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The fate of SOFC anodes under biomass producer gas contaminants

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ABSTRACT

Biomass gasification integrated with Solid Oxide Fuel Cells (SOFCs) offers a tremendous opportunity to generate highly efficient power in sustainable and environmental friendly manner. The comprehensive survey of the up-to-date literature on the influence of producer gas contaminants (particulates, alkali metals, tar, H_2S and HCl) on SOFC anodes presented in this review reveals that state-of-the-art Ni/YSZ anodes are less tolerant to the contaminants and more stringent cleaning is required for them as compared to Ni/GDC anodes, while other anodes have been scarcely studied. The most striking finding is that Ni/GDC anodes seem to be rather more tolerant to the contaminants as recently understood. This remarkable opportunity needs to be further explored via detailed experiments which would lead to design the economically viable gas cleaning systems. The available gas cleaning technologies are also analysed and the most suitable cleaning options for each of the contaminant are suggested.

1. Introduction

The global energy demand is rapidly increasing and approximately 80% of the global primary energy supply will be covered by the fossil fuels by 2040 [1]. The fear of their limited availability and their concentration in few countries lead to the uncertainty in their prices. At the same time the use of fossils is increasing the negative impact on the environment. The CO_2 emissions have increased by 44% by 2011 as compared to 1993 levels [2] resulting in climate change and global warming. Due to these reasons it is becoming crucial to utilize the alternative energy sources to reduce the dependence on fossil fuels.

Biomass is considered one of the potential sustainable energy sources which is available worldwide and considered as environment friendly being carbon neutral. Generally fossil fuels are mainly converted into electricity. At present 77.2% accounts for the electricity generation out of the total energy consumption covered by fossil fuels [3]. Demand of electricity is expected to increase 2.3–3.4% annually in the coming decade [1]. Among the various biomass conversion processes, biomass gasification in conjunction with high temperature Solid Oxide Fuel Cells (SOFCs) has recently received significant attention since it offers the possibility of highly efficient electricity production as well as heat as a by-product in an environment friendly manner. An advanced biomass gasification integrated with SOFC system offers the opportunity to reach significantly high electrical efficiencies up to 55% even in small modular solutions as compared to traditional large power plants which reach 40% electrical efficiency. The system efficiency can reach even higher up to 60% or more when the exhaust heat from SOFC is used in combined cycle applications or for cogeneration [4].

Gasification converts the biomass into combustible mixture of gases referred to as producer gas consists of mainly hydrogen, carbon dioxide, carbon monoxide, methane, nitrogen, water vapor and additionally minor contaminants. SOFC can electrochemically convert H_2 and CO present in the producer gas into electricity while CH_4 is internally reformed into more H_2 and CO. This is due to reason that SOFC operates at high temperature and contains nickel catalyst in their anode. The contaminants present in the producer gas from wood gasification include particulates, tar, alkali metals, sulfur compounds mainly H_2S, halides mainly HCl and nitrogenous compounds mainly NH_3. Ammonia also dissociates to form H_2 at the anode and hence is a fuel for SOFC [5,6]. The remaining contaminants could reduce the lifetime of the components of the biomass gasification-SOFC systems due to corrosion and depositions and at the same time can damage catalysts especially Ni of anode hence reducing the performance of the

Abbreviations: ASR, Area Specific Resistance, $\Omega\ cm^2$; CGO, Ceria Gadolinia Oxide; COS, Carbonyl Sulfide; EDS, Energy Dispersive Detector; ESP, Electrostatic Precipitators; FICFB, Fast Internally Circulating Fluidized Bed; HHV, Higher Heating Value; PAH, Poly-Aromatic Hydrocarbons; ppm, Parts per Million volume (in this text); ppmw, Parts per Million Weight; Ni/YSZ, Nickle/Yttria-Stabilized Zirconia; Ni/GDC, Nickle/Gadolinia Doped Ceria; LHV, Lower Heating Value; LSM, Sr Doped Lanthanum Manganite; RF, Radio Frequency; ScSZ, Scandia-Stabilized Zirconia; SEM, Scanning Electron Microscopy; S/C, Steam-to-Carbon ratio; WGSR, Water Gas Shift Reaction

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SOFC. The producer gas from the gasifier would need to be cleaned sufficiently in order to avoid any degradation caused in the SOFC. Anyhow, various cleaning methods downstream are available for the cleaning of the producer gas for SOFC.

Biomass gasification technology and SOFC are briefly discussed in Sections 2 and 3 respectively. Section 4 focuses on the most recent and relevant literature regarding the impact of producer gas contaminants on SOFC anodes. The achievements attained on the understanding of various aspects of the influence of particulates, alkali metals, tar, H_2S and HCl on SOFC anodes under different operating conditions are summarized. Based on the available information, the probable tolerance limits of these contaminants are concluded and their most suitable cleaning options are also suggested. Analysis of the reviewed literature and the future research perspective is given in Section 5 before the paper concludes in Section 6.

2. Biomass gasification technology

In thermo-chemical process of gasification, the biomass is converted into a gaseous mixture (producer gas) through partial oxidation inside a gasifier. In successive steps, biomass is dried and pyrolysed into gases and char which react further with gasifying agent hence producing producer gas as shown in Fig. 1. Composition of the producer gas is mainly composed of H_2, CO, CH_4, CO_2, N and water vapor along with trace contaminants which include particulates, tar, alkali metals, sulfur compounds (H_2S), halides (HCl) and nitrogen containing compounds (NH_3). The composition of the producer gas generally depends upon the type of biomass feedstock, gasifier type, gasifying agent and operating parameters of the gasification process. Specific to contaminants, the amount of particulates and tar in the producer gas mainly depend upon the type of the gasifier used, while alkalis, H_2S and HCl mainly depends on the type of biomass used as a feedstock.

