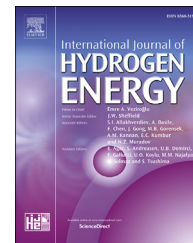




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

CrossMark

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

Guangyong Wang, Shaoping Xu^{*}, Chao Wang, Junjie Zhang, Zijun Fang

State Key Laboratory of Fine Chemicals, Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, China

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 (H₂S) and organic-sulfur (thiophene) removal at 600–680 °C and the excellent desulfurization performance was maintained with wide range H₂O content (27.0–40.7%). Meanwhile, tar was mostly eliminated and H₂ 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.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Biomass as a sustainable and CO₂-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 H₂ and CH₄ as well as a low content of N₂. 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

^{*} Corresponding author.

E-mail address: huizixu@hotmail.com (S. Xu).

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

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

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/Al₂O₃, 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 (Ni₃S₂) could be formed at moderate temperature, in low and high P_{H₂S}/P_{H₂} 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 H₂S-containing feeding gas over nickel catalysts showed that the introduced H₂S was almost completely eliminated at 200–400 °C [24], along with the catalyst deactivation by sulfur-poisoning [25]. H₂S concentration was decreased to below 20 ppmv after raw syngas (with a few hundred ppmv of H₂S) going through the secondary tar reforming catalysts bed (Ni/Al₂O₃ and Ni/CaO–Al₂O₃) [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. NiAl₂O₄-based glass-ceramic, with NiAl₂O₄ phase as clusters dispersed within the glassy matrix, showed improved resistance to aggregation and a high conversion of H₂S 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 H₂S 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_xFe_{1-x})₂SiO₄ as the main phase with small quantities of MgSiO₃ and FeO_x 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 H₂S and 19.7 ppmv thiophene in Ar, provided by Dalian Special Gases Co., Ltd.) and H₂, were controlled by mass flow controllers and admitted to the reactor at an hourly space velocity of 5000 h⁻¹. The removal of H₂S 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 (H₂S 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.

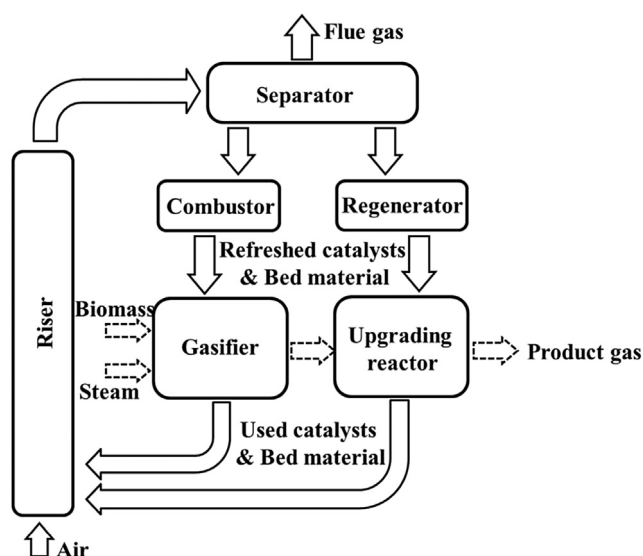
Desulfurization and tar reforming of biogenous syngas in DDLG with Ni/olivine as bed material

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

Table 1 – Proximate and ultimate analysis of the pine sawdust.

Proximate analysis (wt.%, ad)				Ultimate analysis (wt.%, daf)				
Moisture	Ash	Volatile	Fixed carbon	Carbon	Hydrogen	Oxygen ^a	Nitrogen	Sulfur
8.26	0.61	78.40	12.73	47.75	6.98	44.84	0.07	0.36

^a By difference.

**Fig. 1 – Concept of the DDLG gasification system.**

particles as circulating bed materials, respectively. The hot syngas from the bubbling-fluidized bed gasifier of the gasification loop is further upgraded in the moving bed upgrading reactor of the upgrading loop. Both loops have an identical fast fluidized bed riser followed by a separator. The fine bed material, i.e. SiO₂ in this study, with the residual char from the gasifier and the coarse bed material, i.e. Ni/olivine as both desulfurization and tar reforming catalyst, from the upgrading reactor are together transported by the riser and again divided through the separator into the combustor before the gasifier and the regenerator before the upgrading reactor, respectively. In the combustor, the char is burnt out with air and the fine bed material is heated and returned to the gasifier to provide the heat the endothermic gasification needed. In the regenerator, the used Ni/olivine is refreshed in air flow and delivered back to the upgrading reactor. The quality and quantity of the fine and coarse circulating bed materials in both loops are monitored. In this way, the intricate reaction network is decoupled and the gasification and the raw syngas upgrading could be optimized independently.

