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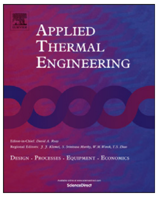

The fate of tars under solid oxide fuel cell conditions: A review

Ming Liu*, P.V. Aravind*

Process and Energy Department, 3ME, Delft University of Technology, Leeghwaterstraat 44, 2628CA Delft, Netherlands

HIGHLIGHTS

- Latest studies on the interaction between tar and SOFC are reviewed.
- The fate of tars under SOFC conditions are studied.
- Tar classification and model tar compound for SOFCs are discussed.
- Tar removal methods are reviewed and discussed.

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ABSTRACT

Biomass is a renewable and low-carbon energy source. Its use via gasification is an attractive way for solid oxide fuel cells (SOFCs). However, tars are the major bottleneck as tars produced from biomass gasification may have detrimental effects on the SOFC. This work comprehensively reviews the fate of tars under SOFC conditions. Specifically, it summarizes tar evolution during biomass gasification, discusses currently available studies on the interaction between tars and SOFC anodes or anode materials. In addition, readily available gas cleaning technologies for reducing tar content are discussed. Future research perspectives are also addressed.

1. Introduction

Solid oxide fuel cells (SOFCs), often with Ni-based anode materials, commonly operate at 600–1000 °C. The catalytic anode material and high operating temperature make SOFCs can potentially work with other fuels, such as methane, biosyngas, in addition to hydrogen. As an option for hydrogen/syngas production, biomass gasification is a promise because of the high conversion efficiency and carbon neutrality [1]. System thermodynamics indicate that the electrical efficiency of biomass-to-electricity can be as high as 70% [2]. Therefore, biomass-powered SOFC energy systems are a promise to meet a sustainable energy future. However, tar, which is unavoidable during biomass gasification, inhibits the development of such energy systems because when presenting within the fuel tar may deteriorate all the downstream processes and equipments including SOFCs. Tars can condense and block the delivering pipe, get reformed, and are also likely to cause carbon deposition. It is clear that tar condenses at ambient temperature; however, the fate of tars and their effects under SOFC conditions are not fully clear.

This work summarizes the achievements obtained thus far for understanding the tar relevant issues and their fate under SOFC conditions. Specifically, it summarizes tar evolution during biomass gasification, discusses the effects of different types of anodes or anode materials on biosyngas use, and addresses the role of SOFC conditions, including operating temperature, cell voltage, steam concentration, and tar components, among others, on the interaction between tars and SOFC anodes/anode materials. In addition, available gas cleaning technologies for reducing tar content are discussed. Future research perspectives on the issues of tars for the combination with SOFCs are also addressed.

2. Background

2.1. Tar

Tar is a complex amalgamation of condensable hydrocarbons, including one-ring to 5-ring aromatic compounds, other oxygen-

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* Corresponding authors. Tel.: +31 152786987; fax: +31 152782460.
E-mail addresses: ming.liu@tudelft.nl, lming928@hotmail.com (M. Liu), p.v.aravind@tudelft.nl (P.V. Aravind).

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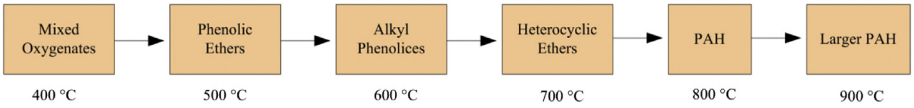

Fig. 1. Tar maturation scheme (redrawn based on Ref. [5]).

containing hydrocarbons, and complex polycyclic aromatic hydrocarbons (PAH) [3]. Tar could be defined as an organic compound with a molecular weight larger than benzene [4]. Lighter tar compounds generally are unavoidable in biomass gasification because pyrolysis always occurs and higher tar can be cracked/reformed into lighter tars. Tars formed during biomass gasification are due to a series of complex reactions, and their compositions are highly dependent on the operating conditions, particularly the temperature, as depicted in Fig. 1 [5].

The amount of tar in a gas stream is strongly dependent on the gasification technology applied. It can be as high as several hundred g Nm^{-3} for updraft gasifiers, whereas it is around 15 g Nm^{-3} for fluidized bed gasifiers and is less than 2 g Nm^{-3} for downdraft gasifiers [6]. Air gasification produces low reactivity tars, whereas steam gasification produces a liquid tar with a low molecular weight [7]. Tar composition can vary substantially when different gasification technologies and operating conditions are employed. In general, tar is predominantly comprised of benzene and toluene which account for 50% as demonstrated in Table 1 [5,8,9].

