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Trace metals emission in syngas from biomass gasification

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ABSTRACT

In this paper, trace metals (As, Be, Cd, Cr, Hg Ni, Pb, Se and V) emission from the atmospheric entrained flow gasifier REGA at Karlsruhe Institute of Technology, Germany is presented. Elemental composition and metals concentration in glycol (model fuel) and straw char samples were determined. In order to achieve well defined and reproducible operating conditions, gasification experiments were carried out with glycol and slurry (straw char mixed with glycol) as fuel. Trace metals emission and distribution into particle and gas phase in syngas from gasification were measured according to US EPA method 29. During glycol gasification, metals concentration in syngas ranged from 0.1 μg/Nm^3 (V) to 4.6 μg/Nm^3 (Cr). In slurry gasification, metals concentration in syngas ranged from 2.4 μg/Nm^3 (Hg) to 53.2 μg/Nm^3 (Ni). Trace metals tend to volatilize more in reducing gasification environment. Tendency of metals to speciate into particle phase increased in slurry gasification than glycol gasification due to increased in particle concentration and unburned carbon content in syngas. The increase of particle and carbon content in syngas possessed strong influence in distribution behavior of As, Be and Pb, however, such influence was less for other metals studied. Mercury in syngas was speciated predominantly into elemental form followed by oxidized form whereas share of particle bond mercury was the least.

1. Introduction

Biomass is a renewable, low carbon fuel that can be used as a substitute of fossil fuels promoting environmental and social benefits. Biomass is the fourth major sources of primary energy uses following coal, petroleum and natural gas [1]. The simplest utilization of biomass i.e. burning, largely practiced in the developing countries, is an unsustainable combustion practice which releases pollutants of serious health and environmental concern. Bio-chemical processes like biomethanization and thermo-chemical methods such as combustion, pyrolysis and gasification are used in recovering energy from biomass [2–4]. Biomass gasification is one of such promising technologies to produce syngas in an energy efficient manner. The gasification of ligno-cellulosic biomass has high conversion efficiency among various thermo-chemical conversion technologies [5]. Due to several advantages, biomass gasification technology has drawn an attention around the world [3,5,6]. As for example, over the past decades the North Dakota Energy and Environmental Research Center has developed and applied the gasification of solid fuels (coal, biomass, coal–biomass blends), cleaned syngas and converted syngas to useful energy [7].

Biomass based energy has been prioritized in current European Union (EU) strategies to mitigate climate change and improve energy security. The member states of the EU are committed to acquire 20% of their energy requirements from renewable sources, including biomass, by the year 2020 [8]. German government's Energy Concept (2010) aims to increase the share of regenerative energies up to 18% of the end-use energy by the year 2020. Influenced by these activities, biomass gasification research and development work has increased intending on improving efficiency; reduce pollutants release during the process utilization. In spite increasing use, one of the environmental aspects that have not been studied comprehensively is the fate of trace metals during biomass gasification process.

Biomass contains trace quantity of metals [9]. Biomass burning, both natural and anthropogenic means has been reported as a source of atmospheric metals including mercury emissions [10–12]. Trace metals introduced into a gasification system, mainly from feedstocks, undergo transformation and removal within the system and the left over enters the chemical conversion steps together with syngas or if syngas is used as fuel in gas engines leaves the system with flue gas. Some trace metals in syngas cause fouling and corrosion of the gas turbine blades [13]. Trace metals in syngas also affect the catalyst in the system and results in low biomass to fuel conversion. Specifically, as for example, alkali metals (Na, K) and heavy metals V, and Zn species can damage materials in heat and power plants, cause abrasion, corrosion and erosion of internal parts, influences energy and mass flow in the system. Further, deposition of alkali species such as NaCl, Na_2SO_4, and Na_2CO_3, can poison and deactivate catalysts [14] and fuel cells. To achieve an economically acceptable service lifetime of catalyst, Hg and As concentration in syngas at the inlet should be reduced to < 5 ppb [15,16]. The catalyst deactivation by other trace heavy metals such as Pb and Cd in off-gas

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has been reported, however, the quantitative data is lacking. Nevertheless, trace metals in biomass gasification are to be controlled, as minimum as possible, to increase the lifetime of the facility itself, increase biomass to fuel conversion and to create the cleaner environment.

To some extent, trace metals emission in combustion flue gas is known [17–19]. However, their behavior in gasification environment is unclear. Considering the difference in off gas chemistry, an apparent difference in trace metal emission behavior between combustion and gasification atmosphere can be rationally anticipated. Behavior of trace metals during gasification process utilization has been studied by some researchers [20,21]. However, most of these studies are carried with fuels containing relatively higher amount of trace metals, mainly coal. Very few studies [9] have investigated trace metals emission during gasification from fuels with relatively lower content of trace metals such as biomass and thus their behavior is still scarcely known. Before biomass gasification technology is used widely, understanding biomass characteristics and metals content in feedstocks and behavior in production process, input and output streams are vitally important, which is lacking in the existing literature. In this paper for the first time we have presented trace metals emission and distribution from gasification of straw char at 60 kW atmospheric entrained gasifier.