In the experimental DDLG set-up (Fig. 2), the gasifier is a bubbling fluidized bed reactor with a down-zone of 56 mm i.d. and 80 mm height and an up-zone 98 mm i.d. and 190 mm height. The upgrading reactor is a gas–solid radial cross flow moving bed reactor, which has an annular bed with an i.d. 28 mm, an o.d. 100 mm and a height 250 mm. The hot syngas from the gasifier flows into the inner space of upgrading reactor and goes across radially through the bed material. The riser is a fast fluidized bed reactor with 20 mm i.d. and

2600 mm height. The combustor and regenerator are moving bed reactors, with identical i.d. 80 mm and a height 140 mm and a height 190 mm, respectively. The fine and coarse bed material particles from the riser are separated from the flue gas in the separator and then fluidized by the air flow introduced into the regenerator. The coarse particle drops down through the bottom tube of the separator into the regenerator and the fine particle outflows the separator into the combustor based on their different masses and terminal velocities. All the reactors are made of 310S stainless steel and heated by independent electrical furnaces to compensate heat loss with a K-type thermocouple inserted in the middle of each furnace closing to the outer wall of the reactors. The circulating rate of fine bed material and that of coarse bed material are controlled by the rotary valve between the gasifier and the riser and that between the upgrading reactor and the riser, respectively.

Prior to each test, 3.0 kg SiO₂ of 60–100 mesh as the fine bed material and 5.5 kg mixture of Ni/olivine (with a density of 1200 kg/m³) and SiO₂ (with a density of 1280 kg/m³) of 20–40 mesh as the coarse bed material were added into the gasifier and upgrading reactor, respectively. The bed materials were bubbling fluidized and fast fluidized/transported with air in the gasifier and riser, respectively. The circulating rate of fine bed material was maintained to be 3.0 kg/h and that of coarse bed material 4.5 kg/h. All of the reactors were electrically heated to desired temperatures and then the fluidization air of the gasifier was replaced by preheated steam. When the temperatures of all reactors reached stable, gasification began by feeding pine sawdust into the gasifier at a rate of 0.3 kg/h. The product gas was extracted from the upgrading reactor with the help of a vacuum pump and cooled in four sequential glycol-cooled (–12 °C) condensers, in which the condensable components and particulate matter were separated from the permanent gas. The effluent product gas underwent further aerosol removal and was measured by a wet type gas flowmeter and analyzed every 10 min by a gas chromatography GC 7890II equipped with a TCD and a FID. The flue gas from the separator was cooled down and the entrained dust was scrubbed in a venturi gas scrubber with water. The tar and sulfur in the product gas were separately sampled via two sampling points before the condensers. The tar sampling was performed by condensing and dissolving the tar components out of the product gas with six 250 ml impinger bottles basing on the protocol CEN/TS 15439 [41–43]. The impinger bottles were located in a cooling bath cooled down to –12 °C by a cryostat, with bottles 1–5 filled with toluene and bottle 1, bottle 5 and bottle 6 glass beads. The liquid phases in the impinger bottles were unified after sampling and the aqueous phase was separated from the toluene phase. The amount of water was then determined to calculate H₂O content in the

