Materials and methods

### 2.1. Test rig for measurements of catalytic activity

Fig. 1 shows a flow chart of the employed test rig. Gases (3) are introduced into the reactor via mass flow controllers (MFCs). As it can be seen, there is a possibility of introducing six different gases into the reactor simultaneously. All gases as well as the mixture of steam and carrier gas can be directed into a bypass to avoid contact with the catalytically active material. This is important to calibrate the gas measurement system and verify its functionality immediately before the start of each experiment. Calibration and review of measurement accuracy was conducted by the certified Test Laboratory for Combustion Systems of the Vienna University of Technology.

DeminerIALIZED water (2) and the model tar toluene (1) were evaporated separately and transported together with carrier gas into the reactor. The mass flow controllers as well as the evaporator for the water were controlled by a computer which also recorded the data. Water was brought into the system from a reservoir through pressurized nitrogen. The nitrogen pushed liquid water out of the reservoir and into an evaporation unit. The amount of water which was brought to the evaporator was adjusted using a mass flow controller for liquids from Bronkhorst. Evaporation of water was realized with a controlled evaporator mixer (CEM) from Bronkhorst, which was heated up to a temperature of 135 °C. Steam became mixed with the carrier gas in the evaporator and was therefore continuously dragged through the reactor system. Tar was transported into an evaporator by a syringe pump and also mixed with carrier gas. The tar evaporator was heated up to a temperature of 165 °C. The pipes from the evaporators to the reactor were trace heated to ensure that no condensation took place. Trace heating was realized at temperatures of 135 °C for the steam pipes and 145 °C for the toluene pipes. In all experiments nitrogen, N<sub>2</sub>, was used as inert carrier gas since it is not reactive with the used model compounds at the investigated conditions. It

Download English Version:

<https://daneshyari.com/en/article/7063284>

Download Persian Version:

<https://daneshyari.com/article/7063284>

[Daneshyari.com](https://daneshyari.com)