The Karlsruhe Institute of Technology (KIT), Germany has developed a two-stage process "*bioliq*®" for the production of synfuel from biomass [22,23]. The process involves: 1) pyrolysis of straw and other lignocellulosic agricultural byproducts at a regional plant, 2) biosyncrude® gasification and syngas conversion in a central plant. The energy-rich suspension, obtained from pyrolysis plants is gasified in an entrained-flow gasifier and converted into syngas, a chemically reactive mixture of CO and H_2. Pyrolysis is the starting point in the biomass gasification process, *bioliq*®. The biomass char, oil obtained from pyrolysis are gasified to produce fuel gas that can be used to produce heat, electricity, or converted into syngas. In this paper characteristic of feedstocks namely glycol (model fuel) and straw char is presented. Further, experiments were carried out to determine emission concentration of trace metals in syngas and their distribution into particle and gas phases at the atmospheric entrained flow gasifier REGA.

2. Experimental

2.1. Pilot-scale gasifier-REGA

Fig. 1 shows the process configuration of a 60 kW pilot-scale atmospheric entrained flow gasifier REGA (Research Entrained Flow GAsifier) at Karlsruhe Institute of Technology (KIT), Germany. At REGA basic research on the influence of atomization and fuel specification on the syngas quality is carried out. The ceramic tube reactor of the gasifier is 3 m long with inner diameter of 28 cm. The gasifier walls can be heated up to 1200 °C. The adiabatic temperatures were 2000 °C (Test 1–1), 1700 °C (Tests 1–2, 1–3) and 1700 °C (Tests 2–1, 2–2, 2–3). Experiments were carried out with fuels: i) glycol ii) and slurry (glycol + straw char 10 wt.%), with feeding rate of 12.6 kg/h and 12.4 kg/h in Test 1 and 10.05 kg/h in Test 2. The air numbers were 0.57 and 0.46 in Test 1 and 0.52 in Test 2. Air enriched with oxygen (53.8 vol.% and 69.3 vol.% in Test 1 and 41.2 vol.%. in Test 2) were used as gasification agent. Syngas after the reactor was cooled by a tube-in-tube heat exchanger and a scrubber. During experiment, the gasification process was monitored by the reactor temperature and syngas composition. Experimental parameters and syngas composition in this study are summarized in Table 1. The syngas composition differs due to different feedstocks: glycol and slurry and different experimental conditions in Test 1 and Test 2.

2.2. Feedstocks characteristic

The feedstocks employed for biomass gasification were straw char and glycol. In order to achieve well defined operating conditions glycol was considered as model feedstock. The energy-rich straw char (mixed with glycol) obtained from pyrolysis were gasified in an entrained-flow gasifier and converted into synthesis gas, a chemically reactive mixture of CO, H_2 and so on. The main reason to use glycol as a model fuel was the oxygen content, which is comparable to pyrolysis oil from biomass [24]. The physico-chemical characteristics: elemental (C, H, N, S, O) composition, heating value, chlorine content, and volatiles in feedstocks used in the gasification process were analyzed.

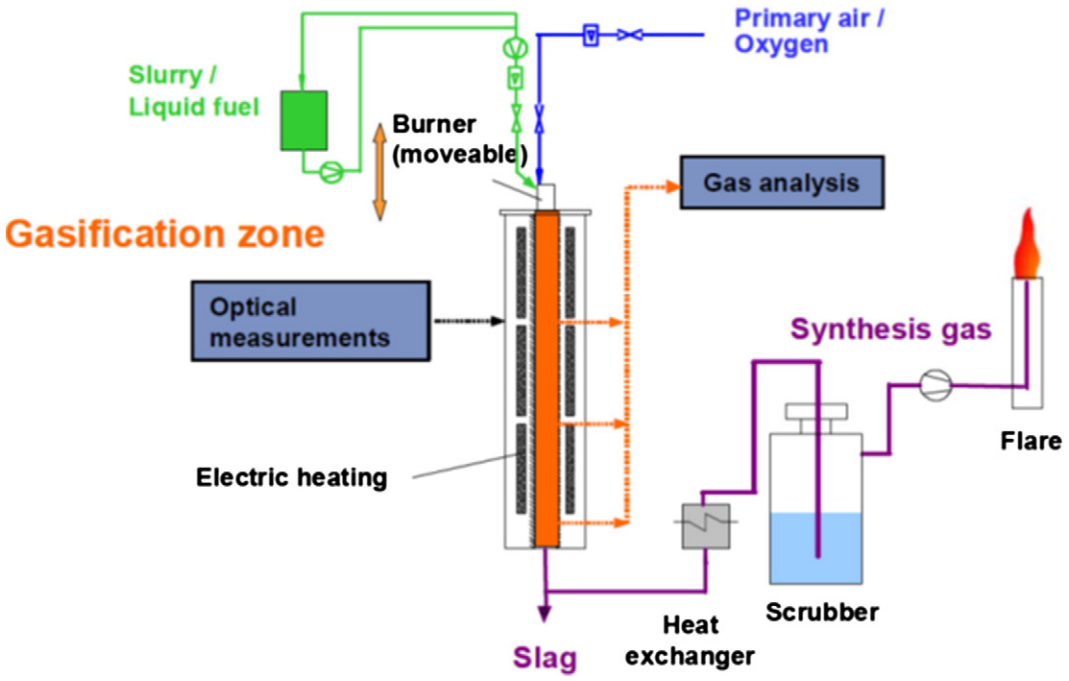

Fig. 1. Process flow diagram of the pilot-scale gasifier REGA [22].