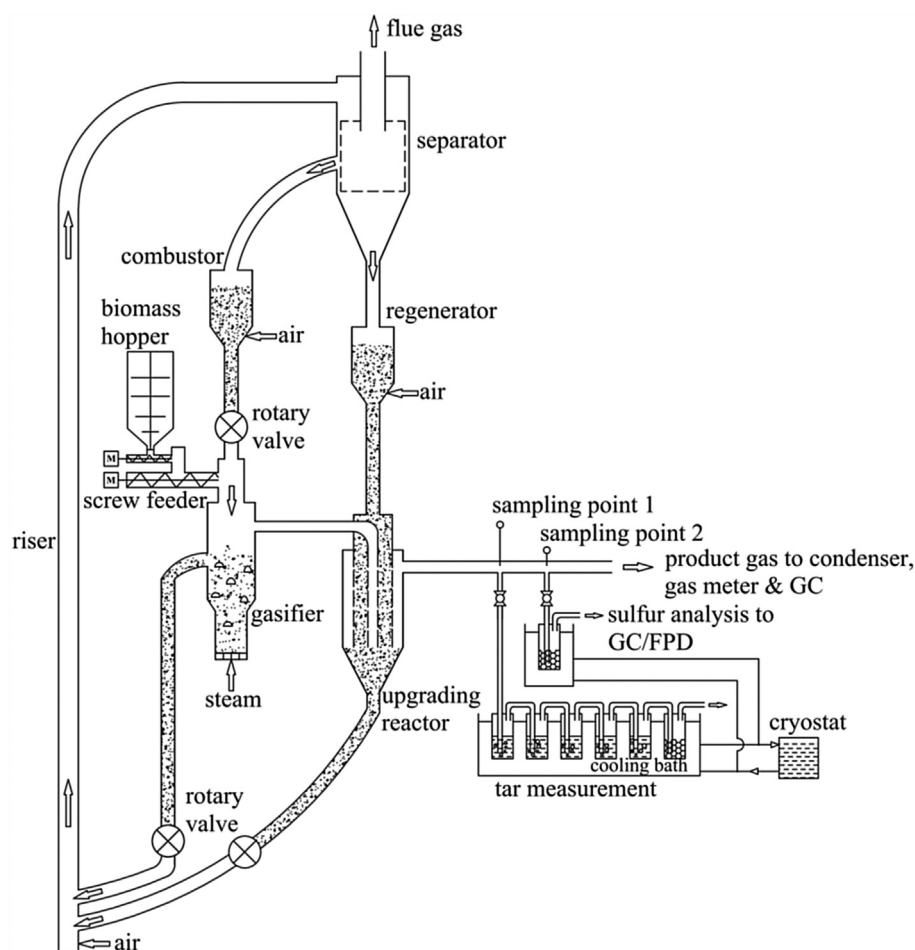


Fig. 2 – Schematic of the lab-scale DDLG facility.

product gas. The tar was obtained by evaporating off the toluene solvent at 50 °C under reduced pressure. The sulfur compounds were sampled by separating the condensable components from the permanent gas in an impinger bottle filled with glass beads, cooled down to –12 °C. H₂S and thiophene in the effluent permanent gas were then measured by a GC 9790 equipped with a packed column (GDX-303, 2 m × 3 mm) and a FPD. As mentioned above, all data samplings were conducted at around 1 h after the pine sawdust was fed into the gasifier when the experiments were in stable state (as shown in Fig. S1 in the Supplementary material). The general parameters are summarized in Table 2.

Results and discussion

Sulfidation and regeneration behaviors of Ni/olivine

The feeding gas mixture of 63 vol.% SG and 37 vol.% H₂ underwent desulfurization over Ni/olivine in the fixed-bed reactor. As shown in Fig. 3a, H₂S in the gas was effectively removed over Ni/olivine-1300. Thiophene conversion over Ni/olivine-1300 was also studied (Fig. 3b) with temperature rising between 500 °C and 700 °C and back down to 500 °C in a step of 100 °C. It was found that higher reaction temperature favors

thiophene elimination. Thiophene conversion increases with reaction time at 500 °C over the fresh desulfurizer, while an increase of conversion followed by decrease appears at both 600 and 700 °C. The results imply that thiophene conversion was determined by the reduction of NiO to Ni at lower temperature, which is the active site for thiophene conversion [29,30].

Table 2 – General parameters of the DDLG system.

Fine bed material	60–100 mesh SiO ₂
Fine bed material inventory (kg)	3.0
Fine particles circulating rate to biomass feeding rate (kg/kg)	10
Coarse bed material	20–40 mesh catalyst + SiO ₂
Coarse bed material inventory (kg)	5.5
Coarse particles circulating rate to biomass feeding rate (kg/kg)	15
Biomass feeding rate (kg _{fuel,db} /h)	0.3
Steam to biomass mass ratio (S/B) (kg _{H₂O} /kg _{fuel,db})	0.4–0.7
Gasification temperature (°C)	780
Gas Upgrading temperature (°C)	520–740
Char combustion temperature (°C)	800
Catalyst regeneration temperature (°C)	840
Operating pressure	Atmospheric

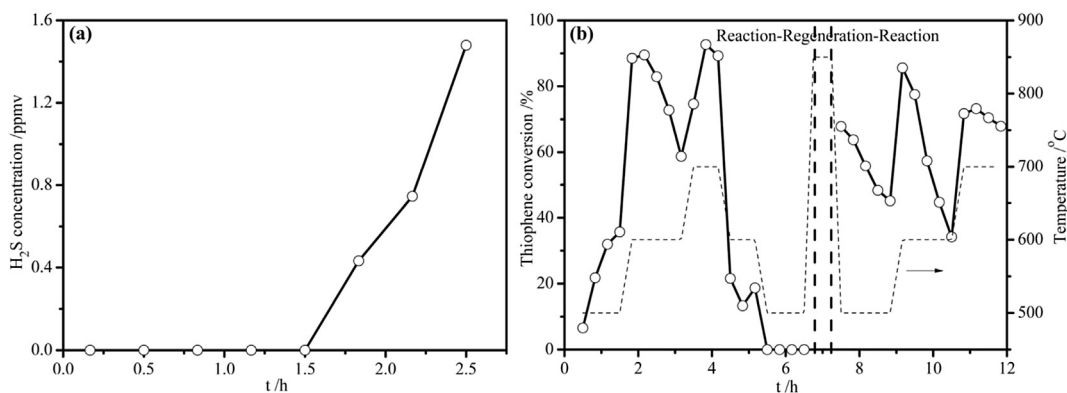


Fig. 3 – Desulfurization over Ni/olivine-1300 in SG/H₂: a) H₂S removal at 500 °C; b) thiophene conversion during programmed temperature test, before and after regeneration in air flow.

More Ni could be achieved by extending the exposure time and increasing the reaction temperature, promoted by the H₂ content in the feeding gas. The decrease of thiophene conversion with time at higher temperature mainly resulted from sulfur-poisoning of Ni.

