



Full Length Article

Fate of inorganic elements during fast pyrolysis of biomass in a cyclone reactor



Henrik Wiinikka*, Ann-Christine Johansson, Linda Sandström, Olov G.W. Öhrman

SP Energy Technology Center AB, Box 726, SE 941 28 Piteå, Sweden

HIGHLIGHTS

- Inorganic elements are predominantly concentrated in the solid residue during cyclone pyrolysis.
- 1–10 wt% of the ingoing amount of Zn, K, and Fe was found in the pyrolysis oil.
- <1 wt% of the refractory inorganic elements were found in the pyrolysis oil.
- The inorganic content could be affected by oil fractionation.

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ABSTRACT

In order to reduce ash related operational problem and particle emissions during pyrolysis oil combustion it is important to produce pyrolysis oil with very low concentration of inorganics. In this paper, the distribution of all major inorganic elements (S, Si, Al, Ca, Fe, K, Mg, Mn, Na, P, Ti and Zn) in the pyrolysis products (solid residue and two fractions of pyrolysis oil) was investigated during pyrolysis of stem wood, bark, forest residue, salix and reed canary grass. The raw materials were pyrolysed in a cyclone reactor and the produced pyrolysis oils were recovered as two oil fractions, a condensed fraction and an aerosol fraction. The inorganic composition of the ingoing raw material, the solid residue and the two pyrolysis oil fractions were analysed with inductively coupled plasma spectrometry techniques.

All major inorganic elements, except sulphur, were concentrated in the solid residue. A significant amount of sulphur was released to the gas phase during pyrolysis. For zinc, potassium and iron about 1–10 wt% of the ingoing amount, depending on the raw material, was found in the pyrolysis oil. For the rest of the inorganics, generally less than 1 wt% of the ingoing amount was found in the pyrolysis oil. There were also differences in distribution of inorganics between the condensed and the aerosol oil fractions. The easily volatilized inorganic elements such as sulphur and potassium were found to a larger extent in the aerosol fraction, whereas the refractory elements were found to a larger extent in the condensed fraction. This implies that oil fractionation can be a method to produce oil fractions with different inorganic concentrations which thereafter can be used in different technical applications depending on their demand on the inorganic composition of the pyrolysis oil.

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1. Introduction

Fast pyrolysis of biomass produces a renewable liquid fuel called pyrolysis oil (or bio-oil). Combustion of pyrolysis oil to generate heat and power in boilers, engines and gas turbines is claimed to be the major field of usage [1]. It is also possible to catalytically upgrade (i.e. deoxygenate) the pyrolysis oil to products more compatible with current fuels. The deoxygenation can be performed with [2] or without [3] hydroprocessing. Another field

of application recently proposed by Bridgwater [4] is decentralised production of pyrolysis-oil or pyrolysis-oil-char slurries for transportation to a central process plant for pressurised oxygen blown gasification [5] and synthesis of hydrocarbon transportation fuels. Common features for the combustion applications and the upgrading with catalysts are that the processes demand oil with a very low content of particles and inorganics. The reason for this is that ash related operational problems such as particle emissions, particle deposits on heat transfer surfaces and high temperature corrosion or catalyst deactivation are closely related to the concentration of inorganics in the fuel. Therefore, Lehto et al. [6] recommended to reduce the solid content of the pyrolysis oil to <10.1%

* Corresponding author.

E-mail address: henrik@etcpitea.se (H. Wiinikka).

by weight if possible, and to ensure that inorganics in the form of ash and sand are present in as low concentration as possible. Furthermore, particles in the pyrolysis oil could also increase the instability of the oil, observed e.g. as an increased viscosity and tendency for phase separation with time [7].

Earlier, pyrolysis oil research has mainly been focused on the manufacturing (e.g. mass and energy balance) and the characterisation of the organic part of the oil (e.g. ultimate analysis, heating value, molecular composition) and surprisingly few investigations have been focused on the fate of inorganics during real pyrolysis oil production. Agblevor and Besler [8], investigated the influence of inorganics (K, Ca, Na, P, Cl, and Si) on the quality of fast pyrolysis oil produced by bench scale (80–100 g/h) fluidised bed pyrolysis of switchgrass (ash content 4.92 wt%). Their results showed that most of the inorganics (97.5 wt%) are present in the char, and that carryover of char fines during the condensation step is the source of metals in the oil. Furthermore, although the pyrolysis oil is acidic (pH 2.4–3.0), the basic potassium and calcium compounds in the fines do not appear to leach into the oil during storage in cold conditions [8]. Agblevor and Besler also showed that hot gas filtration is a promising method for reducing the inorganic content in pyrolysis oil [8].

