

Modeling of alkali metal release during biomass pyrolysis

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Abstract

The release of alkali metals during biomass pyrolysis was numerically and experimentally studied. The concentration of sodium and potassium in the gas phase above a biomass particle was measured; quantitative and time resolved data were acquired by means of the Laser-Induced Breakdown Spectroscopy (LIBS) technique. LIBS made it possible to extend the measurements of alkali metal concentration to the sooty pyrolysis stage. Data from the measurements revealed a staged release of alkali metals from biomass. Two distinct peaks of concentrations were observed, one associated with the pyrolysis stage and the other with the gasification stage. Since during the pyrolysis stage a large temperature gradient exists inside the particle, numerical simulations were carried out to explain the experimental measurements and extract the kinetic data. Using a detailed particle model, the rates of potassium and sodium release from the particle during the pyrolysis stage were attained. For sodium release the activation energy was found to be in the range of 218 to 248 kJ/mole and for potassium release it was found to be between 168 and 198 kJ/mole. Furthermore, equilibrium calculations were performed to identify the stable sodium and potassium compounds and their phases during the pyrolysis stage of the particle.

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1. Introduction

Owing to the presence of high amount of alkali metals (potassium and sodium) in some biomass sources, the release of alkali metals during biomass

pyrolysis and gasification can cause serious damage to the gasification systems. The problems can lead to reduced heat transfer, disturbance of the gas flow, physical damage to the gasifier parts, corrosion and erosion of the parts due to fouling, slagging, and agglomeration [1–5]. To prevent the damage caused by these species it is important to understand the release of alkali metals during thermochemical conversion of biomass.

Recent studies identified staged release of sodium and potassium from biomass during the

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biomass pyrolysis stage and the char gasification/combustion stage [6,7]. During these different stages, the composition of potassium and sodium compounds can be different. Potassium in biomass is mostly in the form of ionic salts [3,8] and depending on the presence of water vapor, the main form of potassium compound in gas phase can change between KOH and KCl [3]. Sodium in biomass usually exists at lower concentration compared with potassium and behaves similarly as potassium. Sodium compounds in the gas phase are mostly NaCl and NaOH [8]. Sodium can also react with sulfur to form sulfates. Cl and S can increase the mobility of sodium and potassium; however, there are studies showing that Cl and S can be released at low temperature, between 200–700 °C, while the potassium content of biomass remains intact at these temperatures [9–12]. While the main Cl compounds at low temperature are HCl and methyl chloride (CH₃Cl) [10,13], at temperatures higher than 700 °C, Cl will be released mainly in the form of alkali metal chlorine [14]. Higher release of sodium compared with potassium has been reported at low temperature pyrolysis [15]. The higher release of sodium at temperature below 700 °C can be associated with the sublimation of NaCl, while the sublimation of KCl will occur at temperatures higher than 700 °C [15]. Part of the potassium release during pyrolysis can be redeposited as discrete particles of KCl and K₂CO₃ bounded to the organic matrix of biomass. Later in the process at higher temperatures, the initial release of potassium to the gas phase is due to the sublimation of these discrete KCl particles [11]. By increasing the temperature, it was shown that the release of K will increase [16,17].

The above mentioned studies show that there is a strong dependency of the amount and the composition of alkali metals compounds on temperature, gas composition and the stage of biomass conversion. Despite these efforts, quantitative and time resolved data on the gas phase concentrations and release kinetics of alkali metals during biomass pyrolysis is rare. The focus of this paper is on the release of sodium and potassium during the pyrolysis stage of biomass at different temperatures. To this end, a joined experimental and numerical study was performed. Experimental data was attained by placing a biomass particle in the hot flue gas of a methane flame and Laser-Induced Breakdown Spectroscopy (LIBS) was employed to measure the time-resolved concentration of potassium and sodium at the boundary of the particle at different temperatures and gas compositions. The LIBS method has the advantage of providing in-situ and time resolved data during the sooty pyrolysis stage, while other techniques may fail due to the laser scattering in this condition. Previous studies on the release of sodium from a coal particle with

Table 1

Temperature profile along radius of the burner exit plane for various test cases.

ϕ	Temperature profile along radius [K]			Label
	$r = 0$	$r = 20$ mm	$r = 33$ mm	
0.9	1596	1515	577	F1
	1483	1272	562	F2
	1408	1100	567	F3
1.2	1518	1491	718	F4

planar laser-induced fluorescence (PLIF) [7,18] was limited to the combustion and gasification stage due to the high level of laser scattering during the pyrolysis stage. A recent study on release of potassium from a pine wood particle by LIBS technique has also shown the capability of the technique for quantitative measurement of alkali metal release [19]. The experimental data is used in a detailed numerical model of the particle to estimate the chemical kinetics of alkali metals release. Furthermore, the kinetic data was supplemented by equilibrium calculations to study the stable species in the gas phase under the experimental conditions.

2. Experimental measurements

The LIBS technique was adopted to measure quantitatively the concentration of alkali metals during thermochemical conversion of biomass. LIBS provides high temperature plasma using a high energetic laser pulse. The existing species in the focus point of the laser are dissociated to atoms and the excited atoms deliver a spectral signature that can be detected by a spectrometer and can be calibrated to provide quantitative data of the element concentration. By employing the LIBS technique, temporal release of potassium and sodium was measured in the flue gas of methane combustion with different concentrations of O₂, diluted by carbon dioxide, at four different temperatures. The hot flue gas was provided from a laminar multi-jet burner flame.

The particle samples were cylindrical pellets from Swedish wood with a diameter of 8 mm and height of 4 mm. The ultimate analysis of the samples shows 50.6% C, 6.6% H and 42.8% O on dry ash free basis. The mass fractions of sodium and potassium in the dry particle are 0.03% and 0.05%, respectively. The details of the experimental set-up and the measurement technique can be found in Ref. [6]. The experimental conditions are presented in Table 1. Two equivalence ratios, ϕ , and four different temperatures are studied. Temperatures at the exit plane of the burner at three locations, center, middle and outer limit, are presented in the table. An example of the raw experimental data of potassium concentration for two cases, F1 and F4,

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