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Sulfur containing organic compounds in the raw producer gas of wood and grass gasification

M.D. Kaufman Rechulski [a], T.J. Schildhauer [a,*], S.M.A. Biollaz [a], Ch. Ludwig [a,b]

[a] General Energy Research Department (ENE), Paul Scherrer Institute (PSI), CH-5232 Villigen PSI, Switzerland
[b] School of Architecture, Civil and Environmental Engineering (ENAC-ISTE), Swiss Federal Institute of Technology at Lausanne (EPFL), Station 2, CH-1015 Lausanne, Switzerland

HIGHLIGHTS

- The method presented allows the measurement of organic sulfur compounds in biomass gasification gas.
- Many organic sulfur species are found in biomass gasification gas, which are usually not reported.
- Only measuring thiophene, benzo[b]thiophene and dibenzothiophene can be misleading.
- The amount of other organic sulfur compounds can be above the limits for catalytic processes.

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ABSTRACT

The detailed description of gas streams in biomass gasification plants is necessary for the correct design and operation of these units. Sulfur containing compounds are usually present in biomass gasification gas, since sulfur is typically found in the feedstock. Sulfur compounds are important contaminants present in the gas streams, since even at concentrations as low as a few ppm they poison catalysts causing significant technical challenges to the production process. The determination of contaminants is often challenging due to their low concentration and the presence of steam and tars in the gas streams. Here a method is presented, which allows the qualitative and quantitative analysis of an extensive number of organic sulfur compounds found in low concentration in biomass gasification gas. The method is a combination of an adequate sampling technique (based on the liquid quench of the sampled gas) and a sensitive analytical equipment (gas chromatograph coupled with a sulfur chemiluminescence detector, CG/SCD). This work shows that several organic sulfur species are found in biomass gasification gas, which are usually not reported, but have to be considered for the design of biomass-based gasification plants. The presence of these compounds is discussed considering the feedstock used, gasification conditions and the sampling technique. Moreover, the results presented here evidence that only measuring thiophene, benzo[b]thiophene and dibenzothiophene in the producer gas can be misleading, since the sum of concentrations of all other organic sulfur compounds could be above the tolerable limits for total sulfur in gasification-based processes.

1. Introduction

1.1. Sulfur compounds in gasification plants

Gasification of lignocellulosic biomass is an efficient route for the production of heat, electricity, fuels and chemicals. Gasification gas has been used as fuel for gas engines [1,2], turbines [2–4], fuel cells [5] and as feed stock for chemical processes, such as methanol synthesis [6,7], methanation [8–10] and Fischer–Tropsch [11] plants. It is important to characterize and quantify the contaminants in the gasification producer gas to properly design and operate the processes using it. If the producer gas is to be used in catalytic reactors, the presence of sulfur compounds is a problem, given that they commonly poison catalysts [12,13]. Tolerances to total sulfur content of the producer gas can be less than 1 ppm_v depending on the application [14].

The techno-economic requirements of the production process and the nature of the sulfur compounds in the producer gas determine the gas cleaning technology which has to be employed [14,15]. Therefore it is highly important to identify and quantify these species. Two gas cleaning technologies are being widely proposed. One is based on a catalytic process and the other on absorber columns [16]. In the first case, catalysts are used to convert

* Corresponding author. Tel.: +41 563102706; fax: +41 563102199.
E-mail address: tilman.schildhauer@psi.ch (T.J. Schildhauer).

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Nomenclature

F	molar flow
f_{gas}	apparent gas phase partition factor
X	molar fraction in the liquid phase
Y	molar fraction in the gas phase

Subscripts and superscripts

$_G$ or *gas*	gas phase
$_{GL}$	mass transfer between gas and liquid phases
$_i$	generic compound
$_{in}$	entering the sampling system
$_L$	liquid phase
$_{out}$	leaving the sampling system

high molecular weight hydrocarbons into hydrogen, carbon monoxide or lower molecular weight hydrocarbons via hydrogenation and/or steam reforming [16]. Analogously, sulfur-containing organic compounds are converted into hydrogen sulfide and similar compounds as for the hydrocarbons [17,18]. Typically, the catalysts are based on transition metals from groups eight to ten, periods four to six [17,18]. One of the challenges currently faced is to design inexpensive catalysts which are active in the presence of both hydrocarbons and sulfur compounds, and can be commercially operated at relatively mild conditions [19].

