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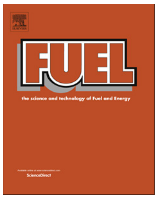

Effect of pressure on tar decomposition activity of different bed materials in biomass gasification conditions

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HIGHLIGHTS

- The tested bed materials were sand, dolomite, MgO, olivine and olivine/kaolin.
- Dolomite and MgO had the highest tar decomposing activities.
- The catalytic activities of dolomite and MgO reduced with increasing pressure.
- Pure olivine was inactive and behaved similarly to sand in laboratory-scale tests.

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ABSTRACT

The objective of this study was to compare the tar decomposing activity of different bed materials and to investigate the effect of pressure on their activity at pressures up to 10 bar. Gasification experiments were first conducted in an atmospheric pressure bubbling fluidised-bed gasifier, while the influence of pressure was studied in a laboratory-scale fixed-bed reactor with simulated gasification gas. The tested bed materials were sand, dolomite, MgO, olivine A and a 50/50 wt.% mixture of olivine B and kaolin. At atmospheric pressure both in gasification and laboratory-scale experiments, dolomite and MgO were the most active bed materials. In air/steam-blown fluidised-bed gasification conditions, all the studied bed materials were capable of reducing the tar content in reference to the base case sand; the reductions amounted to 87%, 83% and 54% with dolomite, MgO and olivine B/kaolin mixture, respectively. Increasing pressure decreased the tar decomposing activities of dolomite and MgO. On the other hand, higher pressure enhanced thermal tar decomposition reactions over sand and olivine A. In pressurised conditions at 5 bar, the carbonate and oxide forms of dolomite (calcium either as $CaCO_3$ or CaO) had similar activities implying that the observed loss in activity at higher pressures was more attributed to the pressure rather than the calcination.

1. Introduction

Gasification of biomass converts solid biomass to gas containing mainly syngas compounds, CO and H_2, but also impurities, such as tar compounds. Tars have been identified as the main challenge in biomass-based gasification processes causing blocking and fouling of downstream units. One possibility to cut down the tar content in biomass-derived gasification gas is to use catalytically active bed materials already in the gasifier. Lower tar concentration in the gas at gasifier outlet facilitates the further clean-up and end-use of the gas, for example by preventing blinding of the hot gas filter or inhibiting coke formation in the reformer. In-situ tar control in the gasifier with catalytic bed materials is often combined with secondary tar removal methods, such as catalytic reforming or scrubbing, to ensure an effective tar reduction for applications that are less tolerant to tars.

Different catalysts to be incorporated in a fluidised-bed gasifier for tar decomposition have been extensively screened by a number of researchers, and the main findings have been summarised in reviews provided by e.g. Abu El-Rub et al. [1], Sutton et al. [2], Dayton [3] and Shen and Yoshikawa [4]. Low cost natural minerals, which include e.g. dolomite, limestone, magnesite and olivine, are typically employed as bed materials – either alone or mixed with

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Abbreviations: CFB, circulating fluidised-bed; FID, flame ionization detector; FT, Fischer–Tropsch; FTIR, Fourier transformation infrared spectrometer; GC, gas chromatograph; GC–MS, gas chromatograph–mass spectrometry; TC, thermal conductivity.

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sand. Among these, dolomite ($CaCO_3{\cdot}MgCO_3$) is favoured because of its high efficiency in tar removal, which has been demonstrated both in gasifier conditions, in a secondary reactor and in laboratory-scale studies with tar model compounds, as outlined in [1–4]. The disadvantage of dolomite is related to its fragile nature due to which it is easily elutriated from the gasifier bed [5]. This in turn leads to higher consumption of make-up bed material and increased costs. However, attrition problem does not prevent using dolomite even in commercial scale gasifier in Skive, Denmark [6]. Another drawback associated with dolomite is that it has been reported to be catalytically active only in calcined form [7], which has been suggested to limit its use to relatively low pressures (close to atmospheric) in biomass gasification processes [3,8]. Under typical conditions prevailing in a fluidised-bed gasifier at atmospheric pressure, at ca. 800–900 °C, both $CaCO_3$ and $MgCO_3$ are calcined into their oxide forms (CaO and MgO) releasing the CO_2 [9]. When the pressure is raised, the partial pressure of CO_2 increases and when it exceeds the calcium calcination/carbonation equilibrium, calcium is converted to carbonate while magnesium still usually occurs as oxide. Simell et al. [7] found that in pressurised conditions, the catalytic tar reforming activity of dolomite is almost completely lost when the calcium is carbonated. Only in the so-called transition region, where the CO_2 partial pressure was close to the calcination/carbonation equilibrium, were the calcium-based bed materials (including dolomite) still found to exhibit some catalytic activity over the inert reference SiC.