Another investigation regarding the transfer of inorganics (i.e. K, Ca, Na, and Mg) into the pyrolysis oil was performed by Jendoubi et al. [9] who pyrolysed beech wood (ash content 0.57 wt%) and straw (ash content 6.78 wt%) in a bench scale fluidised bed reactor (1.5 kg/h). The pyrolysis oil was collected in a series of condensers producing heavy, light, and aerosol oil fractions. Also these results indicated that most (>99 wt%) of the inorganic elements are trapped and concentrated in the char particles [9]. Furthermore, the results also showed that most of the inorganic species (>60 wt%) in the total oil were found in the aerosol oil fraction [9]. The authors proposed several different explanations for this behaviour [9], (i) micro-char particles, which contain inorganics, are transported within bio-oil aerosols, (ii) inorganics (in soluble form or organically bound) are transported with aerosols formed by a mechano-chemical process such as micro-explosions in the pyrolysis step, and (iii) char particles act as condensation nuclei for the bio-oil in the condenser, forming the aerosols. However, the authors also proposed a simpler explanation connected to the experimental equipment used in their experiment [9]. Submicron solid particles and liquid droplets had similar hydrodynamic behaviour as the carrier gas and these were captured by an electrostatic precipitator that was used in the experimental set-up to collect the aerosol fraction whereas tubular condensers collected the heavy and light fractions of the oil.

Recently Leijenhörst et al. [10] performed a literature review of how inorganic elements are transferred to the oil during pyrolysis. An important mechanism in the release of inorganic elements from the biomass to the vapour phase was found in reactions between the organic volatiles produced and the inorganic elements present in the solid material. Furthermore, experiments regarding the transfer of inorganic elements during pyrolysis of 16 biomass materials were also investigated in three different fast pyrolysis plants [10]. A 200 kg/h (biomass input) pilot plant and a 5 kg/h bench scale plant based on the BTG rotating cone technology (hot sand as heat carrier) was used to pyrolyse raw material mainly from woody biomass and agricultural residues whereas residues from biochemical processes was pyrolysed in a 0.5 kg/h screw conveyor (indirect heated). Leijenhörst et al. [10] concluded that incomplete solid separation from the gaseous stream prior to condensation is the main route for the transfer of most alkali earth metals (Ca, Mg), transition metals (Fe, Cu, Ni, Cd, Cr, Co, Mn, and Zn), post transition metals (Al, Pd), phosphorus and alkali metals (Na, K), although sodium and potassium are also transferred notably by reactions with volatiles.

Reaction with organic volatiles is also the main route for sulphur transfer to the oil.

The focus of the present study is the influence of raw material type on the fate of inorganics during fast pyrolysis of biomass in a pilot plant cyclone reactor. Five different types of biomasses were pyrolysed under identical conditions in an externally heated cyclone reactor (20 kg/h). No sand is used as heat transfer media in the cyclone reactor which is a difference to most of the technologies earlier used to investigate the fate of inorganic elements during fast pyrolysis [8–10]. The risk for contamination of the oil from sand minerals or reactions of the sand minerals with the biomass inorganics is therefore less compared to fluidised bed or rotating cone reactors. The cyclone reactor is therefore an excellent reactor type for investigations of the fate of inorganics during pyrolysis of biomass and Wiinikka et al. have in fact already demonstrated that it is possible to produce very clean oil from pyrolysis of stem wood in the cyclone pyrolyser [11].

The novelties in this work compared to previous reported studies [8,9] are that the fate of all major inorganic elements (S, Si, Al, Ca, Fe, K, Mg, Mn, Na, P, and Ti) and not just selected ones are investigated with a reactor type that does not use sand as heat transfer media. Chlorine was however not included in the study since the concentration of this element in both the raw material and the oil are in general below the detection limit of the analysis and therefore it is hard to experimentally follow what happens with chlorine during the pyrolysis process. The fate of zinc, which is studied in this work, is important since the concentration of zinc is relatively high in biomass and an earlier study by Wiinikka et al. has shown that the release of zinc during combustion of biomass could be significant [12]. Furthermore, in order to evaluate the influence of raw material on the fate of all these elements, pyrolysis of five different raw materials (relevant for pyrolysis oil production in Nordic countries) were investigated using a cyclone pyrolyser for comparison to previous studies performed using fluidised bed technologies. The pilot plant size was also significantly larger, 20 kg/h input of raw material compared to 0.1–1.5 kg/h in some of previous works [8,9] related to studies on inorganics. Finally, similar to the investigation by Jendoubi et al. [9] the oil is fractionated into a condensed and an aerosol fraction and kept separate after the collection step and which not so common in the pyrolysis oil community.

2. Experimental

2.1. Raw materials

Five different biomasses relevant for Nordic countries were used as raw materials representing feedstocks from both the forestry and the agricultural sector. A detail description of the raw material can be found elsewhere [13]. The forest based materials were stem wood sawdust from a mixture of pine and spruce, bark from a mixture of spruce, pine and birch and brown forest residue (FR) from a mixture of pine, spruce and deciduous tree (birch and aspen). Salix (the entire tree) and reed canary grass (RCG) were raw materials of agricultural origin. After drying, the raw materials were milled in a hammer mill until all the materials passed through a 0.75 mm sieve. The physical and chemical compositions of the five raw materials are presented in Table 1.

2.2. The cyclone pyrolyser

The experiments were performed in a 20 kg/h cyclone pyrolyser at SP ETC located in Piteå, Sweden. The pyrolyser has been described in detail elsewhere [11,13] and therefore only a short description is given here. The externally heated cyclone reactor

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