It has been found that nickel catalysts were sulfur-poisoned by the formation of chemisorbed sulfur or nickel sulfide. Such sulfur species on the nickel catalysts are prone to be converted to sulfate between 350 and 900 °C in oxidizing atmosphere, which is relatively stable and considered to be the main obstacle during regeneration [8,44–46]. To help to illustrate the regeneration of sulfur-poisoned nickel catalyst, thermal gravimetric analysis (TGA) of NiSO₄·6H₂O was performed under air flow at a heating rate of 20 °C/min on a DTU-2B thermal balance. As indicated in Fig. 4, the weight loss before 500 °C is due to dehydration of NiSO₄·6H₂O. The weight loss near 850 °C accounting for 30 wt.% of NiSO₄·6H₂O verifies the complete decomposition of NiSO₄ to NiO. This result is in accordance with that the deactivated Ni/olivine-1300 was well recovered after regeneration in air flow at 850 °C for 0.5 h (Fig. 3b). Thus, the spent Ni/olivine is suggested to refresh in this way for sufficient regeneration, considering the more encouraging rate and cost-efficiency of oxidative regeneration compared with reductive regeneration as well [23].

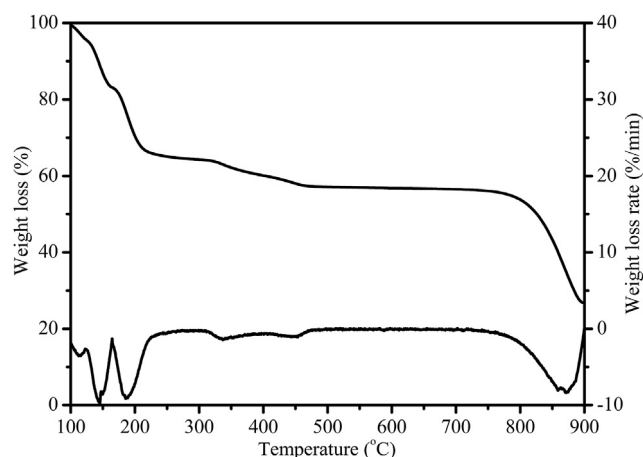


Fig. 4 – TGA and DTG curves of NiSO₄·6H₂O.

Desulfurization of biogenous syngas over Ni/olivine in DDLG

Syngas as-produced from the steam gasification of the pine sawdust in the gasifier was delivered to and upgraded further in the upgrading reactor. As displayed in Fig. 5, at 600 °C and with either 30 wt.% Ni/olivine-850 + 70 wt.% SiO₂ or 30 wt.% Ni/olivine-1300 + 70 wt.% SiO₂ as upgrading bed materials, H₂S and thiophene in the product gas could be effectively decreased to less than several ppmv level, whereas the values with SiO₂ are 146.1 ppmv and 36.1 ppmv, respectively. Ni/olivine-850 shows more pronounced desulfurization performance than Ni/olivine-1300, possibly due to their discrepant redox properties which determine the amount of Ni⁰. It has been reported that calcination temperature of Ni/olivine as high as 1400 °C could lead to NiO integration into olivine structure, which can hardly be reduced [34,36]. Thus, a moderate calcination temperature, i.e. 850 °C here, could be suitable to provide sufficient Ni⁰ as active sites during hot gas upgrading and strong metal-support interaction to bind them as well.

The influence of H₂O content in the syngas on the desulfurization over 30 wt.% Ni/olivine-850 + 70 wt.% SiO₂ in the

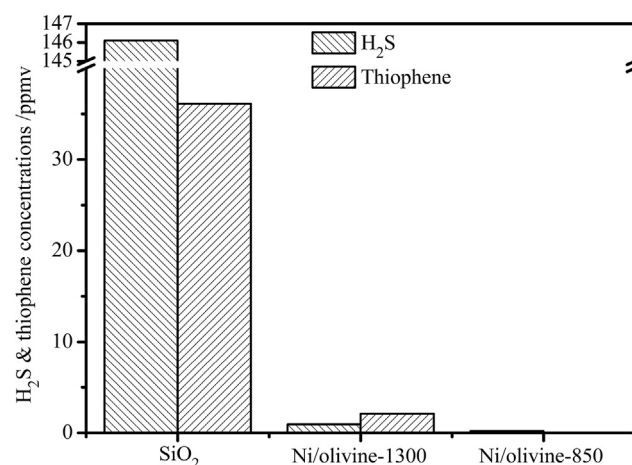


Fig. 5 – Desulfurization over SiO₂, Ni/olivine-1300 and Ni/olivine-850 at 600 °C.

upgrading reactor was evaluated and the result is shown in Table 3. It is found that an excellent desulfurization performance was maintained towards the hot raw gas with wide range H₂O content (27.0–40.7%). The result confirms the different desulfurization mechanism over nickel-based desulfurizer from that over the traditional ZnO-based desulfurizer. H₂O, as a product of the sulfidation of ZnO, could adversely affect the thermodynamic equilibrium of desulfurization and compete with H₂S during adsorption over ZnO-based sorbents [11,47]. In comparison, H₂O is not involved in the sulfidation of Ni, either in terms of bulk sulfide or chemisorbed sulfur. Therefore, Ni/olivine could be a superior sorbent for desulfurization of H₂O-rich raw biogenous syngas.

