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Characteristics of olivine as a bed material in an indirect biomass gasifier

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HIGHLIGHTS

- After a period of activation, olivine shows good characteristics as a catalyst of tar destruction.
- When activated, olivine increases the yield of H_2.
- Enrichment of the olivine by inorganics from the fuel has noteworthy effects on the activity of olivine and the overall process.
- Sulfur addition to the combustion side of the system shows a positive effect on the total tar reduction.
- Addition of silica-sand to the system results in a poorer performance of the system.

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ABSTRACT

The use of untreated olivine as the bed material in a biomass gasifier is investigated in this work, in which activation of the material is the main focus. The experiments were carried out in the Chalmers 2–4-MW_{th} indirect biomass gasification unit and comprised analyses of the gas composition and bed material, as well as changes in tar yield. Starting from the raw material, the first signs of activation, in the form of a reduction in the tar yield, were observed already during the second day of the operation. The tar yield continued to decrease with time, and by the fourth day it was reduced by 30%, as compared to the yield on the first day of the operation. Analysis of the bed samples showed accumulation of inorganics within the bed material, with a share of potassium being present in leachable form. Thermodynamic calculations support the indications from the experiment that potassium can be released under gasification conditions and may play an important role in the activation of olivine. To examine the impacts of S and silica on the activity of olivine, two experiments were conducted. The addition of S to the combustion side gave a positive effect in terms of the tar levels in the raw gasification gas. The addition of silica sand revealed, as expected given the affinity of potassium for silicone, negative influences on the tar yield and gas composition that could not be attributed to mere dilution, as compared with the gas produced during operation with pure olivine.

1. Introduction

Recently, biomass-based fuels have attracted great interest as carbon dioxide-neutral energy sources, as opposed to fossil fuels. In this context, the use of biomass in countries where it is abundant represents a route to reduce the dependency on oil from foreign sources utilizing domestic resources instead. Among the different conversion techniques, thermochemical conversion of biomass *via* gasification is seen as highly promising [1–5].

The primary gas produced *via* the gasification step is commonly referred to as the 'raw gas', and it consists of CH_4, H_2, CO, CO_2, light hydrocarbons, and heavy hydrocarbons. The heavy hydrocarbons are usually referred to as 'tar'; the usual definition is that the tar fraction includes hydrocarbons with a molecular mass greater than that of benzene. This fraction may represent 5–10% of the total energy content of the fed biomass [6]. These tar species start to condense already at temperatures of around 360 °C, and they create operational problems, such as process shut-down and/or downstream catalyst deactivation [2,7–10].

The overall gasification reaction is endothermic and requires energy input. As a solution to the partial burning of the fuel in the presence of pure oxygen or air, with the latter diluting the raw gas with nitrogen, indirect gasification is used. This technology uses the circulating bed material as a carrier of heat between the two reactors. The material is heated up in the combustion process and transferred to the gasifier supplying the heat for the endothermic gasification reactions. By use of catalytically active bed

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materials one can even actively influence the gas composition and tar yield in the produced gas. These materials can be produced synthetically or may have a naturally occurring character, e.g., ores [10]. Given the severity of the conditions in the system, in terms of high temperatures, the presence of ash, and material circulation, the material undergoes significant physicochemical changes. A commonly applied bed material in this process is silica sand, which is a natural material that is relatively cheap, readily available, and not associated with disposal issues. However, silica sand is not expected to influence the chemical reactions within the system so as to increase the quality of the produced gas, e.g., attain high yields of hydrogen and minimize tar content. Moreover, the presence of ash components that chemically bond to the silica sand results in operational problems, such as agglomeration [11–13]. Therefore, alternative bed materials are needed for optimization of the product gas at a reasonable cost.

Natural materials, such as dolomite, magnesite, limestone, and olivine, all of which have tar cracking abilities [14], fulfill the above requirements. In particular, olivine, which is a naturally occurring iron-magnesium mineral, has shown catalytic effects on tar decomposition in several previous studies [15–19]. For this reason, it is used as the active bed material in the plant located at Guessing (Austria), which is operated commercially [20]. One drawback of olivine is its ability to transfer oxygen between the combustion side and the gasification side of the indirect gasification system [16,21], which lowers the lower heating value (LHV) of the product gas. Furthermore, traces of heavy metals in olivine are environmentally problematic, making disposal more difficult.