Biomass is non-fossilized and biodegradable organic material from plant, animal and micro-organisms mainly characterized into four main types, woody plants, herbaceous plants, aquatic plants and manures [7]. Woody biomass and herbaceous biomass with low moisture content (< 40 wt%) are considered most suitable for thermo-chemical conversion of biomass [8]. For biomass gasification integrated with SOFC systems, the selected biomass feedstock must have appropriate physical and chemical properties. Amongst the physical properties, low moisture content and high bulk density are desirable. Thermal efficiency of the gasification reduces if the moisture content is more than 40 wt% [9] due to the energy used for biomass drying inside the gasifier. This also reduces the reaction temperature which results in producer gas with higher tar levels and low LHV [10]. The density on the one hand affects the freight and transportation and on the other hand hinders feeding to the gasifier. As far as chemical properties are concerned, the biomass fuels with high calorific value, low ash, chlorine and sulfur content are to be selected. Where high ash content can cause agglomeration, erosion and corrosion problems, the high sulfur and chlorine content can end up as high H_2S and HCl concentrations in the producer gas which needs to be pre-treated before the SOFC (see Sections 4.4 and 4.5). Table 1 shows the physical and chemical properties of some biomass feedstocks.

The available gasifier systems for biomass gasification are categorized as (i) fixed bed and (ii) fluidized bed gasifiers. Sequential steps of gasification inside the fixed bed gasifier along with the formed products during each step are visualised in Fig. 1. Fixed bed gasifiers are further divided into updraft and downdraft gasifiers.

In updraft (countercurrent) gasifiers [13–15], the biomass moves downward from top while gasifying agent moves upward from bottom and producer gas is collected from the top of the gasifier (Fig. 1a). As the producer gas passes through the low temperature pyrolysis and drying zone, it exits with comparatively high tar load as compared to downdraft gasifiers, although with lower particulate load due to the filtration on the way up. In downdraft (concurrent) gasifiers [16–19], both biomass and gasifying agent (mostly air [20]) move from the top to the bottom of the gasifier (Fig. 1b). The producer gas exits at the bottom after passing through the high temperature oxidation and reduction zones, which results in relatively clean gas from tar as compared to updraft gasifiers.

Unlike fixed bed gasifiers, the biomass fuel and bed material (sand/catalyst) is fluidized with the help of excessive air/gas in fluidized bed gasifiers [21–23] and circulating bed gasifiers [24–26]. These types operate at uniform but lower temperature (< 900 °C) to avoid ash melting. But tar and particulate load in the producer gas is high from fluidized bed gasifiers as compared to downdraft gasifiers. The

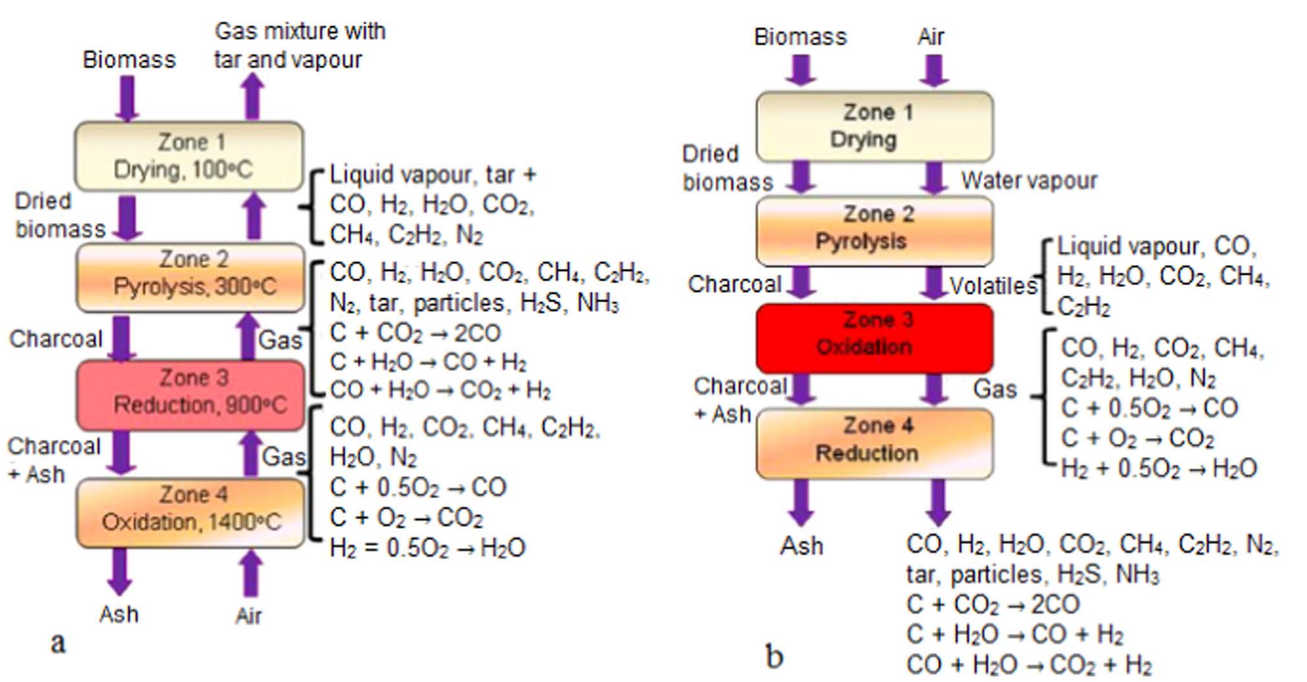

Fig. 1. Sequential steps of gasification in (a) updraft and (b) downdraft gasifier [12].