The influence of the upgrading temperature on the desulfurization over 30 wt.% Ni/olivine-850 + 70 wt.% SiO₂ is shown in Fig. 6. H₂S in the product gas maintains to be less than 0.5 ppmv in the temperature range of 520–680 °C and, dramatically, increases up to 110.3 ppmv at 740 °C, which could result from the variation of chemisorption behavior with temperature since stronger chemisorption between H₂S and Ni is expected at lower temperature [23]. Thiophene concentration, however, decreases with the increase of temperature, indicating that higher reaction temperature promotes thiophene cracking and conversion.

Tar reforming of biogenous syngas over Ni/olivine in DDLG

Catalytic steam reforming of biogenous tar over 30 wt.% Ni/olivine-850 + 70 wt.% SiO₂ was evaluated at the same upgrading temperature range as that for efficient desulfurization (Table 4). Compared with that over SiO₂, the tar content decreases distinctly over Ni/olivine at 600–680 °C, and the carbon conversion and gas yield increase a lot. The results indicate that the tar was mostly destructed to permanent gases. Meanwhile, H₂ concentration increases much, accompanied by evident decrease of CO at 600 °C and CH₄ at 680 °C.

Table 3 – Influence of H₂O content on desulfurization over Ni/olivine-850.

S/B (kg/kg)	0.40	0.45	0.70
Gasifier temperature/°C	780	780	780
Bed material in gasifier	SiO ₂	SiO ₂	SiO ₂
Upgrading reactor temperature/°C	600	600	600
Bed material in upgrading reactor	Ni/olivine	Ni/olivine	Ni/olivine
Tar content in raw gas (g/Nm ³)	61.2	60.3	60.5
H ₂ O content in raw gas/%	27.0	30.4	40.7
Raw gas composition/vol.%			
H ₂	34.9	33.8	36.8
CO	33.3	33.8	32.3
CH ₄	10.1	10.8	10.1
CO ₂	17.2	17.0	16.6
C ₂ H ₄	2.7	3.0	2.9
C ₂ H ₆	0.6	0.6	0.6
C ₃ H ₆	1.0	0.8	0.6
C ₃ H ₈	0.2	0.2	0.1
H ₂ S in product gas/ppmv	<0.1	0.2	0.3
Thiophene in product gas/ppmv	<0.1	<0.1	<0.1

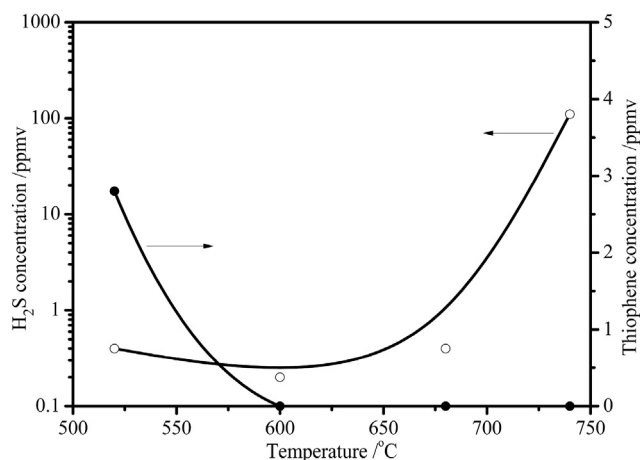


Fig. 6 – Influence of temperature on desulfurization over Ni/olivine-850.

The exothermic WGS reaction is promoted at lower temperature, producing H₂ and CO₂ at the expense of CO and H₂O, while the endothermic CH₄ reforming contributes to H₂ production at higher temperature. Notably, Ni/olivine showed poor catalytic activities for tar steam reforming, WGS and CH₄ reforming at 520 °C. The decrease of reaction rates with lowering temperature could deteriorate the upgrading performance. Sulfur-poisoning of the catalyst could be another important factor, as thiophene of 2.8 ppmv penetrated at

Table 4 – Biomass gasification with raw syngas upgrading over Ni/olivine-850 at different temperatures in DDLG.

