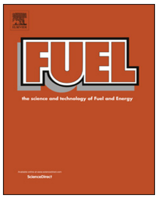
Fuel 225 (2018) 89–94

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

Potassium and soot interaction in fast biomass pyrolysis at high temperatures

Anna Trubetskaya[a,*], Flemming Hofmann Larsen[b], Andrey Shchukarev[c], Kenny Ståhl[d], Kentaro Umeki[e]

[a] *Thermochemical Energy Conversion Laboratory, Umeå University, 90187 Umeå, Sweden*
[b] *Department of Food Science, University of Copenhagen, Rolighedsvej 26, 1958 Copenhagen, Denmark*
[c] *Department of Chemistry, Umeå University, 90187 Umeå, Sweden*
[d] *Department of Chemistry, Technical University of Denmark, Kemitorvet B206, 2800 Kongens Lyngby, Denmark*
[e] *Energy Science Division, Luleå University of Technology, 97187 Luleå, Sweden*

ARTICLE INFO

Keyword:
Soot
Potassium
Biomass
Fast pyrolysis
CO_2 reactivity

ABSTRACT

This study aims to investigate the interaction between potassium and carbonaceous matrix of soot produced from wood and herbaceous biomass pyrolysis at high heating rates at 1250°C in a drop tube reactor. The influence of soot carbon chemistry and potassium content in the original biomass on the CO_2 reactivity was studied by thermogravimetric analysis. The XPS results showed that potassium incorporation with oxygen-containing surface groups in the soot matrix did not occur during high temperature pyrolysis. The potassium was mostly found as water-soluble salts such as KCl, KOH, $KHCO_3$ and K_2CO_3 in herbaceous biomass soot. The low ash-containing pinewood soot was less reactive than the potassium rich herbaceous biomass soot, indicating a dominating role of potassium on the soot reactivity. However, the catalytic effect of potassium on the reactivity remained the same after a certain potassium amount was incorporated in the soot matrix during pyrolysis. Raman spectroscopy results showed that the carbon chemistry of biomass soot also affected the CO_2 reactivity. The less reactive pinewood soot was more graphitic than herbaceous biomass soot samples with the disordered carbon structure.

1. Introduction

Entrained flow gasification (EFG) is a promising technology, which generates high quality syngas and small amounts of tars due to the high operating temperatures. However, the high soot yields lead to intensive gas cleaning and can cause a possible plant shut down. The reduction of soot formation increases the overall production system efficiency and improves the economic feasibility and reliability of the gasification plant. Moreover, the alkali metals released from high ash-containing lignocellulosic materials may form molten ash material, and thus, lead to deposition of slag upon the reactor wall [1,2]. Continuous extraction of the ash slag from the reactor is required to prevent outlet blockages and to ensure steady syngas production.

The released alkali metal ions in the biomass pyrolysis participate in soot formation and conversion reactions. It is known that alkali metal ions enhance CO_2 reactivity of graphite and carbon black [3] and suppress soot formation [4]. The alkali metal ions can form a fly ash or be bonded to oxygen-containing surface groups in the soot matrix [5,6]. The fly ash particles contain K_2S, KOH and K_2CO_3 [6]. The interaction of K_2CO_3 with the low ash-containing coal was investigated under CO_2 gasification condition in a thermogravimetric analyzer by Kopyscinski et al. [7]. The pyrolysis results showed that CO was released from K_2CO_3, which was bound to a carbon surface. In the next step, the oxygen from the carbonate reacts further with the surface carbon and forms CO which leaves the reduced potassium complex of an unknown stoichiometry. In the last step, the transfer of the potassium cluster occurs. During fast pyrolysis, the elemental potassium is unlikely to be released in gas phase at low temperatures. However, little is known about the interaction between the carbonaceous matrix of soot and alkali. In catalytic gasification, the concentration of intercalated species is small, and it decreases with increasing temperature [8,9]. The elemental potassium, bonded to the soot matrix in phenolate groups remained inaccessible for the gaseous reactants, leading to the low catalytic activity [10]. The potassium-carbon complexes form series of stable and metastable phases with different physicochemical properties [11–14]. The K-C_{60} complex was investigated using ^{13}C and ^{39}K solid state NMR [15]. According to the ^{13}C NMR spectra of intercalated graphite (K_1C_{60}) it exists as a single phase characterized by a resonance

