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Research article

Inorganic element transfer from biomass to fast pyrolysis oil: Review and experiments

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ABSTRACT

Fast pyrolysis bio oil is a liquid biofuel produced by fast pyrolysis of biomass materials. Even though pyrolysis oil consists primarily of carbon, hydrogen and oxygen, contaminations in the form of inorganic elements can be transferred from the original biomass feedstock to the pyrolysis oil during its production. These inorganic elements might limit the potential for utilization in high value applications, for example by poisoning the catalysts used in any subsequent processing steps. In this work, the transfer of inorganic elements from biomass to pyrolysis oil has been investigated. First a literature review was performed in order to determine the possible pathways inorganic elements can follow in the pyrolysis process. An important mechanism in the release of inorganic elements from the solid to the vapor phase was found in reactions between the organic volatiles produced and the inorganic elements present in the solid material. Organic volatiles form bonds with inorganic elements on the solid (pore) surface, after which the composed molecule can be released to the vapor phase.

Experimental work on the transfer of inorganic elements during pyrolysis of 16 biomass materials has been carried out. Results show that alkali earth metals (Ca, Mg), transition metals (Fe, Cu, Ni, Cd, Cr, Co, Mn, Zn) and post transition metals (Al, Pb) remain largely on the solid char by-product. Incomplete solid separation from the gaseous stream prior to condensation is then the main route for their transfer to the pyrolysis oil. For the non-metals (S, P) sulfur is transferred primarily due to reactions with organic volatiles, while phosphorus is transferred primarily by physical entrainment of solid char particles. For the alkali metals (Na, K) the entrainment of solid char particles to pyrolysis oil is also the primary pathway, although Na and K are also transferred notably by reactions with volatiles. The influence of the pyrolysis temperature in the normal operating range (400–600 °C) appears to be small. >95 wt.% of all inorganic elements present in the biomass are typically separated from the pyrolysis oil product. Options are available to increase the separation efficiency even further, showing that the presence of inorganic elements should not be a limiting factor for the application of pyrolysis oil.

1. Introduction

A common difficulty for most biomass conversion systems involves the presence of inorganic elements in the biomass materials. These inorganic elements, which primarily form ash upon combustion, can cause fouling of process equipment as well as contamination of the products. Fast pyrolysis of biomass is believed to be a technology able to deal with (most of) the problems associated with biomass ash. The operating temperature of 400–600 °C is sufficient to break down the organic biomass structure, but low enough to avoid melting and evaporation of the inorganic elements. It is often claimed that most inorganics remain in the solid phase (char), and as such can be avoided in the pyrolysis oil product.

Goal of this work was to investigate the fate of inorganic elements present in biomass during the fast pyrolysis process. Despite the importance for the development of pyrolysis oil applications, information in the open literature regarding this matter is still scarce. First the relevant literature will be reviewed, including both fundamental aspects as well as results obtained in representative pyrolysis systems. Then, the results of a series of dedicated experiments carried out in our own laboratories will be reported and discussed.

The tolerance level for the quantities and types of inorganic elements in the pyrolysis oil depends strongly on the intended application. For example poisoning of reform catalysts may occur [1] in gasification systems. Usage of pyrolysis oil with inorganic elements in a gas turbine might result in deposition of these elements on turbine blades [2]. Because of the wide variety in potential applications, no general

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benchmark values can be set for the maximum allowable inorganic content in pyrolysis oil. This work focusses on the question how much of the inorganic elements are transferred to the pyrolysis oil, and why.

For both the literature review and the experimental work discussed hereafter, the transfer degree of each individual inorganic element i from the biomass to the pyrolysis oil is calculated according to Eq. (1).

$$X_i = \frac{\Phi_{PO} \cdot C_{PO,i}}{\Phi_{BM} \cdot C_{BM,i}} \cdot 100\% \quad (1)$$

where X_i presents the transfer degree of element i, φ_{PO} represents the mass flow rate of the total liquid product and φ_{BM} the mass flow rate of the biomass feed to the process on as received basis, both in kg/h. $C_{PO,i}$ is the concentration of element i in mg per kg pyrolysis oil, $C_{BM,i}$ is the concentration of element i in mg per kg biomass material, both also on as received basis. Because $\varphi_{PO}/\varphi_{BM}$ presents the pyrolysis oil yield (Y_{PO}) of the process on as received basis, Eq. (1) can be rearranged to give Eq. (2).

$$X_i = Y_{PO} \cdot \frac{C_{PO,i}}{C_{BM,i}} \cdot 100\% \quad (2)$$

For phase separated pyrolysis oils, the mass flow rate of the total liquid product is the sum of the individual phases (i.e. $\varphi_{PO} = \varphi'_{PO} + \varphi''_{PO}$). The concentration for element i is then the weighted average of the concentration in the individual phases according to Eq. (3).