S/B (kg/kg)	0.45	0.45	0.45	0.45
Gasification temperature/°C	780	780	780	780
Bed material in gasifier	SiO ₂	SiO ₂	SiO ₂	SiO ₂
Upgrading reactor temperature/°C	350	520	600	680
Bed material in upgrading reactor	SiO ₂	Ni/olivine	Ni/olivine	Ni/olivine
Carbon conversion/%	76.4	79.2	90.8	91.6
Product gas yield (Nm ³ /kg)	1.0	1.0	1.5	1.5
LHV (MJ/Nm ³)	14.8	13.9	11.3	11.3
Tar content in product gas (g/Nm ³)	60.3	37.1	2.6	2.7
H ₂ S in product gas/ppmv	146.1	0.4	0.2	0.4
Thiophene in product gas/ppmv	36.1	2.8	<0.1	<0.1
Dry product gas composition/vol.%				
H ₂	33.8	35.1	47.4	45.9
CO	33.8	30.6	17.7	28.9
CH ₄	10.8	10.7	9.8	6.2
CO ₂	17.0	20.0	24.5	18.3
C ₂ H ₄	3.0	2.2	0.1	0.4
C ₂ H ₆	0.6	0.6	0.1	0.2
C ₃ H ₆	0.8	0.7	0.2	0.1
C ₃ H ₈	0.2	0.1	0.2	–

520 °C may result in an increase of sulfur coverage over metallic nickel [8].

Carbon conversion of 76.4% and product gas yield of 1.0 Nm³/kg were achieved during biomass gasification at 780 °C over SiO₂, as shown in Table 4. The results approach or even exceed the published works based on dual bed gasification systems [48,49]. Additionally, with Ni/olivine as the upgrading catalyst, deep sulfur removal and efficient tar elimination were achieved simultaneously at 600–680 °C. The upgraded product gas with gas yield of 1.5 Nm³/kg_{daf}, tar content of 2.6 g/Nm³, H₂/CO mole ratio of 2.7 and sulfur of 0.2 ppmv H₂S and <0.1 ppmv thiophene was obtained in the lab-scale DDLG facility under the temperatures of gasification and raw gas upgrading at 780 °C and 600 °C, respectively. The favorable result indicates that biomass gasification in DDLG with Ni/olivine as 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 [50,51].

Conclusions

Sulfidation and regeneration of Ni/olivine in the fixed-bed reactor showed that Ni/olivine was efficient for both H₂S (inorganic-sulfur) and thiophene (organic-sulfur) removal at moderate temperature. Sulfur-poisoned Ni/olivine was well recovered after regeneration in air at 850 °C.

Biomass gasification in DDLG with difunctional Ni/olivine as in-bed upgrading catalyst was performed. Deep sulfur removal was achieved at 600–680 °C and the excellent desulfurization performance was maintained with wide range H₂O content (27.0–40.7%). But even higher and lower upgrading temperatures were unfavorable for inorganic-sulfur and organic-sulfur eliminations, respectively. Meanwhile, tar was mostly destructed at 600–680 °C and poorly eliminated at the lower temperature.

Acknowledgments

This work is supported by the Natural Science Foundation of China (No. 50776013) and the National High Technology Research and Development Program of China (No. 2008AA05Z407).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2017.05.041>.