In order to maintain the oxide state of dolomite in pressurised conditions, the gasification temperature should be increased which, in practice, is often restricted by ash melting and bed sintering which start to occur at elevated temperatures [8]. In pressurised process development-scale gasification experiments with a CFB gasifier in steam/oxygen-blown mode [8], dolomite was found to be a suitable catalytic bed material when operated at pressures up to 4 bar. Above 4 bar, bed sintering and agglomerate formation were encountered with sand/dolomite mixtures, and they had to be replaced by MgO or MgO/dolomite mixtures. The addition of MgO in the gasifier bed inhibited ash-related issues, and stable operation was achieved even at pressures above 4 bar.

One bed material option, which has been gaining more attention, is olivine. Olivine is a silicate mineral containing magnesium and iron: $(Mg,Fe)_2SiO_4$. It is employed as a bed material, for example, in the demonstration-scale CHP plant in Güssing, Austria, which is based on steam gasification of woody biomass [10]. The clear advantage of olivine compared to dolomite is its high resistance to attrition, which is comparable to that of sand [11]. However, its activity is generally somewhat lower than that of dolomite [5,11–15]. The tar decomposing activity of olivine is related to its MgO and Fe_2O_3 contents [4] and to the coating effect of the olivine particles in fluidised-bed gasification conditions [16,17]. Kirnbauer et al. [16,17] discovered that when olivine was used as a bed material in a dual fluidised-bed gasifier in steam gasification conditions, a calcium-rich layer was formed on top of the olivine particles as they interacted with biomass ash components and possible other additives, such as dolomite. This coating enhanced tar conversion and resulted in an 80% reduction in tars (detected by GC–MS) compared to unused olivine. The formation of coating layer has been explained in detail in [18]. Calcination of olivine may improve its activity. Devi et al. [19,20] discovered that when olivine was calcined at 900 °C in air, its activity towards naphthalene conversion improved. This was suggested to originate from the segregation of iron to the surface of the olivine particles and also from the iron(III) phases formed during calcination. However, high calcination temperature 1500 °C may decrease the porosity and the activity [5].

The catalytic nature of different bed materials at atmospheric pressure has been well covered in earlier studies, but their activity in pressurised gasification conditions is not well known. Systematic comparison of bed material activities in pressurised conditions is lacking, although some publications feature studies performed with one single bed material at a few pressure levels, for example with olivine [21,22]. Pressurised gasification becomes relevant in process concepts where the final steps of the process chain operate at high pressures, such as the FT-synthesis for producing FT-liquids. In those cases, the costs caused by the final compression of the product gas to the synthesis pressure could be reduced by elevating the pressure in the front-end gasification process i.e. in gasification and gas cleaning. As an example, the cost saving potential for a methanol production process based on oxygen/steam-blown gasification of biomass was estimated at around 3–4% reduction in the methanol production costs when the gasification pressure was elevated from 1 bar to 5 bar [23]. Thus, it is of great interest to consider the bed material activities also at higher pressures and to study whether they pose technical challenges to the gasification process operating in pressurised conditions.

In this work, the effect of pressure on the tar decomposition activity of different bed materials was evaluated in biomass gasification conditions. Experiments were divided into two parts. The studies were initiated by bench-scale fluidised-bed gasification experiments at atmospheric pressure with bark pellets as feedstock. After that, laboratory-scale tests using a fixed-bed reactor were carried out with simulated gasification gas in the pressure range of 1–10 bar. A gas composition resembling that obtained in the gasification tests was used as feed gas; the aim was to compare the activity of bed materials as a function of pressure in easily controllable laboratory conditions, not to compare the two reactor technologies.

2. Experimental

2.1. Fluidised-bed gasification tests at atmospheric pressure

2.1.1. Experimental conditions and test procedure

The fluidised-bed gasification tests with different bed materials were carried out in a bench-scale atmospheric pressure bubbling fluidised-bed gasifier (AFB60) with a bed and freeboard diameter of 63 mm and 102 mm, respectively. A more detailed description and a schematic diagram of the used test rig is given in [24]. The experiments were performed in air/steam gasification conditions (75/25 vol.% air/steam) where the air/steam mixture was fed as primary fluidising gas and no secondary or tertiary air was used. Bark pellets (Table 1), which were crushed and sieved to 0.5–1.0 mm particle size, were used as feedstock. Bed materials were

Table 1
Feedstock composition.

Feedstock	Bark pellets
Moisture content, wt.%	8.6
LHV, MJ/kg (dry)	19.9
Proximate analysis, wt.% (d.b.)	
Volatile matter	70.8
Fixed carbon	25.3
Ash	3.98
Ultimate analysis, wt.% (d.b.)	
C	53.2
H	5.5
N	0.3
S	0.04
O (as difference)	37.1
Ash	3.9

d.b. = dry basis

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