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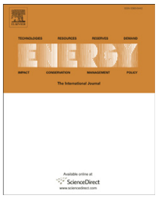

Kinetic study of catalytic gasification of wood char impregnated with different alkali salts

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ABSTRACT

Different concentrations (0.1 and 1 M K^+/Na^+) of salt solutions (K_2CO_3, Na_2CO_3, NaOH and NaCl) were used to impregnate alkali in sawdust. After devolatilization, char samples were gasified at different temperatures (750–900 °C) under CO_2 in a macro-thermogravimetric analyzer for gasification kinetics. Morphologically, three classes of chars could be identified. Chars experiencing the highest catalytic influence were in Class-2 (0.5 M K_2CO_3 and 1 M NaOH) with a swollen and molten surface. In contrast, Class-1 (wood char like) and Class-3 (with salt deposits) chars showed moderate and low catalytic effect on gasification reactivity respectively. It is believed to be related to char surface swelling and alkali salt used. At 850 °C or below, the reactivity increased linearly (Class-1 and Class-3 Char) with initial alkali content up to 2200 mmol alkali/kg of char (except for NaCl). The same reaction rate was maintained until 3600 mmol/kg of char of alkali loading (Class-2) and then decreased. However, no trend was observed at 900 °C due to drastic change in reactivity of the samples, probably due to alkali transformation. Among the salts, K_2CO_3 (0.5 M) was found to be the most suitable for catalytic gasification due to its high catalytic activity in combination with relatively low carbon leaching.

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1. Introduction

Being a renewable source of energy, biomass has the potential to transform the fossil fuel based transport sector into a sustainable one. To bring this to reality, gasification technologies coupled with Fischer–Tropsch (F-T) or, methanol synthesis can play an important role for efficient conversion of biomass. As one of the most efficient technologies for thermochemical conversion, entrained flow gasification has attracted the attention of the researchers for several years. The benefit of this technology lies in its scalability and high fuel conversion efficiency [1]. The main reason for the high conversion efficiency is its high operating temperature. However, it is desirable to operate the gasifier at a lower temperature provided the conversion remains the same. A lower gasifier temperature could potentially lead to energy savings resulting in an overall higher efficiency. To achieve high conversion at lower operating temperature, addition of metal catalysts could be a promising option. The potential of metal catalysis is evident from the effect of the inherent minerals in the biomass ash during gasification [2,3]. As cheap disposable catalysts, alkaline earth metal ores (i.e. dolomite, calcite etc.) were proposed to be used in fluidized beds for mainly tar cracking and syngas upgrading [4]. In contrast, pure salts of alkali and alkaline earth metals are known for high catalytic activity on char gasification [4–6], tar destruction and cleaner syngas generation, albeit expensive if disposed [4]. Furthermore, a number of studies [5,7,8] confirmed that alkali species (K, Na) are more catalytically active than alkaline earth species (Ca, Mg) during gasification. Particularly, it is of great importance to have high catalytic activity for fuel conversion during entrained flow gasification to compensate for the residence time. In addition, alkali species form slag at low temperatures compared with the ores and alkaline earth species [9], which allow the recovery of alkali salts at a lower temperature.

Hence, the major issues with the use of alkali catalysts for gasification remain in the selection of a suitable alkali salt for entrained flow gasification and its recovery. One proven technology for alkali catalyzed entrained flow gasification with catalyst

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recovery is black liquor gasification, which has been extensively demonstrated in pilot scale [10,11]. Black liquor, being a by-product of the pulping process, contains high concentrations of Na, present both as lignin bonded Na^+ ions and inorganic salts in a very concentrated aqueous solution. The black liquor gasification process runs at around 1000 °C with a carbon conversion efficiency of 99% and produces a tar and soot-free syngas [12]. The high carbon conversion and high quality syngas are, to a large extent, the effect of catalysis provided by the alkali present in the fuel. The inorganic material in the fuel is completely recovered in an aqueous solution using this technology, which enables catalyst recycle. However, the dependence on the pulp and paper mill makes the technology non-flexible in terms of location, and integration with an existing pulp mill is a complex task. Therefore, we would like to suggest the use of alkali catalyzed entrained flow gasification for renewable feedstock such as woody biomass as a stand-alone process. To assess the technical feasibility of such a process, the primary requirement is for alkali species to have similar catalytic activity on woody biomass.

In case of black liquor, alkali species are inherent in a homogenized liquid mixture which gives it high catalytic activity. In contrast, the forest biomass is inhomogeneous solid which needs to be impregnated with alkali species for uniform dispersion. A few studies on alkali impregnation [2,7,13,14] in wood investigated the kinetics, comparison of catalytic activity of various alkali salts and char morphology during char gasification. Perander et al. [2] observed a linear increase in reactivity with the increase in alkali impregnation per kg of biomass. Yet, no general conclusion can be drawn regarding the optimal amount of catalyst impregnation for desired reactivity and the aftermath of alkali impregnation on biomass such as energy penalty. The best available information is from catalytic gasification of coal char [15], indicating an atomic ratio of metal to carbon of 0.1 for reactivity saturation. However, this projection might not be necessarily true for biomass due to the structural difference between coal and lignocellulosic char (e.g. pore size distribution, ash composition, and size of aromatic clusters) [16]. In essence, there is a fundamental need to assess the type of alkali salts and the degree of impregnation with respect to reactivity for successful entrained flow catalytic gasification. As noted above, catalyst recovery is also an important aspect in selection of catalyst.