REFERENCES

- [1] Zeng X, Shao R, Wang F, Dong P, Yu J, Xu G. Industrial demonstration plant for the gasification of herb residue by fluidized bed two-stage process. *Bioresour Technol* 2016;206:93–8.
- [2] Moneti M, Carlo AD, Bocci E, Foscolo PU, Villarini M, Carlini M. Influence of the main gasifier parameters on a real system for hydrogen production from biomass. *Int J Hydrogen Energy* 2016;41:11965–73.
- [3] Cai J, Wang S, Wang Q, Cao K. The characteristics of biomass gasification in multistage heating and gradient chain gasifier. *Int J Hydrogen Energy* 2016;41:15674–81.
- [4] König CFJ, Schildhauer TJ, Nachttegaal M. Methane synthesis and sulfur removal over a Ru catalyst probed in situ with high sensitivity X-ray absorption spectroscopy. *J Catal* 2013;305:92–100.
- [5] Norbeck JM, Park CS, Raju ASK. Method to produce methane rich fuel gas from carbonaceous feedstocks using a steam hydrogasification reactor and a water gas shift reactor. 2014. U.S. Patent 8,771,388B2.
- [6] Li CZ, Xu G. Decoupled thermochemical conversion-preface. *Fuel* 2013;112:607–8.
- [7] Pfeifer C, Koppatz S, Hofbauer H. Steam gasification of various feedstocks at a dual fluidised bed gasifier: impacts of operation conditions and bed materials. *Biomass Convers Biorefin* 2011;1:39–53.
- [8] Seiffert M, Rönsch S, Schmersahl R, Zeymer M, Majer S, Pätz C, et al. Bio-SNG-Demonstration of the production and utilization of synthetic natural gas (SNG) from solid biofuels. 2009. Final project report. TREN/05/FP6EN/S07.56632/19895.
- [9] Köchermann J, Schneider J, Matthischke S, Rönsch S. Sorptive H₂S removal by impregnated activated carbons for the production of SNG. *Fuel Process Technol* 2015;138:37–41.
- [10] van der Meijden CM. Development of the MILENA gasification technology for the production of Bio-SNG [Thesis]. Eindhoven University of Technology; 2010.
- [11] Zuber C, Husmann M, Schroettner H, Hochenauer C, Kienberger T. Investigation of sulfidation and regeneration of a ZnO-adsorbent used in a biomass tar removal process based on catalytic steam reforming. *Fuel* 2015;153:143–53.
- [12] Aznar MP, Caballero MA, Gil J, Martín JA, Corella J. Commercial steam reforming catalysts to improve biomass gasification with steam-oxygen mixtures. 2. Catalytic tar removal. *Ind Eng Chem Res* 1998;37:2668–80.
- [13] Rapagnà S, Gallucci K, Marcello MD, Matt M, Nacken M, Heidenreich S, et al. Gas cleaning, gas conditioning and tar abatement by means of a catalytic filter candle in a biomass fluidized-bed gasifier. *Bioresour Technol* 2010;101:7134–41.
- [14] Pfeifer C, Reinhard Rauch A, Hofbauer H. In-bed catalytic tar reduction in a dual fluidized bed biomass steam gasifier. *Ind Eng Chem Res* 2004;43:1634–40.
- [15] Gil Javier, Caballero MA, Martín JA, Aznar Mariápar, Corella J. Biomass gasification with air in a fluidized bed: Effect of the in-bed use of dolomite under different operation conditions. *Ind Eng Chem Res* 1999;38:4226–35.
- [16] Sutton D, Kelleher B, Doyle A, Ross JRH. Investigation of nickel supported catalysts for the upgrading of brown peat derived gasification products. *Bioresour Technol* 2001;80:111–6.
- [17] Wang JB, Xiao B, Liu SM, Hu ZQ, He PW, Guo DB, et al. Catalytic steam gasification of pig compost for hydrogen-rich gas production in a fixed bed reactor. *Bioresour Technol* 2013;133C:127–33.
- [18] Li D, Tamura M, Nakagawa Y, Tomishige K. Metal catalysts for steam reforming of tar derived from the gasification of lignocellulosic biomass. *Bioresour Technol* 2015;178:53–64.
- [19] Abu ElRub Z, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes. *Ind Eng Chem Res* 2004;43:6911–9.
- [20] Rhyner U, Edinger P, Schildhauer TJ, Biollaz SMA. Experimental study on high temperature catalytic conversion of tars and organic sulfur compounds. *Int J Hydrogen Energy* 2014;39:4926–37.