---

[*] Corresponding author.
E-mail address: anna.trubetskaya@umu.se (A. Trubetskaya).

https://doi.org/10.1016/j.fuel.2018.03.140
Received 26 November 2017; Received in revised form 2 March 2018; Accepted 20 March 2018

at 174 ppm at temperatures above 420 K [13]. At lower temperatures, two resonances of intercalated graphite at 187 ppm (K_3C_{60}) and 143 ppm ($K_\delta C_{60}, \delta \leqslant 1$) were identified by ^{13}C NMR [13]. X-ray photoelectron spectrum of potassium doped double-walled carbon nanotubes showed two peak components at the binding energy of 293.3 and 296 eV (K $2p_{3/2}$ and K $2p_{1/2}$ of the K-oxides and K-cations) [16]. The X-ray photoelectron bands at 294.6 and 293.4 eV were assigned to ionic potassium intercalated within the graphite layers and to oxidized potassium at the surface of graphite [17]. The modeling using density functional theory method (DFT) confirmed the existence of an electron transfer from soot to gaseous oxygen through the active K^+ sites [18]. In this DFT model, soot structure was represented by graphene layers and potassium was modeled perpendicular to the plane of the soot model and near the zigzag and armchair edges of the soot. The DFT model for the C–C armchair face showed that the potassium intercalation in phenolate groups (C-O-K) inhibits the gasification reaction, confirming previous experimental observations [3,19].

This work aims to investigate the interaction between potassium and carbonaceous soot matrix in detail. The specific objectives of this study were to: (1) investigate the interaction of potassium with the carbonaceous matrix of soot produced at high temperatures (1250°C) in a drop tube reactor, and (2) understand the formation mechanism of potassium-carbon complexes in fast pyrolysis and their effect on the soot reactivity using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), ^{13}C solid state NMR, X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

Table 1
Proximate and ultimate analysis.

Fuel	Pinewood	Beechwood	Wheat straw	Alfalfa straw	Leached wheat straw
		Proximate analysis			
Moisture, (wt% as received)	5.1	4.5	5.5	5.2	4.3
Ash (550°C), (wt% dry basis)	0.3	1.4	4.1	7.4	2.1
Volatiles, (wt% dry basis)	86.6	79.4	77.5	75.9	82.2
HHV, (MJ kg^{-1})	21.6	20.2	18.8	19.7	19
LHV, (MJ kg^{-1})	20.2	19	17.5	16.9	17.2
		Ultimate analysis, (wt%, dry basis)			
C	53.1	50.7	46.6	42.5	46.2
H	6.5	5.9	6.1	6.7	6.8
O	40	41.9	42.5	43.1	44.9
N	0.06	0.13	0.6	0.3	0.05
S	< 0.01	0.01	0.1	0.03	0.02
		Ash compositional analysis, (mg kg^{-1}, dry basis)			
Cl	0.01	0.02	0.1	0.5	0.01
Al	10	10	150	600	100
Ca	600	2000	2500	12,900	1300
Fe	20	10	200	–	350
K	200	3600	11,000	28,000	1200
Mg	100	600	750	1400	350
Na	30	100	150	1000	50
P	6	150	550	1900	80
Si	50	200	8500	2000	6200
Ti	2	< 8	10	30	10

2. Materials and methods

2.1. Raw biomass characterization

Pinewood, beechwood, wheat straw and alfalfa straw were chosen for the fast pyrolysis study in a drop tube reactor (DTF). Fuel selection was based on the differences in the ash composition and plant cell compounds (cellulose, hemicellulose, lignin, extractives), as shown in the supplemental material (Table S-1). The ultimate and proximate analysis of pinewood, beechwood, wheat straw, leached wheat straw and alfalfa straw is shown in Table 1.

