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Use of alkali-feldspar as bed material for upgrading a biomass-derived producer gas from a gasifier

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HIGHLIGHTS

- The alkali-feldspar showed high potential for WGS even at low temperature.
- No reduction of the methane content in the cleaned gas.
- The elimination of most of the C_2H_2 and C_3H_6 already at 800 °C.
- Tar selectivity: exclusively pure ring-compounds in the reformed gas.
- Fresh olivine was less efficient than feldspar in reducing tars.

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ABSTRACT

Gasification of biomass has strong potential for biofuels production. However, one challenge to its competitiveness is the efficient elimination of the tars present in the raw gas. The use of active bed materials in tar reforming is an appealing approach and can be employed as part of primary and/or secondary measures. Here, the activity of an alkali-feldspar [(K, Na)$AlSi_3O_8$] ore was assessed in relation to upgrading the producer gas from the Chalmers 2–4 MW indirect biomass gasifier. This material was tested in a single bubbling bed reactor previously developed for studies involving catalytic tar reforming. The bed of feldspar was fluidized with raw gas. The material was tested at three temperatures: 700 °C, 800 °C, and 900 °C. The results indicate that alkali-feldspar shows: (1) a high potential for the Water–Gas Shift reaction even at low temperature ($H_2/CO \sim 3$); (2) no reduction of the methane content in the cleaned gas and net formation of methane at 900 °C; (3) the elimination of most C_2H_2 and C_3H_6 already at 800 °C; and (4) a striking tar selectivity, which resulted in the reformed gas having exclusively pure ring-compounds. In the same reactor set-up at 800 °C, fresh olivine was comparatively less efficient than feldspar in reducing tar levels. At 900 °C, the feldspar decomposed 47% excepting benzene. Moreover, it retained its mechanical integrity, withstood longer reducing periods (3 h), and displayed neither signs of agglomeration nor loss of activity, despite the formation of a carbon deposit. The deposits were readily removed by introducing an oxidizing atmosphere. Furthermore, the raw feldspar showed a low capacity for oxygen transport, advantageous in this application. Taken together, our results indicate that this material is clearly promising and warrants further investigations.

1. Introduction

The thermochemical transformation of biomass *via* gasification results in the formation of a so-called ‘producer gas’ or raw gas that can be used subsequently to synthesize a variety of biofuels and value-added chemicals and/or for the polygeneration of combined heat and power (CHP) [1–9]. The use of biomass in such applications is attracting increasing interest as a means for reducing the demand for fossil fuels and paving the way towards a more sustainable society. The gasification products include permanent gas components, such as H_2, CO, CO_2, CH_4, and light hydrocarbons, as well as undesirable condensable hydrocarbons (tars), which are formed during the primary step of biomass conversion. While the definition of a tar varies slightly between different studies, in this work, a tar is defined as an aromatic hydrocarbon with a molecular mass greater than that of benzene [10–13]. These molecules have a high dew-point, and the larger tars, e.g., pyrene, start to condensate already at 400 °C. Thus, they are often prone to deposit on cooler surfaces e.g. on gas ducts/piping or

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Nomenclature

BB	bubbling bed
CFB	circulating fluidized bed
CHP	combined heat and power
CLC	chemical-looping combustion
CLR	chemical-looping reforming
DAF	dry ash-free (fuel)
FCC	fluid catalytic cracking
GC	gas chromatograph
IR	infrared
PSD	particle size distribution
SEM	scanning electron microscopy
SNG	substitute natural gas
SPA	solid-phase adsorption
SPE	solid-phase extraction
WGS	Water–Gas Shift (equilibrium)

heat exchanger surfaces leading to fouling or precluding the instruments efficiency. If reaching the downstream fuel synthesis equipment, these can even contribute to deactivate catalysts.

There are two principal approaches to treating the raw gas generated by gasification: hot gas cleaning; and wet cleaning with solvents. Hot gas methods include thermal cracking at high temperatures (>1100 °C) and catalytic tar destruction using catalyst particles at moderate to high temperatures (700–900 °C). The latter can be implemented in the gasifier bed as a primary measure and/or in downstream reactors as secondary measures, most often in a fixed-bed manner [14–16]. Since tars can contain up to 10% of the total energy value of the fed biomass, their elimination should ideally involve recovery of some of the energy to the raw gas, so as to promote the efficiency of the resulting cold gas [17,18]. In this context, catalytic gas conditioning is a particularly interesting alternative, as the heavy hydrocarbons are degraded into smaller and more-desirable molecules, often having higher energy contents, while the temperatures required for the reactions enable thermal integration with the gasification step. Moreover, the process does not create an additional waste stream of costly solvent, as is the case with scrubbing techniques. The reactions involved also often permit an adjustment of the cleaned gas composition, which in turn facilitates the downstream gas treatment and/or fuel synthesis steps.