This study aims at assessing the type of alkali salts and the degree of impregnation as the catalyst for entrained flow gasification of biomass. Unlike other studies, we evaluated not only char gasification reactivity but also the loss of organic components during leaching. Four salts of two alkali metal elements (K and Na) at different concentrations of water solution were used for impregnation of wood particles. Then, the char gasification reactivity and kinetics were evaluated under CO_2 between 750 °C and 900 °C using a macro-thermogravimetric analyzer. The results may serve as a basis for the development of alkali catalyzed entrained flow gasification of woody biomass. The practical implications of alkali impregnation were discussed along with an attempt to find parameters to explain and quantify the gasification reactivity. .

2. Experimental

2.1. Materials

Pine sawdust in the particle size range of 355–400 μm was used for catalyst impregnation with K_2CO_3 (99.8% purity), Na_2CO_3 (99.9% purity, anhydrous) and NaOH (98% purity) from VWR Chemicals. Selective tests were also performed with NaCl (100% purity, VWR) salt. Pine sawdust was selected for its abundance in Sweden along with significantly low ash content (<0.5%) to observe the effect of impregnation. ICP-SFMS (Method SS EN ISO 17294-1, 2 and US EPA Method 200.8) and ICP-AES (Method SS EN ISO 11885 and US EPA Method 200.7) were used for the determination of metal species in biomass and char by ALS Scandinavia. Total organic carbon (TOC) in the residual solution from impregnation was determined by ALS Czech Republic following the water analysis method based on CSN EN 1484. Scanning electron microscopy was performed on the sample using FEI Magellan 400 XHR-SEM (FEI Company, USA). Ultimate analysis (CHNS) was carried out by the Mikroanalytisches Laboratorium (University of Vienna, Austria). Each analysis was conducted three times with a sample size of 0.75–3 mg in tin vials (4 × 6 mm) using Eurovector EA 3000 CHNS-O Elemental Analyzer by flash combustion® applying 25 kPa oxygen at 1000 °C.

2.2. Experimental procedure

2.2.1. Impregnation of alkali salts

Sawdust particles were impregnated with alkali salts by wet-impregnation method. To compare the impregnation efficiency of different salts, salt solutions with different levels (1 M and 0.1 M) of the molar concentration of alkali ions were prepared for K_2CO_3, Na_2CO_3 and NaOH while only one concentration (1 M) was used for NaCl. Here, 69.1 g of K_2CO_3 was dissolved in 1 L of aqueous solution to have 1 M equivalent of K^+ ions (i.e. equivalent to 0.5 M solution of K_2CO_3) available for impregnation. The biomass submerged in the solution was stirred overnight by an overhead stirrer (VELP Scientifica) at 500 rpm. To prevent forming a stagnant biomass layer at the bottom of the beaker, the ratio of solution to biomass was kept at 16 ml/g.

After the overnight impregnation at room temperature, the solid biomass was recovered by vacuum filtration. The filtrate was also sent for analysis to determine any loss of carbon from biomass. The collected biomass from the filter paper was dried overnight on a glass tray at 105 °C before devolatilization.

2.2.2. Char preparation and gasification

The experiments were conducted in a macro-thermogravimetric analyzer (macro-TGA) with continuous recording of mass loss by a precision balance (A&D INSTRUMENTS LTD. FZ-120i-EC). Around 2 g of biomass sample was devolatilized at the temperature of 600 °C for 4–5 min with the flow of CO_2 at 5 NL/min in an alumina crucible to produce char. Devolatilization was considered to be completed when the mass changes among the measurements were less than 3 mg. CO_2 was used to inhibit the breakdown of carbonate ions present in the impregnated biomass. It can be assumed that the mass loss occurred mainly due to devolatilization as gasification rate is sufficiently low at the temperature of 600 °C (also verified experimentally earlier by Kirtania et al. [17]). Before removing the char from the TGA, the sample was cooled to the room temperature with N_2 flow. However, chars from two samples (0.1 M K_2CO_3 and 0.1 M Na_2CO_3) needed to be cooled under CO_2 to avoid the self-ignition under air (See section 3.1 for more details). Then it was ground and sieved to condition the size of char particles.

A sample basket made of platinum wire mesh (220 μm mesh opening) was used to hold the samples during gasification instead of the crucible to minimize the mass diffusion effect and to avoid any alkali-ceramic reactions [17,18]. Therefore, the choice of particle size (250–300 μm) was limited by the screen size of the mesh. Gasification experiments were performed at 750, 800, 850 and 900 °C to determine the apparent gasification reactivity for comparison among different samples. All the samples were subjected to gasification by lowering the sample basket in the heated zone purged with pure CO_2. A more detail description of the

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