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CO_2 gasification of biomass: The effect of lime concentration in a fluidised bed

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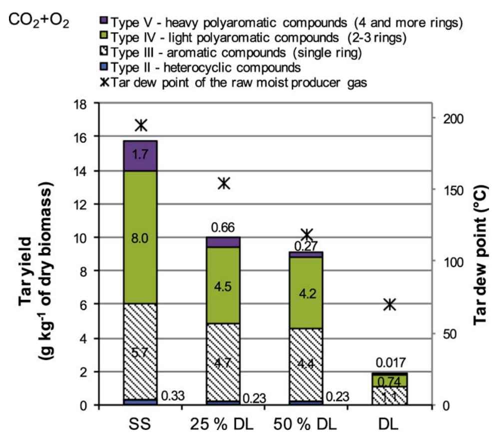
HIGHLIGHTS

- CO_2 lime-catalysed gasification was compared to H_2O lime-catalysed FB gasification.
- The effect of lime concentration in FB is less pronounced in CO_2 gasification.
- Higher concentration of lime in a fluidised bed is needed in the CO_2 atmosphere.
- More than 8-fold decrease in tar yield was achieved by using lime in the FB.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluidised bed (FB) technology can be advantageously used for the gasification of solid fuels. Calcined carbonate materials, such as limestone or dolomite, can be used directly in the fluidised bed of the gasification reactor to reform tars in situ and to enhance carbon conversion and cold gas efficiency of the gasification process. However, they exhibit poorer mechanical stability, they tend to be attrited and carried over from the reactor, and their catalytic activity decreases over time. Therefore, a portion of the material has to be replenished continuously or periodically. To decrease the amount of carbonate material that has to be replenished, a lower amount of lime (calcined limestone or dolomite) can be used in the FB, diluted by a mechanically robust material, such as silica sand or olivine. According to the literature, even concentrations in the order of 10–35% wt. of carbonate material in the FB of silica sand have a substantial effect on the decomposition of tars during steam or air gasification. However, the effect of the concentration of lime in the FB has not yet been described for CO_2 gasification. In this paper, we focus on the effect of the ratio of calcined dolomitic limestone and silica sand in the FB (0%, 25%, 50% and 100% vol. of dolomitic limestone) for $CO_2 + O_2$ gasification of biomass and compare it with $H_2O + O_2$ gasification at the temperature of 850 °C. The experiments were performed in a semi-autothermal spouting FB reactor, gasifying 1.4 kg h^{-1} of woody biomass. The effects of the concentration of dolomitic lime in the fluidised bed differed for $H_2O + O_2$ and $CO_2 + O_2$ gasification. When gasifying with $H_2O + O_2$, optimal results were found with 50% vol. (35% wt.) lime in the FB, when the yield of tar was similar to the use of

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pure lime in the FB. When gasifying with CO_2+O_2, a substantial decrease in tar yield was observed when using 50% vol. (35% wt.) lime in the FB (compared to the use of pure silica sand); nevertheless, the use of undiluted lime in the FB remains the best option to attain minimal tar yield when gasifying with a CO_2+O_2 gasifying agent. In this case, the tar yield was decreased 8.7-fold, and the tar dew point was decreased by 124 °C (to 71 °C) compared to the non-catalysed case with silica sand being the fluidised bed of the gasifier.

1. Introduction

Several measures to reduce CO_2 emissions have to be applied concurrently to meet the goals set by the Paris Agreement to limit global warming to well below 2 °C above pre-industrial levels by 2100 [1,2]. Both CO_2 capture and storage (CCS) technologies [3,4] and renewable sources of energy can play a significant role in this effort. [5] One possible option that could contribute to CO_2 emissions reduction is the generation of useful products from the captured CO_2 to effectively close the carbon loop [6], although this CO_2 capture and utilisation (CCU) strategy has its efficacy limitations when compared to CCS [7]. Biomass gasification employing CO_2 as a gasifying agent can potentially serve as a first step in the conversion of captured CO_2 to synthetic fuels [8] via generating a syngas rich in CO that is further processed to synthetic fuels. The efficiency of this concept can be potentially improved by the additional use of hydrogen produced from the off-peak renewable electricity [9]. Because of the above-stated reasons, the use of CO_2 as gasifying agent for biomass gasification has received increased attention [10–20] recently.

