



Fate of sulphur during simultaneous gasification of lignin-slurry and removal of hydrogen sulphide over calcium aluminate supported nickel oxide catalyst



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ABSTRACT

The simultaneous process of synthesis gas production via lignin slurry gasification and high-temperature removal of hydrogen sulphide from the synthesis gas over calcium aluminate supported nickel oxide catalyst (NiO/CaAl₂O₄) was investigated. The goal of this study was to clarify the effects of the operating temperature (750–950 °C), moisture content of the lignin slurry (73–90 wt%), and catalyst loading (0.00–0.61 g-catalyst/g-feedstock) on the sulphur balance of the process and to determine the appropriate catalyst loading with cleaner biosyngas via utilisation of the sensible heat for smaller additional heat, which is maintained at the temperature of the gasifier. The biosyngas generated from gasification of lignin slurry, which contained hydrogen sulphide (H₂S) and carbonyl sulphide (COS), was subjected to sulphur removal catalysed by NiO/CaAl₂O₄; a sulphur yield on NiO/CaAl₂O₄ of 0.14 mmol/g-lignin was achieved at the moisture content of 80.0 wt%, the reaction temperature of 900 °C, and the catalyst loading of 0.16 g-catalyst/g-feedstock. For the catalytic H₂S removal system applicable to solid oxide fuel cells, the performance efficiency was introduced to discuss the optimal catalyst loading amount; the performance efficiency was 0.63–0.72 S-mol%·g-lignin/kJ for the catalytic operations while 0.33 S-mol%·g-lignin/kJ for non-catalytic operation.

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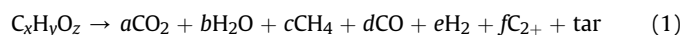
1. Introduction

Biogenous synthesis gas (biosyngas) is attractive because of the growing need for reduction of fossil diesel fuel use, as a sustainable hydrogen (H₂) resource for fuel cells, and for mitigation of carbon dioxide emission. There are two routes for biomass conversion into hydrogen-rich gas, namely (i) Thermo-chemical conversion and (ii) Bio-chemical/biological conversion. In the several kinds of biomass-based H₂ production methods as presented in Table 1, the biomass gasification methods are anticipated to become a dominant technology for H₂ production based on the B1-H₂ scenario developed as the Environmentally Compatible Energy Strategies (ECS) project at International Institute for Applied Systems Analysis

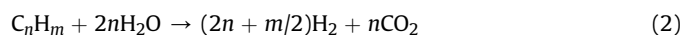
(IIASA) (Barreto et al., 2003). Hydrogen is consumed in fuel cells, such as polymer electrolyte fuel cells (PEFC) and solid oxide fuel cells (SOFC); thus, the demand for H₂ should increase with progressive development of this technology (Balat and Kirtay, 2010).

At the same time, sulphur compounds such as hydrogen sulphide (H₂S) and carbonyl sulphide (COS) are formed during bio-hydrogen production processes. The reactions of biomass gasification can be divided into gas formation and gas equilibrium stages. Following reaction pathways are possible (Moon et al., 2013):

(Pyrolysis)



(Steam-tar reforming)



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Table 1
Biomass-based hydrogen production methods.

Method	Condition (Bičáková and Straka, 2012; Kalinci et al., 2009)	Characteristics (Bičáková and Straka, 2012; Kalinci et al., 2009)	Reference
<i>Thermo-chemical conversions</i>			
Pyrolysis	$T = 500\text{--}900\text{ }^{\circ}\text{C}$	in the absence of air	Al-Rahbi et al. (2016)
Gasification	$T = 800\text{--}1400\text{ }^{\circ}\text{C}$	with or without oxygen	Sun et al. (2013)
Supercritical water gasification	$T > 374\text{ }^{\circ}\text{C}$, $p > 22\text{ MPa}$	reaction in water beyond critical point	Deniz et al. (2015)
<i>Biological conversion</i>			
Fermentative hydrogen production	Ambient temperature and atmospheric pressure	with anaerobic (dark fermentation) and photoheterotrophic (light fermentation) microorganisms using carbohydrate rich biomass	Kumar et al. (2015); Liu et al. (2015)
Photosynthesis process	Ambient temperature and atmospheric pressure	in the presence of many phototrophic organisms, such as purple bacteria, green bacteria, Cyanobacteria and several algae with the aid of solar energy	Nyberg et al. (2015); Hwang et al. (2014)
Biological water gas shift reaction	Ambient temperature and atmospheric pressure	with photo heterotrophic bacteria such as <i>Rubrivivax gelatinosus</i>	Yang et al. (2012)

T = temperature, p = pressure.