Tar would normally condense at ambient temperature. The condensate may deposit on the piping and in other downstream component such as heat exchangers, and further likely lead to shut-down of the gasifier and damage the SOFCs. However, reforming of tars (often associated with the water–gas shift reaction (WGS), Eq. (4)) can occur under dry and wet conditions, which respectively use CO_2 (Eq. (1)) and steam (Eqs. (2) and (3)). Reforming process is highly endothermic and favors the forward reaction at elevated temperature, but it encounters the risk of carbon deposition via decomposition (Eq. (5)), the Boudouard reaction (Eq. (6)) and/or reversible carbon reforming (Eq. (7)). Carbon deposited can be in the form of pyrolytic, encapsulating and whisker in the steam reforming of tars/hydrocarbons [10]. Similar to graphite, pyrolytic carbon is produced from the decomposition of hydrocarbons, but differs from graphitic carbon in disordered layers. Encapsulating carbon is in a "gum" CHx film or a few layers of graphite that covers the catalyst. Whisker type, considered the most destructive to catalysts, is generated by the reaction of hydrocarbons or CO at one side of the nickel particle with the nucleation of graphitic carbon on the other side of the nickel particle [10]. Whisker carbon is a main product of carbon formation in steam reforming with metal-based catalysts, and possesses a high mechanical strength which can destroy the catalyst particle [11].

Table 1
Typical composition of tars from biomass gasification [5,8,9].

Compound	Composition (wt.%)
Benzene	37.9
Toluene	14.3
Other one-ring aromatic hydrocarbons	13.9
Naphthalene	9.6
Other two-ring aromatic hydrocarbons	7.8
Three-ring aromatic hydrocarbons	3.6
Four-ring aromatic hydrocarbons	0.8
Phenolic compounds	4.6
Heterocyclic compounds	6.5
Others	1.0

$$C_mH_n + mCO_2 \rightarrow n/2H_2 + 2mCO \tag{1}$$

$$C_mH_n + mH_2O \rightarrow (m + n/2)H_2 + mCO \tag{2}$$

$$C_mH_n + 2mH_2O \rightarrow (2m + n/2)H_2 + mCO_2 \tag{3}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

$$C_mH_n \leftrightarrow mC + \frac{n}{2}H_2 \tag{5}$$

$$2CO \leftrightarrow C + CO_2 \tag{6}$$

$$CO + H_2 \leftrightarrow C + H_2O \tag{7}$$

2.2. SOFC

2.2.1. Working principle

In an SOFC with an oxide-ion-conducting electrolyte, the fuel enters the anode chamber and is oxidized at certain sites. Oxygen enters the cathode chamber and is ionized and transported through the electrolyte to the anode (Fig. 2). The anode disperses the fuel gas over its interphase with the electrolyte, catalyzes the electrochemical reactions, and conducts the electrons that are freed. These electrons flow through an external circuit, delivering electric power. The cathode distributes the oxygen at its interphase with the solid electrolyte, and conducts the electrons from the external circuit. Oxide ions pass through the solid electrolyte to the anode. The solid electrolyte contains many oxygen vacancies which allow oxygen ions to pass through. The solid electrolyte mainly prevents the two electrodes to come into electronic contact by blocking the electrons, and allows the flow of oxide ions from the cathode to the anode and to balance the overall electrical charge. A schematic view on the function of an SOFC is shown in Fig. 2.

In addition to operating conditions, the electrochemical performance of an SOFC is highly dependent on the material properties and the electrode microstructure. The electrolyte should be ionic conductive and minimum electronic conductive, whereas the

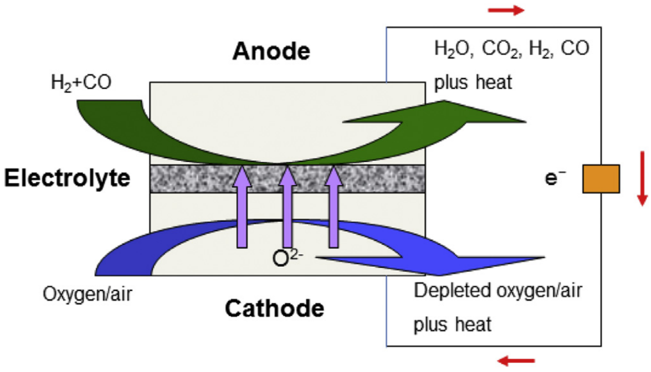

Fig. 2. A view of SOFC working principle.