An application of catalytic gas cleaning that is currently attracting attention is a concept that exploits the advantages of the circulating fluidized bed (CFB) principle, referred to as chemical-looping reforming (CLR). The process originated from the petrochemical industry and was based on the development of fluid catalytic cracking (FCC) to convert high-molecular-weight hydrocarbons in oil refineries [19]. The idea was reintroduced by Mattisson et al. [20,21] for hydrogen production in the context of CO_2 capture and climate change mitigation. The principle involves a dual-fluidized bed configuration in which catalytic hydrocarbon reforming is achieved in one vessel and the deactivated catalyst is subsequently regenerated in another vessel. Regeneration involves the removal of principally carbon deposits formed during hydrocarbon reforming, as well as other impurities (e.g., sulfur) carried over by the particles to the regenerator [10]. In previous related research conducted at Chalmers University of Technology with laboratory-scale reactors, a dual fluidized bed reactor with a reformer and a regenerator was convincingly applied to the upgrading of a biomass-derived producer gas, with the emphasis being placed on tar destruction [22–27]. This technique can be deployed as a secondary gas cleaning measure or can be introduced as a primary measure in existing processes, whereby the catalyst will undergo cyclical exposure to raw gas and to a regenerating agent, e.g., air or oxygen-depleted air. This is, for instance, the case with indirect gasification using a gasifier-boiler loop [3,8,28].

2. Theory

In fluidized bed gasification, the main focus of studies to enhance the conversion of tars has been the use of metal oxide catalysts. In practical terms, these catalysts can be used either in a primary or in a secondary measure. For instance, oxides of iron, aluminum, nickel, manganese, and magnesium have been proven to be efficient for tar degradation [10,16,22,25,29–36]. In particular, the iron-magnesium silicate olivine has been successfully employed in indirect gasifiers [9,36,37]. Furthermore, in a recently submitted paper, Marinkovic and colleagues used bauxite – an aluminum ore – in the Chalmers indirect gasifier and showed a clear effect on tar reduction [35]. Despite having proven catalytic activity, such materials contain sufficient concentrations of metal (a major contributor to the catalytic effect) to enable the carry-over of oxygen from the oxidizing vessel to the reducing vessel, wherein fractions of the valuable gases are inevitably burned off. For example, despite its positive catalytic efficiency, olivine can transport oxygen. Koppatz et al. showed that the olivine used in their work had an oxygen transport capacity of 2.2%, resulting in a lower heating value for the producer gas [37]. Other groups have obtained values one order of magnitude lower; for example, an olivine material used in the Chalmers gasifier resulted in an oxygen transport capacity of around 0.15% [36]. Studies conducted with the iron titanium oxide ilmenite have reported that although the tar levels are reduced, a considerable part of the gas is combusted in the gasifier. For activated ilmenite, the oxygen transport capacity varies slightly with the activation procedure; for instance a value of 2.1% is stated in [38]. Larsson et al. reported a decrease in the heating value of the gas from 17 MJ/m^3 to 12.5 MJ/m^3 using only 12% ilmenite in an inventory of silica sand, as compared to using silica sand alone [17]. One can conclude that this drawback related to a lower heating value of the gas through oxygen transport is to some extent counterbalanced by the increase of heating value associated with the catalytic reforming of hydrocarbons. One way to address the oxygen transport problem would be to reduce the catalyst before it comes in contact with the reforming gases. An alternative strategy would be to find a substitute material that has negligible oxygen carrier capacity but that still displays an active phase for tar elimination.

Finally, it has been shown that the effects of the natural constituents of the bed materials described above are augmented by the introduction along with the bed material of low-cost substances, such as alkali salts [39,40]. Alkali salts should be added in a controlled and well-defined manner, as they are associated with corrosion of the heat exchanger tubing and bed agglomeration [41,42]. For both olivine and bauxite, the uptake and release of alkali through interactions of the bed material with the biomass ash have been shown to have significant impacts on the observed gas upgrading performance [35,36].