Ash transformation during dual fluidized gasification of biomass

Högskolan i Borås och SP Technical Research Institute propose this present project aiming to investigate the fate of ash-forming matter in dual fluidized bed gasification. The amount applied for is 699 500 SEK.

1. Background, problem, and limitation

The steam gasification of biomass in dual fluidized beds is a promising technology to produce energy from biomass [1]. Two interconnected fluidized beds are used in this process as shown in figure 1. In one of the fluidized beds (the gasification reactor), steam is used to gasify biomass to produce a gas of high energy value (12-20 MJ/Nm$^3$ [2, 3]). In this process, char is obtained as by-product. The char together with the bed material (e.g. silica sand or olivine) are circulated to the other fluidized bed (the combustion reactor). In the combustion reactor, air is used to combust the char to generate heat which heats up the bed material. The hot bed material and any uncombusted char are recirculated to the gasifier to provide the heat needed for biomass gasification. Thus, a single fuel particle in this process undergoes conversion under alternating oxygen-rich and oxygen-free atmospheres.

![Figure 1. Dual fluidized bed gasification process.](image)
Dual fluidized bed gasification (DFBG) is prone to problems associated with the release and transformation of some ash-forming elements from biomass. Some of these ash-related problems are fouling [4, 5] and corrosion [6, 7] of heat transfer surfaces, and agglomeration of bed material [8, 9]. In addition to ash-related problems in fluidized beds, the release of S species such as H$_2$S into the product gas from biomass gasification poisons catalysts used in various downstream processes [10, 11]. The severity of ash-related problems during thermal conversion of biomass depends among others on the fraction of ash-forming elements in the fuel transferred to the vapour [12, 13]. In turn, the fraction of these elements in the fuel transferred to the vapour depends on fuel characteristics and operating conditions [13-16]. Some of the fuel characteristics include the concentration and association of the ash-forming elements in the fuels, and the size of fuel particles [14, 15, 17]. Operating conditions include the heat transfer to the fuel particles, the temperature and atmosphere in the reactor, and the residence time of the fuel particles in the reactor [14, 18, 19].

The temperatures in the gasification and combustor reactors are in the ranges 800-850 °C and 850-900 °C respectively [20]. Studies show that at given operating conditions, the amount of ash-forming elements released from biomass is strongly determined by the absolute and relative concentrations, and association of ash-forming elements in the fuel [14-17, 21, 22]. Ash-forming elements can be organically and/or inorganically associated in biomass [15, 23, 24]. The organically associated elements are mostly metal cations that are bonded to anionic groups of the organic fuel matrix [23]. The inorganically associated elements in biomass may exist as soluble salts, and/or minerals [23]. The fraction of ash-forming matter that exists as soluble salts and/or is organically bonded is believed to be very reactive during thermal conversion processes [25-28]. The fraction of ash-forming matter that exists as minerals is less reactive during thermal conversion processes [28, 29]. Therefore in order to predict the behaviour of ash-forming matter during thermal conversion processes and effectively mitigate ash-related problems, it is important to determine both the concentration and the association of ash-forming elements in the fuel.

The concentration of ash-forming elements in biomass can be determined by standard fuel analyses methods. Chemical fractionation (CF) is widely used to determine the form of ash-forming elements in biomass [12, 23, 25, 26, 29]. This technique relies on the solubility of ash-forming matter (in biomass) in solvents of increasing aggressiveness. The solvents used in order of increasing aggressiveness include water (H$_2$O), 1 M ammonium acetate (NH$_4$Ac), and 1 M hydrochloric acid (HCl). The fraction dissolved by water is mostly alkali salts: e.g. alkali carbonates, chlorides, sulfates, and phosphates. NH$_4$Ac(aq) dissolves exchangeable ions of some elements such as Ca, K, Na, and Mg. This fraction is believed to be organically associated. The fraction leached out by HCl(aq) is mostly carbonates, sulfates, and phosphates of alkali and alkaline earth metals. Ash-forming matter that is insoluble in any of these solvents consists of silicates and other minerals. Many studies on CF of virgin biomass fuels and ash samples from stand-alone combustion and gasification processes has been reported in literature [23, 25, 28, 29]. Werkelin et al. [29] observed that all of the Cl and most of the K, Na, and P in woody biomass were leached out with water. Most of the Ca was leached out with HCl(aq) while most of the S and Si was
insoluble in all the solvents. Zevenhoven et al. [28] used CF to study the tendency of various forms of ash-forming matter in biomass to cause bed agglomeration during fluidized bed combustion. The results showed that the soluble fraction of K and Ca in the investigated fuels may be responsible for the formation of a sticky layer on bed particles that ultimately leads to agglomeration. The results from the referred works are largely applicable to stand-alone combustion and gasification processes in which virgin biomass is predominantly under a single atmosphere reactor until it is converted. However for DFBG (in which biomass particles undergo conversion under alternating oxygen-free and oxygen-rich atmospheres) these results are somewhat limited to the gasification of virgin biomass. It has been observed during thermal conversion processes that, the inorganically associated fraction of ash-forming matter in biomass may undergo transformation and become organically associated and vice versa [15, 30]. It is thus possible that during DFBG, the concentration and association of ash-forming matter in the char (obtained from the steam gasification of the virgin biomass) leaving the gasification reactor into the combustion reactor may be different from those in the virgin biomass. Similarly, the concentration and association of the ash-forming matter in the ash and/or unconverted char leaving the combustion reactor into the gasification reactor may be different from those in the char leaving the gasification reactor into the combustion reactor. Therefore in order to predict the transformation and release of ash-forming matter in biomass during DFBG, it is important to ascertain the concentration and forms of ash-forming matter in the fuel at each step of the process.

