Full Length Article

Bed material as a catalyst for char gasification: The case of ash-coated olivine activated by K and S addition

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GRAPHICAL ABSTRACT
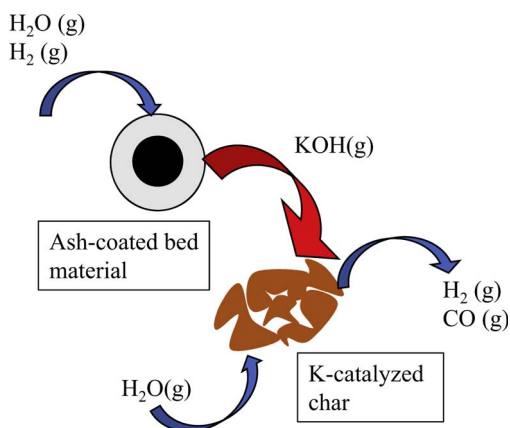
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ABSTRACT

In this paper, the ability of an ash-coated olivine to catalyze the steam gasification of biomass-derived char is investigated in a laboratory reactor. The olivine investigated is a sample from the Chalmers dual fluidized bed gasifier and it has been activated by the in-bed addition of S and K_2CO_3. The char and bed material samples were analyzed by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS). It is shown that the ash layer coating of the olivine can catalyze the steam gasification of char by transferring catalytic potassium (K) to the char particles. The mobilities of the catalytic species from the olivine ash-layer are discussed. This work furthers the current understanding of the catalytic activities of ash-coated bed material particles during the thermochemical conversion of carbonaceous feedstocks in fluidized beds. In addition, it complements the existing literature on catalytic bed materials, which to date have focused on tar removal and improving gas quality.

1. Introduction

The steam gasification of char is a chemical reaction that is relevant for a number of thermochemical processes, such as gasification and chemical looping combustion (CLC). The reactivity of char towards steam depends on its morphological structure, as well as on its content

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of catalytic inorganic matter [1]. The artificial addition of catalytic inorganic matter to carbonaceous feedstocks has been widely investigated as a strategy for accelerating the relatively slow kinetics of the gasification reaction. In this context, various catalysts, ranging from transition metals (e.g. Fe, Ni, Co, Cu) to Alkali and Alkaline Earth Metals (AAEM), have been investigated [2]. Wet impregnation and mechanical mixing of the char and catalyst are the most commonly used contact methods [1].

In fluidized bed gasifiers, the catalyst is usually introduced in the form of a bed material rather than being premixed with the fuel; the main goal being to improve the gas quality by, for example, reducing the amount of tar. Accordingly, there is an extensive body of literature on *in situ* tar reduction [3,4], whereas the influence of the bed material on char gasification has been largely overlooked. As pointed out by Nzihou et al. [2], catalytic char gasification is usually masked by the catalytic effects of the bed materials towards tar reactions.

Investigations that have focused on the interactions between the bed material and char have shown that the gasification rate can be enhanced indirectly by the bed material. For instance, lower inhibition of the char gasification reaction by, e.g., H_2 and tar species, can be attained when the bed materials influence the concentrations of inhibiting species around the char particle [5]. In a previous study that examined the use of various bed materials in the Chalmers gasifier [6], the correlation between the concentrations of inhibiting gases and char conversion was found to be weak, leading to the suspicion that there is an additional catalytic activity of the bed material towards the char gasification reaction.

Keller et al. [7] have demonstrate the possibility for a bed material to catalyze the char gasification reaction by transferring potassium (K) from the bed material to the char particle. Their investigation was carried out in the context of CLC and used a manganese ore that was pre-soaked in K_2CO_3. After the bed material was soaked, the K was uniformly distributed over the cross-section of the manganese particles, and the bed material became a source of catalytic K for the char gasification reaction during the subsequent CLC experiment.

In the case of fluidized bed gasification, the catalytic activity of naturally occurring bed materials, such as olivine, has been attributed to an external layer that is rich in catalytic ash elements [8,9]. It is generally accepted that ash-coated olivine can effectively lower the tar content of the product gas, as well as catalyze the water–gas shift (WGS) equilibrium [6,10,11]. However, the interactions that occur between the ash-layer and the char have not been explored previously.