(Char gasification)



(Boudouard)



(Methanation)

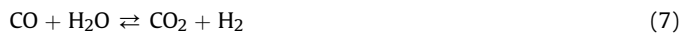


(H₂S formation)



The produced sulphur and biosyngas proceed to equilibrium following the reactions:

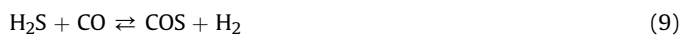
(Water-gas shift)



(Steam-methane reforming)



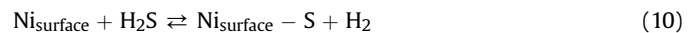
(H₂S-CO equilibrium)



The crude biohydrogen produced from gasification of biomass must be cleaned to obtain pure biohydrogen. The desulphurisation processes can be categorised into three different methodologies, i.e. adsorption (hot-gas cleaning or dry desulphurisation), absorption (wet desulphurisation), conversion sulphur removal as shown in Table 2. The dry desulphurisation cleaning approach has several advantages: i) the sensible heat of the product gas is available for use in the gasification operation or processes at a subsequent stage and ii) the drain of the process is more easily treated (Hanaoka et al., 2004). In fact, an analysis of the market potential and economics presented by McMullan et al. (2001) showed that a significant economic advantage was derived from the increase in efficiency and the reduced capital cost of heat exchangers, gas cleaning systems, and water treatment for a Shell gasifier for an entrained flow-based integrated gasification combined cycle (IGCC)

system compared with that for wet gas cleaning. Hot gas cleaning is superior to wet gas cleaning in terms of the efficiency (in %LHV) as well as the cost of electricity (in EURO/MWh).

Nickel oxide-based catalysts are often used as gasification and/or steam reforming catalysts; however, these catalysts are prone to deactivation of the active sites by hydrogen sulphide during the gasification process (Struis et al., 2009). These catalysts, however, can be used as high-temperature desulphurisation catalysts because their operating temperature is relatively high (Vamvuka et al., 2004). The main desulphurisation reaction that occurs with the Ni type catalyst, as proposed by Ashrafi et al. (2008) is:



which is the surface reaction (two-dimensional surface sulphide) that occurs at lower sulphur concentration. From the perspective of price, the nickel-based catalysts are attractive for sulphur removal due to the lower price. During desulphurisation using calcium oxide (CaO) adsorbents, the concentrations of H₂S and COS in syngas depend on the operational conditions, such as the operating temperature, steam fraction, and catalyst amount (or molar ratio of CaO to sulphur) (Fujioka et al., 1994). Moreover, several investigations similarly reported that sulphur removal depends on the operating temperature (Kienberger et al., 2013). Thus, the influence of such factors on the gasification and desulphurisation operations should be investigated.

Thus, the goal of this study is to utilise the sensible heat cascade for the desulphurisation of biomass-gasification-derived biosyngas. As the first step, high-temperature sulphur removal from biosyngas in the furnace is proposed using a catalyst comprising nickel oxide supported by calcium aluminate (NiO/CaAl₂O₄). In this study, the effects of the operating temperature ($T = 750\text{--}950\text{ }^{\circ}\text{C}$), moisture content in the lignin slurry (MC = 73–90 wt%), and catalyst loading (CL = 0.00–0.61 g-catalyst/g-feedstock abbreviated as g-cat/g-feed) on the production of sulphur from gasification of wet-lignin are clarified to determine the biosyngas sulphur yield/concentration and sulphur distribution (or sulphur balance before and after the gasification reaction) in the products. Then, subsequent sulphur removal on the catalyst surface is also investigated. Based on the results, we discuss a system for the removal of sulphur compounds during biohydrogen production, which may be applicable to SOFC operation. For the catalytic H₂S removal system, the performance efficiency, the characteristic index for both sulphur removal and thermal efficiency (or additional external heating), is introduced to discuss the optimal catalyst loading amount.

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