2.2. Pyrolysis with drop tube furnace

Soot and char samples were obtained from pyrolysis experiments in a drop tube reactor (DTF). Soot samples were generated at 1250°C to obtain a maximal soot yield. The DTF setup and operating conditions were described in detail by Trubetskaya et al. [20]. The reactor consists of an alumina tube (internal diameter: 54 mm, tube length: 1.06 m) heated by four heating elements with independent temperature control. Gas flow rate into the reactor is regulated by mass flow controllers (EL-FLOW® Select, Bronkhorst High-Tech B.V.). The experiments were conducted by feeding ≈5 g of biomass at a rate of 0.2 g min^{-1}. Both primary (0.18 l min^{-1} measured at 20°C and 101.3 kPa) and secondary (4.8 l min^{-1} measured at 20°C and 101.3 kPa) feed gases were N_2. The residence time of fuel particles was estimated to be about 1 s, taking into account density changes during pyrolysis. Soot particles passing the cyclone (cut size 2.5 μm) were captured from the product gas flow by a grade QM-A quartz filter with a diameter of 50 mm (Whatman, GE Healthcare Life Science).

2.3. Solid residue characterization

2.3.1. Ash compositional analysis

The ash compositional analysis was performed by ICP-OES (DIN EN 15290). Prior to the analysis, soot samples were pre-heated in oxygen at 10°C min^{-1} up to 550°C and kept at that temperature for 7 h.

2.3.2. Potasium ion selective electrode

The potassium ion-selective membrane electrode Orion 93–19 (Thermo Scientific, USA) was used to determine the amount of leached potassium in deionized water. The electrode potential was measured at room temperature using the Benchtop Meter Orion 720A (Thermo Scientific, USA). Five-points calibration was conducted using potassium chloride solutions with ionic strengths of 10^{-5}, 10^{-4}, 10^{-3}, 0.01 and 0.1 M.

2.3.3. X-ray diffraction

The XRD analysis of the soot matter was conducted using a Bruker D8 AXS X-ray diffractometer with (Cu-Kα1, λ = 1.54056 Å and Cu-Kα2 radiation, λ = 1.54439 Å) operating in Bragg–Brentano (reflection) mode, using a secondary graphite monochromator, and a scintillation detector, in the range 5 to 80 degrees for 12.5 h. Soot samples were placed in small cups which were rotated during the XRD analysis. The multiple fitting of XRD pattern, crystallite size analysis and peak searches were done using PowderPlot software and Crystallographica Search-Match software (Version 3,1,0,0). The instrumental reflection broadening was subtracted from the experimental pattern by the PowderPlot software.

2.3.4. Raman spectroscopy

Raman spectroscopy was performed using an inVia Raman microscope (Renishaw, UK) operating with a 514 nm laser line at a power of 30 mW. The measurements were performed in static mode with a centre at 1600 cm^{-1} resulting in a 960–2200 cm^{-1} spectral region. The laser power was set to 100% in the software and roughly 30% in the hardware. 1 s exposure time was used in normal confocality mode. A 20x lens and 8–15 μm step size (X and Y directions) were used for mapping, to generate 100–200 spectra/image for each soot sample. Deconvolution of the Raman spectra were conducted using the peak fit pro tool in the OriginPro software (OriginLab, USA) by combination of five Gaussian-shaped bands (D4, D3, D2, D1, and G) following Sadezky et al. [21] and as described in the supplemental material (Section S-10.1). The mean crystal size in the *a*-direction (L_a) with the fitting constants $C_0 = -12.6$ nm and $C_1 = 0.033$, which are valid for the laser