Absorber columns are another gas cleaning technology often proposed. In this case, the absorbing liquids such as polyethylene glycol dimethyl ether or methanol remove the contaminants [15,20]. Both physical and chemical absorption are possible. A challenge is to design and operate the unit so that it selectively removes the contaminants from the producer gas such as sulfur-containing molecules. Absorber columns usually have to be operated at temperatures below ambient and high pressures. Moreover, the absorbing media might be expensive, have to be recycled and might generate liquid waste (especially if the producer gas cleaned contains steam). As a result, absorber columns usually require large auxiliary units, making the technology economically viable mainly for large-capacity plants, often above the sustainability threshold of biomass-based processes [10]. The selection between these two technologies or others depends on various factors, ranging from the scale of the plant, the characteristics of the producer gas, the requirements of the downstream units and the availability of the technology [15,18]. They have however an important impact on the techno-economic viability of the overall process.

The sulfur content of the producer gas of gasifiers has been studied by several authors, both for coal [21–23] and biomass [14,24–26] feedstocks. The knowledge accumulated from coal gasification assists the understanding of the processes involved in biomass gasification, since the former case has been investigated in detail and the physicochemical conditions of the gasifiers can be similar. It is well known that H_2S is found in higher concentration in the producer gas, followed by COS and CS_2 [22]. For coal gasification, the presence of other organic compounds such as mercaptans, thioethers and thiophenic species has been extensively reported [21]. Regarding biomass gasification, little information is available on organic sulfur species other than CS_2 and thiophene [24].

When designing the desulfurization of the producer gas of biomass gasification, most authors assume that H_2S is the only sulfur-containing compound present in the gas, due to its relative high concentration and the difficulty in measuring other sulfur compounds [27–29]. Considering the long term operation of these plants, this assumption can be misleading, since technologies for removal of H_2S are not necessarily effective with other sulfur-containing compounds [24]. The result is that the total sulfur content in the gas might remain above the technical recommendations. The goal of this work is to show that several organic sulfur species are found in biomass gasification gas and therefore to provide a more representative input for the design of biomass-based gasification plants.

1.1.1. Sulfur compounds in gasification fuels

In order to understand the presence of sulfur species in the producer gas, it is important to take into account the sulfur content of gasification fuels.

1.1.1.1. Coal. It is generally accepted that sulfur found in coal can be divided into three categories: pyrites, sulfates and organic sulfur [30]. The distribution varies greatly with the origin and with the rank of the coal [31]. The total amount of sulfur in coal can be as high as tens of weight percent, usually equally divided between organic and inorganic sulfur-containing compounds [30]. According to Calkins [30], inorganic sulfur in coal is predominately pyrite (FeS_2). Other sulfide minerals include dimorphic mercasite (FeS_2), sphalerite (ZnS), galena (PbS) and others [30]. Sulfates are generally found in ionic form such as barite ($BaSO_4$), gypsum ($CaSO_4{\cdot}2H_2O$), anhydrite ($CaSO_4$) and others [30]. The organic sulfur compounds can be grouped in aromatics and non-aromatics. Examples of aromatic sulfur species are thiophene, benzo[b]thiophene, dibenzothiophene, their methylated and/or partially hydrogenated thiophenic analogs as well as thiophenic species containing heterocyclic atoms among others [30,32]. Non-aromatic sulfur structures are mercaptans, thioethers and disulfides [30]. Organic sulfur in coal has been reported to be 40–70 % of thiophenic structure [31].

1.1.1.2. Vegetable biomass. Sulfur is a secondary macronutrient for plants, it is essential for plant growth. It is mainly taken up by the roots in the form of sulfate $\left(SO_4^{2-}\right)$ or by the canopies as SO_2 [33]. SO_4^{2-} is transported to the leaves by the xylem and phloem [34], re-distributed to younger leaves at the shoots, where it is reduced to sulfide and then incorporated into amino acids. The most important of them are cysteine and methionine, which will form proteins. In vegetative plants, sulfur is concentrated in apices of shoots and roots, while in generative plants, sulfur is required at reproductive tissues [33,35]. As much as 65% of the total sulfur in plants is inorganic, mainly as sulfates [36]. Woody biomass contains little protein, the total sulfur content in trees is usually 0.1–0.3 g per kg of dry matter. In leafy biomass of agricultural interest, the sulfur content is usually one order of magnitude higher [37].

In wood, the presence of organic sulfur is dependent on the stem region analyzed, generally sulfur content is lower in the core of trunks than in the outer layers (bark) [38]. Struis et al. [39] reported the presence of organic disulfide, methylthiol and organic sulfonate or organic sulfate in samples of Norway spruce, both in the sap and heartwood, but in different concentrations. Thiophenic compounds are not commonly found in woody biomass. In vegetable biomass, they have been found in roots and seeds of *Tagetes* species such as *Tagetes Erecta* and *Tagetes patula* [40] and in the roots of *Echinops ellenbeckii* [41], which are herbaceous flowering plants belonging to the daisy family.

1.1.2. Sulfur in the producer gas of coal and biomass gasification

In gasifiers, sulfur atoms from the fuel are distributed in the gasification products. Sulfur-containing species are found in the