The aim of this work was to provide conclusive evidence that the active ash-layer in olivine can catalyze the steam gasification reaction, and that this catalysis occurs by a process similar to that described by Keller et al. [7]. For this purpose, steam gasification experiments were carried out in a laboratory reactor with untreated and ash-coated olivine, respectively. Char and bed material samples were examined to elucidate the mobility of catalytic species from the bed material to the char in a gasification environment.

2. Theoretical background

2.1. Char reactivity

In the present work, char reactivity is characterized as the overall reactivity (R_m), which is normalized to the initial mass of char, and it is defined according to Eqs. (1) and (2).

$$R_m(t) = -\frac{1}{m_o}\frac{dm_c(t)}{dt} \tag{1}$$

where m_o is the initial mass char, $m_c(t)$ is the remaining unconverted char, and $X_c(t)$ is the degree of char conversion at time t.

$$X_c(t) = \frac{m_o - m_c(t)}{m_o} \tag{2}$$

For a given fuel, the reactivity of the char is strongly influenced by the char preparation method [12–14], e.g., the heating rate [13–15], cooling step after devolatilization [16], and devolatilization temperature [15,17], as this determines the porosity [13,14] and alkali content [15,17] of the produced char. Therefore, the quantification of reactivity is here applicable only for comparisons of experimental cases. For dedicated kinetic investigations relevant to fluidized bed gasification (i.e., in-bed pyrolysis), the reader is referred to other studies [18] for different types of biomasses, and to the study of Lundberg et al. [19] for the reactivity of large wood particles.

Using a fluidized bed of non-catalytic silica sand, Lundberg and colleagues found that the reactivity (R_m) curves of centimeter-sized wood pellets peaked at a conversion rate of around 5%, which was followed by a steady decrease of the gasification rate [16]. Similar curves were observed by Ahmed and coworkers for the steam gasification of woodchips in a drop tube reactor [20]. For large char particles, the gasification rate is typically dominated by the mass transfer at the beginning of the conversion [16,19]; and the shape of the reactivity curve is influenced by the development of the reactive surface and that of the ash content, as conversion proceeds [13].

When there is artificial addition of AAEM catalysts to the char, a direct correlation between the catalyst load and the reactivity of the char is commonly observed [21–23]. For a similar catalyst load, K-catalysts have higher catalytic activity than Ca-based catalysts [23–25]. The reactivity curves (R_m) exhibit different shapes, e.g., a wide maximum [21], a maximum in the late conversion range [22], or even a sustained gasification rate [26]. Zhang et al. [24] have described the different locations of the maximum as a function of the concentration of active AAEM elements in the char. Furthermore, Lobo [26] proposed that the achievement of a steady gasification rate over wide ranges of conversion rates can be explained by the action of a stable catalytic front.

2.2. Active ash layer in olivine

Olivine is a magnesium-iron silicate material that can contains some impurities, such as Ni and Cr. In a combustion/gasification environment with ash-containing fuels, the untreated olivine particles become coated with ash-forming elements. The morphological features of an already developed layer are typically: (1) an inner layer that is homogeneous and melt-like type; followed by (2) a more heterogeneous outer layer [27]. The inner layer may comprise two zones: an innermost Ca-rich region surrounded by a Mg-rich region, which is thought to be formed as Mg ions are expelled from the olivine structure when Ca ions are incorporated into the structure [28]. The composition of the outermost layer is closer to that of the fly ash [27].

In dual fluidized bed (DFB) gasifiers, where the bed material circulates between a combustor and a steam gasifier, ash-coated olivine transports inorganic species between the reactors, by means of the ash layer. The transport of K from the combustor to the gasifier has been confirmed by Kirnbauer et al. [29], who investigated the flows of inorganic matter in the Güssing gasification plant. Apart from the transport of K, Marinkovic et al. [8] have demonstrated the transport of sulfur from the combustor to the gasifier, which in the Chalmers gasifier results in a higher concentration of H_2S in the raw gas than can possibly be ascribed to the fuel. Marinkovic et al. [8] describe that S acts as a