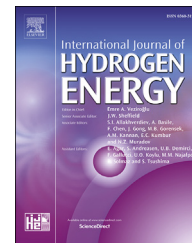




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# Desulfurization and tar reforming of biogenous syngas over Ni/olivine in a decoupled dual loop gasifier

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## ARTICLE INFO

### Article history:

Received 20 March 2017

Received in revised form

27 April 2017

Accepted 5 May 2017

Available online 23 May 2017

### Keywords:

Biomass gasification

Desulfurization

Tar reforming

Nickel catalyst

## ABSTRACT

For the production of bio-SNG (substitute natural gas) from syngas of biomass steam gasification, trace amounts of sulfur and tar compounds in raw syngas must be removed. In present work, biomass gasification and in-bed raw gas upgrading have been performed in a decoupled dual loop gasifier (DDLG), with aggregation-resistant nickel supported on calcined olivine (Ni/olivine) as the upgrading catalyst for simultaneous desulfurization and tar elimination of biogenous syngas. The effects of catalyst preparation, upgrading temperature and steam content of raw syngas on sulfur removal were investigated and the catalytic tar reforming at different temperatures was evaluated as well. It was found that 850 °C calcined Ni/olivine was efficient for both inorganic-sulfur (H<sub>2</sub>S) and organic-sulfur (thiophene) removal at 600–680 °C and the excellent desulfurization performance was maintained with wide range H<sub>2</sub>O content (27.0–40.7%). Meanwhile, tar was mostly eliminated and H<sub>2</sub> content increased much in the same temperature range. The favorable results indicate that biomass gasification in DDLG with Ni/olivine as the upgrading bed material could be a promising approach to produce qualified biogenous syngas for bio-SNG production and other syngas-derived applications in electric power, heat or fuels.

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## Introduction

Biomass as a sustainable and CO<sub>2</sub>-neutral feedstock can be converted to heat, electricity or fuels [1–3]. Production of substitute natural gas (SNG) from biomass is attractive because that the SNG could be distributed in the existing gas grid and thus facilitate biomass logistics by eliminating the need for long transportation distances [4,5]. Biomass steam gasification in dual bed gasification systems leads to producer gas, the biogenous syngas, with a relatively high content of H<sub>2</sub> and CH<sub>4</sub> as well as a low content of N<sub>2</sub>. Such

properties are necessary for an efficient Bio-SNG production [6–8]. The syngas contains still trace amounts of sulfur and tar compounds which could poison the catalyst and deteriorate the operation of the downstream methanation [9]. Therefore, low temperature scrubbing was commonly adopted before methanation to remove the tar, sulfur and even moisture [8,10], in which the syngas was cooled, cleaned at relatively low temperature, reheated and then sent to methanation reactor. Compared to the gasification–scrubbing–methanation process, an integrated gasification–methanation process with hot gas-cleaning

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<http://dx.doi.org/10.1016/j.ijhydene.2017.05.041>

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could significantly improve the efficiency of the SNG production by avoiding cooling and reheating of the syngas and lower the investment-costs as well [4,5,11].

Tar removal from the hot syngas by tar steam reforming at 600–1000 °C utilizing its steam content and sensible heat [12] was generally achieved over in-bed catalysts, i.e. the active bed materials (olivine, dolomite, Ni/olivine, Ni/MgO, etc.) of the gasifier [13–15], or over the secondary catalyst bed (Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/dolomite, char, etc.) downstream the gasifier [16–19]. The relatively cheap and efficient nickel catalysts are attractive in these processes. However, they are vulnerable to sulfur-poisoning below 900 °C [20]. A chemisorption layer of hydrogen sulfide over supported nickel catalyst and bulk sulfide (Ni<sub>3</sub>S<sub>2</sub>) could be formed at moderate temperature, in low and high P<sub>H<sub>2</sub>S</sub>/P<sub>H<sub>2</sub></sub> ratios, respectively [21].

The excellent affinity between nickel and sulfur compounds, typically in terms of chemisorption of sulfur on the nickel surfaces rather than the conversion of Ni to Ni sulfides [22,23], could be used for deep sulfur removal from hot syngas. Methanation of H<sub>2</sub>S-containing feeding gas over nickel catalysts showed that the introduced H<sub>2</sub>S was almost completely eliminated at 200–400 °C [24], along with the catalyst deactivation by sulfur-poisoning [25]. H<sub>2</sub>S concentration was decreased to below 20 ppmv after raw syngas (with a few hundred ppmv of H<sub>2</sub>S) going through the secondary tar reforming catalysts bed (Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/CaO–Al<sub>2</sub>O<sub>3</sub>) [26–28], although a poor desulfurization behavior was found when the nickel catalysts were introduced in gasifier, mainly due to the severe conditions of the gasifier [26]. Moreover, nickel was considered to be active for organic sulfur elimination as well [29,30] and might be capable of simultaneous removal of inorganic and organic sulfur compounds, which is superior to the commonly ZnO-based desulfurizers [31].