$$C_{PO,i} = \frac{\Phi'_{PO,i} \cdot C'_{PO,i} + \Phi''_{PO,i} \cdot C''_{PO,i}}{\Phi'_{PO,i} + \Phi''_{PO,i}} \quad (3)$$

2. Literature review

To investigate the transfer of inorganic matter from biomass during fast pyrolysis, the concentrations and forms of the individual inorganic elements in biomass materials needs to be considered. Important in this respect is that biomass is a term used for a wide variety of materials, of which both organic and inorganic structures vary greatly. These variations, along with variations in operating conditions of the pyrolysis processes, lead to quite broad ranges in transfer degree. Section 2.1 provides details regarding the form in which the inorganic elements are present in the biomass. The behavior of the inorganic elements during the pyrolysis process is discussed in Section 2.2, including fundamental aspects (Section 2.2.1), the transfer in fast pyrolysis setups (Section 2.2.2) and attempts to steer the transfer degree of inorganic elements during pyrolysis (Section 2.2.3).

2.1. Inorganic elements in biomass

Biomass materials can contain a large number of different elements depending on the biomass variety, environmental conditions (soil quality, water quality), harvesting methods and time. Vassilev et al. [3] examined peer-reviewed data from 93 biomass varieties, both with respect to their organic and inorganic composition. Common elements found in biomass, in decreasing order of abundance, are C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn and Ti. Analysis of trace elements in biomass ashes produced from 8 biomass varieties further showed the presence of As, Ba, Co, Cr, Cu, Mo, Ni, Se, Sn, U, V and Zn [4]. The inorganic elements present in biomass are typically measured by using inductively coupled plasma (ICP) technique, which is the same technique as is often used for the pyrolysis oil product.

Inorganic elements can be present in biomass in numerous forms. The simplest form is as a free ion, dissolved in fluid matter inside the biomass material. Salts are also found, often in structured mineral form (e.g. NaCl). Furthermore, covalent bonds between inorganic elements and the organic biomass structure are seen as well (e.g. proteins). Table 1 gives an overview of the dominating forms for the various elements, along with examples of typical inorganic and organic components. A more detailed description of these findings is provided hereafter.

The alkali metals Na and K are present in biomass materials mainly as salts [5]. They often occur in free ion form (Na^+, K^+) with counter ions such as chloride (Cl^-) or malate ($C_4H_4O_5^{2-}$) and are dissolved in the fluid matter trapped within the biomass cell structure. Alternatively the alkali metals appear in solid salt structures fixed on the cell wall. Bonds of Na and K inside the organic matrix, for example in carboxylate form, can be present as well [3], but are less common.

Contrary to the alkali metals, the alkali earth metals Ca and Mg do form predominately bonds with the organic parts of the biomass [6], and are less commonly present in free ionic form.

Transition metals such as Fe, Cu, Ni, Cd, Cr, Co, Mn and Zn are not always found in biomass, nor are the post transition metals Al and Pb necessarily present. When these elements are detected, their concentrations are usually very low; therefore these elements are

Table 1
Typical mineral forms in biomass materials.

Group	Examples of organic forms	Examples of inorganic forms	Dominant forms
Alkali metals (Na, K)	Oxalate [3]	Cation in fluid matter (Na^+, K^+) [3] KCl, NaCl [3,5] $NaNO_3$, KNO_3 [5]	Na and K mostly in the form of ionic salts [5]
Alkali earth metals (Mg, Ca)	Oxalate [3]Carbonate [3]	Cation in fluid matter (Mg^{2+}, Ca^{2+}) [3] $CaCl_2$ [3,5] $MgCl_2$ [3,5] $Ca_3(PO_4)_2$ [5] [7] $Mg_3(PO_4)_2$ [5]	Mg and Ca form to large extent complexes with organic counterions [6]
Transition metals (Fe, Cu, Ni, Cd, Cr, Co, Mn, Zn)	Fe-Chelates [3],Mn-Carbohydrate [3]	Cation in fluid matter (Fe^{2+}, Mn^{2+}, Cr^{3+}) [3] Metallic form [3], Iron oxide [5]	Often in small (<2 μm) crystal structures [7] Often introduced by harvesting and/or treatment
Post transition metals (Al, Pb)	–	Aluminum hydroxide ($Al(OH)_3$) [3] Kaolinite [5]	Highly variable Mostly inorganic forms, often introduced by processing
Non-metals (P, S)	Covalently bound P, S [3] Proteins [3]Amino acids with P or S [5]	Sulfate anion (SO_4^{2-}) [3] Sulfite (SO_3^{2-}) [3] Phosphate anion (PO_4^{3-}) [3] [5]	In straw 40–50 wt.% as sulfate, 40–50 wt.% as organic sulfur [8]P mainly in organic form in cottonseed hull (87 wt.%) [11] and pecan shell (74 wt.%) [11]P mainly inorganic in corn stover (97 wt.%), sewage sludge (86 wt.%), cow manure (90 wt.%) swine manure(99 wt.%) [11]