To enhance the reactivity of CO_2, increase the conversion of fuel-carbon into gas and to reform tars during fluidised-bed gasification [21], a catalyst can be used directly in the gasifier. Carbonate materials are described as acting as catalysts for solid fuel gasification and towards tar reforming. [22–24] They are generally used as calcines because, in the carbonated form, their catalytic activity towards tar reforming is reported to be substantially lower [25] or even entirely lost [26]. In calcines (mostly CaO or MgO), the basic active sites are the O^{2-} ions, with the most active sites being located at the defects of the polycrystalline solid (corners, edges, terraces), for which each anion is coordinated with only three or four metallic cations [27,28]. The equilibrium of (endothermic) decomposition of $CaCO_3$ and $MgCO_3$ to CaO or MgO depends on the temperature and partial pressure of CO_2 in the reactor. During atmospheric gasification, the partial pressure of CO_2 usually is lower than 0.4 bar. The corresponding equilibrium temperature for 0.4 bar CO_2 partial pressure is 670 °C for pure $MgCO_3$ and 840 °C for pure $CaCO_3$ [29,30]. In the presence of impurities [31–33], as well as for reducing conditions [34–39], the corresponding decomposition temperatures of the carbonates, particularly of $CaCO_3$, can be lower.

Carbonate materials can be used in the FB alone or diluted by an inert material, for example, silica sand. The dilution of the carbonate material in the FB can be advantageous for *(i)* reducing the amount of fines produced by attrition and carried over from the reactor and *(ii)* taking advantage of the better mechanical properties of silica sand in the FB [40]. It is also possible that the two materials synergistically combine during long-term operation, to form mechanically robust particles with a Ca-rich catalytic coating layer, as reported by Kuba et al. [41–44], for ash enhancement of quartz or olivine during long-term operation of the dual FB gasifier.

Some publications describe the use of mixtures of dolomites or limestones with silica sand in the FB for gasification with air or steam $+O_2$ mixture as gasifying agents. Narváez et al. [45] introduced pre-calcined dolomite to the fluidised bed by feeding it with biomass (1–5% wt. of the fuel feed) during gasification at 800 °C with air. The tar content in the exit gas in this experiment was lowered by 40%, to 4.0 g m_n^{-3}, compared to the case without dolomite. Olivares et al. [46]

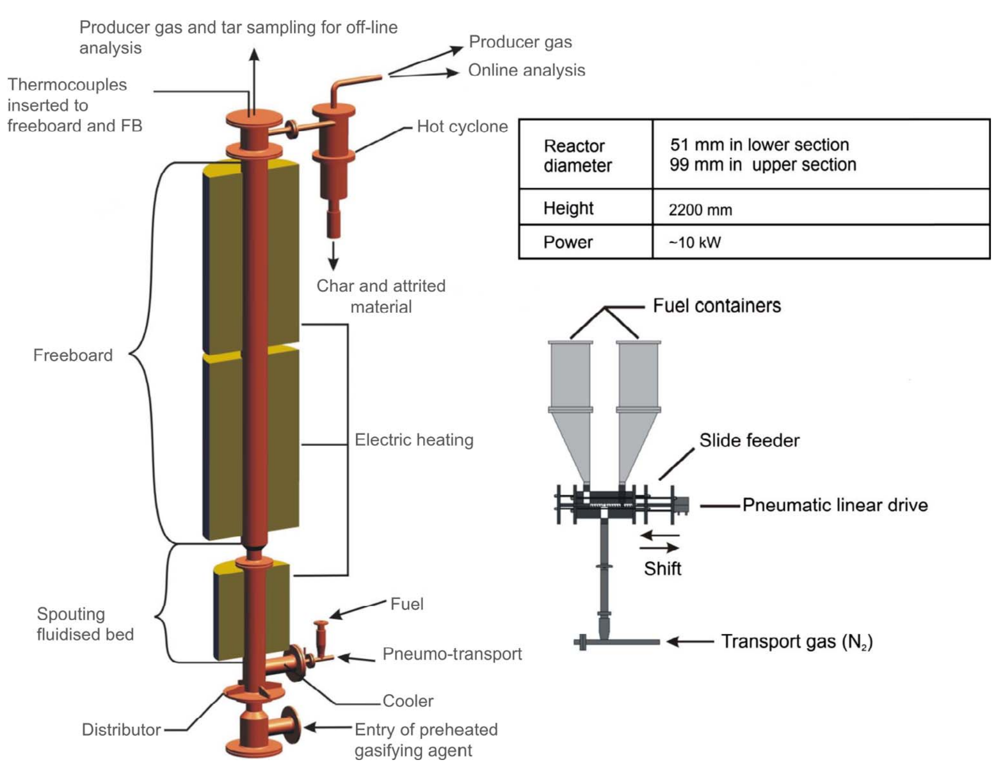

Fig. 1. Experimental facility – spouting FB reactor (reprinted from [52]).