However, the development of regenerable Ni-based desulfurizer has been impeded by the strong tendency of nickel to aggregate during the regeneration process, which causes loss in metal surface area and sulfur capacity [32]. Some efforts have been tried to achieve discrete nickel deposition on/in the inert structure to restrain its sintering. NiAl<sub>2</sub>O<sub>4</sub>-based glass-ceramic, with NiAl<sub>2</sub>O<sub>4</sub> phase as clusters dispersed within the glassy matrix, showed improved resistance to aggregation and a high conversion of H<sub>2</sub>S at 600 °C [33]. Ni/SBA-16, with nickel isolated and stabilized in cubic structured mesoporous silica SBA-16, was prepared to suppress the sintering and sulfur capacity loss, which could remove H<sub>2</sub>S from hot syngas to less than 60 ppbv with 3 wt.% sulfur loading capacity at 300 °C throughout five-cycle test [32]. NiO was grafted with or integrated into calcined olivine support (Ni/olivine) to prevent attrition, sintering and volatilization of the nickel [14,34,35]. The Ni/olivine as a cheap steam-reforming nickel-based catalyst could provide high stability and resistance for repeated high temperature processing in oxidizing (900 °C) and reducing (850 °C) atmosphere during circulation [36].

To suppress nickel aggregation by intensifying metal-support interaction, in present study, a difunctional Ni/olivine has been prepared for both desulfurization and tar reforming of biogenous syngas. A novel decoupled dual loop gasifier (DDLG) has been developed to facilitate biomass gasification and in-bed hot gas upgrading. In the DDLG,

different from the common dual bed gasification systems [6,7,37,38] and our early set-ups [39,40], an additional upgrading loop parallel with the gasification–combustion loop has been introduced. In this way, raw gas upgrading, i.e. desulfurization and tar reforming, could be optimized independently. Specifically, inorganic-sulfur and organic-sulfur removal, tar reforming and water gas shift reaction (WGS) have been investigated in DDLG with Ni/olivine as upgrading bed material.

## Experimental

### Materials

A natural occurring olivine from the Chinese city of Yichang, containing (Mg<sub>x</sub>Fe<sub>1-x</sub>)<sub>2</sub>SiO<sub>4</sub> as the main phase with small quantities of MgSiO<sub>3</sub> and FeO<sub>x</sub> species [35], was used as the catalyst support after calcination at 1000 °C for 4.5 h. The catalyst with 6 wt.% Ni supported on the olivine, marked as Ni/olivine-1300, was prepared by incipient wetness impregnation of the olivine with an aqueous solution of nickel nitrate, followed by calcination at 1300 °C for 4.5 h, and used as the desulfurizer. The catalyst with the same Ni loading on the olivine, i.e. Ni/olivine-850, was prepared by the incipient wetness impregnation followed by calcination at 850 °C for 4.5 h, and used as both the desulfurizer and the tar reforming catalyst. The biomass feedstock used in this work was pine sawdust from Dalian City, Liaoning Province and its proximate and ultimate analysis are presented in Table 1. The pine sawdust was crushed and sieved to 20–40 mesh and dried for 4 h at 105–110 °C before tests.

### Desulfurization of sulfur-containing gas over Ni/olivine in fixed-bed reactor

The hot gas desulfurization was investigated at atmospheric pressure in an electric heated fixed-bed tube reactor with 10 mm inner diameter. The desulfurizer was placed in the middle of the reactor embedded with a K-type thermocouple to monitor the reaction temperature. The feeding gases, i.e. a simulation gas mixture (SG, 15.1 ppmv H<sub>2</sub>S and 19.7 ppmv thiophene in Ar, provided by Dalian Special Gases Co., Ltd.) and H<sub>2</sub>, were controlled by mass flow controllers and admitted to the reactor at an hourly space velocity of 5000 h<sup>-1</sup>. The removal of H<sub>2</sub>S and thiophene, i.e. the most abundant components of inorganic-sulfur and organic-sulfur in the biogenous syngas [20], was used for the evaluation of both inorganic-sulfur and organic-sulfur elimination over Ni/olivine. Sulfur compounds (H<sub>2</sub>S and thiophene) concentrations in the effluent gas were determined by a gas chromatography GC 9790 equipped with a packed column (GDX-303, 2 m × 3 mm) and a flame photometer detector (FPD) with the accuracy of 0.1 ppmv.

### Desulfurization and tar reforming of biogenous syngas in DDLG with Ni/olivine as bed material

As shown in Fig. 1, DDLG consists of two circulation loops, i.e. a gasification loop and an upgrading loop with fine and coarse

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