The aim of this project is to investigate the transformation of the forms of ash-forming matter in biomass during DFBG.

2. Hypotheses
   i. The association of ash-forming matter in biomass changes as biomass is thermo-chemically converted
   ii. The relative concentration of ash-forming matter in biomass changes as biomass is thermo-chemically converted

3. Objectives
   i. Determine the concentration and association of ash-forming matter (K, S, Cl, and Ca) in biomass fuels that can be used for DFBG
   ii. Determine the concentration and association K, Cl, S, and Ca in char samples (char 1) produced from steam gasification of virgin biomass at temperatures relevant for DFBG
   iii. Determine the concentration and association of K, Cl, S, and Ca in ash/unconverted char resulting from the combustion of char 1
4. Method

The work will be carried out in two phases as follows:

I. Phase 1. This phase will be carried out at SP Technical Research Institute of Sweden and will consist of the following:
   i. Standard fuel analysis will be carried out on two biomass fuels (Bark and GROT or two fuels selected by Göteborg Energi)
   ii. These fuels will be gasified with steam in a laboratory-scale bubbling fluidized bed reactor. Operating parameters will include two temperature setpoints (800 and 850 °C) and a fixed residence time of 90 seconds. The char samples obtained from this process are denoted char 1.
   iii. Standard fuel analysis will be carried out on the char 1.
   iv. The char 1 will be either partially or completely combusted at 900 °C. The uncombusted char from this process is denoted char 2.
   v. Chemical analysis will be carried out on char 2 as well as the ash resulting from the complete combustion of char 1.
   vi. Leaching according to the standard "SIS-CEN/TS 15105" will be carried out on char 2 and the ash.

II. Phase 2. This phase of the project will be carried out at the University of Borås. The following steps will be considered:
   i. Chemical fractionation of the virgin biomass fuels and char 1 will be done.
   ii. FactSage simulation of the transformation of the ash elements during DFBG will be done.

5. Timeline

The timeline for this project is shown in table 1 below.

<table>
<thead>
<tr>
<th>Phase 1</th>
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<tbody>
<tr>
<td>Period</td>
<td>Activity</td>
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<tr>
<td>20140201-20140301</td>
<td>Preparation of fuels</td>
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<tr>
<td>20140301-20140501</td>
<td>Fuel analysis</td>
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<tr>
<td>20140501-20141101</td>
<td>Gasification/combustion experiments</td>
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<tr>
<td>20141115-20150215</td>
<td>Chemical analysis/leaching of char/ash samples</td>
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<tr>
<td>20150301-20151101</td>
<td>Analysis and writing of report</td>
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6. Importance of the project to “Göteborg Energi”

The GoBiGas project based on DFBG is one of the many areas by which Göteborg Energi (GE) aims to contribute to a sustainable energy supply while preserving the environment. It is GE’s largest investment in the production of biomethane. The efficiency of the DFBG process may be affected by ash-related problems caused by the release and transformation of ash-forming elements from biomass fuels. Ash-related problems are conducive to high maintenance cost, and costly unscheduled shutdowns.

An important measure in predicting the transformation and release of ash-forming elements from biomass (as well as designing suitable control methods for mitigating ash-related problems in fluidized bed) is to determine the concentration and association of ash-forming elements in the fuel at each step of the thermal conversion process. This is the main focus of this project. The results obtained from this project will be useful to GE in improving the efficiency of the GoBiGas power plant.

7. Report

The results from this project will be reported according to the specifications of Göteborg Energi Forskningsstiftelse.

8. Management of the project

The project will be carried out by the following:

- SP Technical Research Institute of Sweden: Kent Davidsson (project leader), Frida Jones, and Placid Tchoffor
- University of Borås: Anita Pettersson, and Farzad Moradian

References