Olivine has been investigated by several groups, with studies being carried out on non-calcined, calcined, and doped material [3,10,22–24], and it is known that olivine needs to undergo activation to produce the catalytic effects on tar species in the raw gas. The changes in activity of olivine is commonly attributed to Fe migration in the particle, which has been shown to be a result of calcination [3], and to the CaO layer that is formed during the interaction with biomass ash [20,21,25,26]. Besides calcium, the fuel contains varying amounts of potassium (K), silicon, and sulfur (S), which may also have effects on the chemistry within the system. On the one hand, high levels of silicon and potassium have negative influences on agglomeration in the system [11,12] and S disrupts catalysis downstream of the gasification process [27]. On the other hand, the presence of potassium increases carbon conversion, as demonstrated by several groups and in different process set-ups [28–31].

In the Chalmers 2–4-MW_{th} dual fluidized bed gasification system, in which silica sand is usually applied as the bed material, the process has been thoroughly evaluated and reported upon [6]. Olivine has been tested on two occasions in consecutive years in the Chalmers unit under comparable operational conditions. The materials used differed in terms of particle size, although they originated from the same mine. The first test lasted only 3 days and was terminated due to operational issues. Therefore, it was repeated in the following year using material with a slightly smaller particle size. Nevertheless, the results from the first run will be used here for comparison, to assess the repeatability of the activation process of olivine in the Chalmers boiler.

In the present work, non-calcined olivine was investigated over the course of 9 days in the Chalmers unit. The focus was on the activation of the material and the consequences for the performance of the gasifier in terms of gas composition, tar load, and efficiency. In this context, the roles of inorganics in the gasification process were investigated through analyses of the physicochemical changes of the interactions between bed material and ash elements. Furthermore, thermodynamic modeling was performed based on the analyses of bed material samples, to predict the behaviors of certain ash components.

2. Experimental setup

The Chalmers boiler and gasifier system (Fig. 1) has been used as the experimental unit in the present work. The boiler is a 12-MW_{th} circulating fluidized bed boiler that provides heat to the Chalmers campus. The gasifier is a 2–4-MW_{th} bubbling fluidized bed coupled to the boiler *via* two loop seals. Detailed description of the system can be found elsewhere [6]. The letters A–D in Fig. 1 represent the locations at which the bed material is sampled in the system. In the present study, the focus was on the collection of samples from Loop Seal 1 (LS1; point B) and Loop Seal 2 (LS2; point C), corresponding to the sites at which the bed material enters and exits the gasifier, respectively.

The heat that is needed for the gasification reaction is provided by the hot bed material that circulates from the boiler to the gasifier. In order to match the normal output of the boiler, fuel is added to both the boiler and the gasifier. Wood chips are used as fuel in the boiler and wood pellets are used as fuel in the gasifier. The results of the analyses of the wood chips and the pellets used in the experiment are given in Table 1. The gas that is produced in the gasifier is fed to the boiler and combusted therein.

The olivine that was used in the present work was delivered by SIBELCO Nordic AB from a pit in Norway and it had a particle diameter that ranged from 180 μm to 355 μm. The chemical composition of the olivine is listed in Table 2. During this series of experiments, the Chalmers system contained approximately 4 metric tons of the material.

Throughout the experiments, the gas composition was monitored online and the results are presented as average values over a period of stable operation. In addition, tar samples were taken at each operational point and the bed material samples were collected from two points in the system. The gas was sampled from a slipstream that is led from the raw gas line. From the same line tar samples were taken for the analysis. In the Fig. 1 sampling point is indicated with red X sign. The composition of the raw gas was measured online using a Varian CP4900 micro-Gas Chromatograph (microGC). Sampling of tar species in the raw gas produced in Chalmers gasifying unit was achieved by solid phase absorption (SPA). In order to capture all the fractions, including benzene, for sampling, amines with an active carbon layer were used. For each operational point a set of 6 amines was taken. Further analyses of the eluted samples were performed in a Gas Chromatograph equipped with Flame Ionization Detection (GC–FID) and average result is used for the presentation of the results. Detailed procedures for the sampling and analyses can be found elsewhere [32]. To structure and present the results of the tar analyses, different approaches are commonly used [33–35]. In the present work, the results are presented according to the following groups: benzene; 1-ring components; naphthalene; 2-ring components; 3-ring and higher components; and phenolic aromatics. In order to be able to relate the composition of the produced gas to the fuel conversion and to avoid wrong conclusions that can be caused by an dilution effect of the product gas, all results were calculated to yields and expressed as $mol/kg_{dry\ ash\ free\ fuel}$ for permanent gases and $g/kg_{dry\ ash\ free\ fuel}$ for tar species. For calculation of the flows, a known amount of helium was used as a tracer gas.

The collected bed materials were analyzed to follow changes in the elemental composition (ALS Scandinavia AB, Luleå, Sweden). Solid samples were first dissolved in $LiBO_2$ according to standardized method. The elemental analysis was then performed using Inductively Coupled Plasma Sector Field Mass Spectrometry