- [21] Rostrup-Nielsen JR. Some principles relating to the regeneration of sulfur-poisoned nickel catalyst. *J Catal* 1971;21:171–8.
- [22] Swisher JH, Schwerdtfeger K. Review of metals and binary oxides as sorbents for removing sulfur from coal-derived gases. *J Mater Eng Perform* 1992;1:399–407.
- [23] Swisher JH, Jhunjhunwala M, Gasper-Galvin LD, Gardner TH, Hammerbeck K. Properties of sulfur sorbents containing dispersed nickel in an Al₂O₃ matrix. *J Mater Eng Perform* 1996;5:247–55.
- [24] Wan AWAB, Othman MY, Ali R, Yong CK. Nickel oxide based supported catalysts for the in-situ reactions of methanation and desulfurization in the removal of sour gases from simulated natural gas. *Catal Lett* 2009;128:127–36.
- [25] Wan AWAB, Ali R, Toemen S. Catalytic methanation reaction over supported nickel-rhodium oxide for purification of simulated natural gas. *J Nat Gas Chem* 2011;20:585–94.
- [26] Pinto F, Rui NA, Franco C, Lopes H, Carolino C, Costa R, et al. Co-gasification of coal and wastes in a pilot-scale installation. 2: effect of catalysts in syngas treatment to achieve sulphur and nitrogen compounds abatement. *Fuel* 2010;89:3340–51.
- [27] Pinto F, Lopes H, Cabrita I, Rui NA, Gulyurtlu I. Effect of catalysts in the quality of syngas and by-products obtained by co-gasification of coal and wastes. 2: heavy metals, sulphur and halogen compounds abatement. *Fuel* 2008;87:1050–62.
- [28] García G, Campos E, Fonts I, Sánchez JL, Herguido J. Gas catalytic upgrading in a two-zone fluidized bed reactor coupled to a cogasification plant. *Energy Fuels* 2013;27:2835–45.
- [29] Bezverkhyy I, Gadacz G, Bellat JP. Interaction of Ni/SiO₂ with thiophene. *Mater Chem Phys* 2009;114:897–901.
- [30] Chang HK, Park JG, Ji CP, Song H, Han SS, Kim JN. Surface status and size influences of nickel nanoparticles on sulfur compound adsorption. *Appl Surf Sci* 2007;253:5864–7.
- [31] Zuber C, Hochenauer C, Kienberger T. Test of a hydrodesulfurization catalyst in a biomass tar removal process with catalytic steam reforming. *Appl Catal B Environ* 2014;156–7: 62–71.
- [32] Li L, King DL, Liu J, Huo Q, Zhu K, Wang C, et al. Stabilization of metal nanoparticles in cubic mesostructured silica and its application in regenerable deep desulfurization of warm syngas. *Chem Mater* 2009;21:5358–64.
- [33] Dolan MD, Ilyushechkin AY, McLennan KG, Nguyen T, Sharma SD. Glass-based processing of mixed-oxide desulfurization sorbents. *Ind Eng Chem Res* 2009;48:10498–503.
- [34] Świerczyński D, Courson C, Bedel L, Kiennemann A, Guille J. Characterization of Ni-Fe/MgO/Olivine catalyst for fluidized bed steam gasification of biomass. *Chem Mater* 2006;18:4025–32.
- [35] Wang G, Xu S, Jiang L, Wang C. Nickel supported on iron-bearing olivine for CO₂ methanation. *Int J Hydrogen Energy* 2016;41(30):12910–9.
- [36] Pfeifer C, Rauch R, Hofbauer H, Świerczyński D, Courson C, Kiennemann A. Hydrogen-rich gas production with a Ni-catalyst in a dual fluidized bed biomass gasifier. *Sci Therm Chem Biomass Convers* 2004. URL, <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.472.5068&rep=rep1&type=pdf>.
- [37] Liu H, Cattolica RJ, Seiser R. CFD studies on biomass gasification in a pilot-scale dual fluidized-bed system. *Int J Hydrogen Energy* 2016;41(28):11974–89.
- [38] Chen H, Zhang X, Wu B, Bao D, Zhang S, Li J, et al. Analysis of dual fluidized bed gasification integrated system with liquid fuel and electricity products. *Int J Hydrogen Energy* 2016;41(26):11062–71.
- [39] Tursun Y, Xu S, Wang C, Xiao Y, Wang G. Steam co-gasification of biomass and coal in decoupled reactors. *Fuel Process Technol* 2015;141:61–7.
- [40] Xiao Y, Xu S, Tursun Y, Wang C, Wang G. Catalytic steam gasification of lignite for hydrogen-rich gas production in a decoupled triple bed reaction system. *Fuel* 2017;189:57–65.
- [41] Kern S, Pfeifer C, Hofbauer H. Gasification of lignite in a dual fluidized bed gasifier-Influence of bed material particle size and the amount of steam. *Fuel Process Technol* 2013;111:1–13.
- [42] Neeft J, Knoef H, Zielke U, Sjöström K, Hasler P, Simell P, et al. Guideline for sampling and analysis of tar and particles in biomass producer gases, version 3.3. Energy project ERK6-CT1999-20002 (Tar Protocol). *Prog Thermochem Biomass Convers* 2008:162–75.
- [43] Van Paasen S, Kiel J, Neeft J, Knoef H, Buffinga G, Zielke U, et al. Guideline for sampling and analysis of tar and particles in biomass producer gases. ECN-C-02–090. 2002. URL, <http://www.ecn.nl/docs/library/report/2003/c02090.pdf>.
- [44] Park JJ, Jung SY, Chang GP, Lee SC, Kim JC. A study on the regenerable Co and Ni-based sorbents to remove hydrogen sulfide at middle temperature. *Top Catal* 2010;53:635–40.
- [45] Dasgupta S, Gupta P, Aarti, Nanoti A, Goswami AN, Garg MO, et al. Adsorptive desulfurization of diesel by regenerable nickel based adsorbents. *Fuel* 2013;108:184–9.
- [46] Siriwardane RV, Gardner T, Poston JA, Fisher EP, Miltz A. Spectroscopic characterization of nickel containing desulfurization sorbents. *Ind Eng Chem Res* 2000;39:1106–10.
- [47] Kim K, Jeon S, Vo C, Park CS, Norbeck JM. Removal of hydrogen sulfide from a steam-hydrogasifier product gas by zinc oxide sorbent. *Ind Eng Chem Res* 2007;46:5848–54.
- [48] Bengtsson K. Twin-bed gasification concepts for Bio-SNG production. Lund: Lund University; 2007. URL, <http://www.chemeng.lth.se/exjobb/E450.pdf>.
- [49] Zhang J, Wu R, Zhang G, Yao C, Zhang Y, Wang Y, et al. Recent studies on chemical engineering fundamentals for fuel pyrolysis and gasification in dual fluidized bed. *Ind Eng Chem Res* 2013;44(31):6283–302.
- [50] Kraussler M, Binder M, Hofbauer H. 2250-h long term operation of a water gas shift pilot plant processing tar-rich product gas from an industrial scale dual fluidized bed biomass steam gasification plant. *Int J Hydrogen Energy* 2016;41(15):6247–58.
- [51] Kalinci Y, Hepbasli A, Dincer I. Biomass-based hydrogen production: a review and analysis. *Int J Hydrogen Energy* 2009;34(21):8799–817.