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Distribution of sulfur species in gaseous and condensed phase during downdraft gasification of corn straw

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ABSTRACT

This study concerns the distribution of sulfur species during the gasification of non-woody biomass. Experiments were carried out in a downdraft fixed bed gasifier using air and steam as oxidizing agents. Based on RSM (response surface methodology), the study investigated three operating parameters, including the ER (equivalence ratio), steam to biomass mass ratio (S:B) and biomass particle size. The independent factors were tested in the range of 0.2–0.4, 0.8–1.2 and 2.5–8.5 mm for the equivalence ratio, steam to biomass mass ratio and biomass particle size. The response variables investigated were gaseous sulfides, including H_2S (hydrogen sulfide), COS (carbonyl sulfide), CH_3SH (methyl mercaptan) and SO_2 (sulfur dioxide), as well as the condensed phase of sulfur that retained in the fly ash and the bottom ash. The results indicate that the three operating conditions significantly affect the distribution of sulfur compounds, and the equivalence ratio is found to be the most important factor.

1. Introduction

Energy crisis has intensified with over exploitation of fossil fuels in the past few decades. Biomass is expected to be one of the most promising resources for the production of future fuels [1]. As for the technologies of converting biomass materials into sustainable and renewable biofuels, TCC (thermochemical conversion) is considered one of the most significant technologies, including pyrolysis, gasification and liquefaction. In terms of the gasification, it is an important technology for converting biomass into fuel gas and subsequent use in heat or power generation, chemical production and large-scale hydrogen production [2]. To this end, many researchers have focused on internal and external factors affecting the gasification performance, which mainly includes types of the reactor [3], operating conditions [4] and feedstock properties [5].

In terms of the biomass properties, most investigations have been performed on woody biomass [6] and non-woody biomass [7,8]. Non-woody biomass is characterized by a relatively higher amount of sulfur and other trace elements, compared with woody biomass. As already discussed in a previous paper [9], in addition to the pollutants of condensable tars and particulate dust, the fuel gas obtained from gasification of non-woody biomass has a comparatively high concentration of sulfides compared with the gasification of woody biomass, which is detrimental to situ or downstream catalysts. Osada et al. carried out systematic studies of the effect of sulfur on the catalytic gasification of lignin in supercritical water [10] and the corresponding reaction pathway [11]. It was observed that the rate of lignin gasification decreased in the presence of sulfur, which was probably caused by the decrease in the number of active ruthenium sites available after the adsorption of sulfur impurities. According to Tomishige et al. [12], the steam reforming Ni catalyst was effective for the removal of tar derived from the pyrolysis of cedar wood, without the addition of H_2S. However, the catalyst was deactivated drastically with the presence of H_2S. Consequently, additional gas cleaning equipment is required to remove the poisonous sulfur species formed during the gasification process, which definitely becomes an extra purifying cost for the application of non-woody biomass. Besides, sulfur species are partly bounded to the ash, causing partial ash sintering or bed agglomeration, which can render the operation unstable as well as damage the reactor and downstream equipments.

In respect to the significant issue, researchers have paid special attention to investigate methods of inhibiting or removing sulfur species during the gasification process. These mainly include: specific catalysts [13], sulfur sorbents [14] and situ desulfurization [15]. Although there have been some experimental investigations concerning the release and removal of sulfur in product gas from biomass gasification as discussed above, few data are available on the combined effects of varied operating conditions on reducing sulfur emissions during the gasification process, which should be

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one of the most economical and feasible methods. Besides, most of the biomass gasification investigations adopt the traditional approach of "one-factor-at-a-time". This kind of method generally employs a limited number of experiments, which could not see the comprehensive perspective of the entire process. And this classical method could not be used to investigate the interactions of different operating parameters on the desired experimental results. Therefore, in respect to these faults of the classical method, RSM (response surface methodology) [16] was adopted in the current study. It could give a comprehensive investigation of experimental parameters and their interactions, whilst quantitatively determining the desirable operating conditions and corresponding results. Consequently, the main objective of this study is to investigate the effect of operating parameters and their interactions on the distribution of sulfides during the gasification of non-woody biomass.

2. Materials and methods

2.1. Materials

As a representative non-woody biomass, corn straw was selected as the feedstock for its relatively high amount of sulfur compared with woody biomass. Before the tests, the samples were first air-dried for 30 days to reduce moisture content to less than 10%. Then after being crushed and sieved, three fractions of particle size were chosen to study the effect of particle size, including 2.5 mm, 5.5 mm and 8.5 mm. In the present study, the elemental compositions of the feedstock were determined using an elementary analyzer (vario MACRO cube, Elementar, Germany) equipped with a TCD (thermal conductivity detector). Other chemical compositions and calorific content were analyzed according to the standard of ISO (ISO 589: 2003, ISO 562: 2010, ISO 1171: 2010 and ISO 1928: 2009). The proximate and ultimate analysis of corn straw is shown in Table 1.

2.2. Experimental design

In the current study, RSM was used to investigate the effect of operating parameters and interactions on the distribution of sulfur compounds during the gasification of non-woody biomass. A FCCCD (face-centered central composite design) [17] was selected to design the experiments. Thanapal et al. [8] investigated the effect of the equivalence ratio and steam fuel ratio on fixed bed gasification performance, and found that the two parameters both greatly affected the peak temperature and the composition of product gas. Yin et al. [18] investigated the effect of particle size on the pilot-scale downdraft fixed-bed gasification process. It was observed that for small particle sizes, the gas compositional content was more varied. Increasing the particle size produced higher gas yields but with a lower calorific value. Therefore, it can be seen that the equivalence ratio, steam to biomass mass ratio and biomass particle size can greatly affect the biomass gasification performance, which were selected as independent factors in the current study. The levels of three operating parameters were determined in the range of 0.2–0.4, 0.8–1.6 and 2.5–8.5 mm for the equivalence ratio, steam to biomass mass ratio and biomass particle size, respectively.

In terms of the response variables, since the sulfides during downdraft gasification of non-woody biomass are mainly released in the product gas and in the solid ash, the response variables investigated were: H_2S, COS (carbonyl sulfide), CH_3SH, SO_2 and the sulfur concentration in the bottom ash and the fly ash. Temperature is another significant factor that affecting the reaction kinetics, thereby influencing the sulfur distribution in the gaseous phase and condensed phase during the gasification process. As the gasification system employed in this study is internal heating, which is mainly affected by the operating parameters of biomass feed rate, air flow rate, steam flow rate, and biomass particle size. Thus, the temperature within the reactor is initially investigated.

Table 1
Proximate and ultimate analysis of the corn straw.

Corn straw			
Proximate (wt.% db[a])		*Ultimate* (wt.% daf[b])	
Volatile matter	75.95	Carbon	43.83
Fixed carbon	13.75	Hydrogen	5.95
Ash	5.93	Oxygen	45.01
Moisture (ar[c])	6.17	Nitrogen	0.97
L.H.V (MJ/kg daf)	17.75	Sulfur	0.13
Bulk density[d] (kg/m^3)	47.39	Chlorine	0.49

[a] Dry basis.
[b] Dry ash free basis.
[c] As received basis.
[d] The mass of particles of the material divided by the total volume they occupy.

2.3. Experimental procedure

All the experiments were conducted on a bench scale downdraft fixed bed gasification system. It mainly consists of a downdraft fixed bed gasifier, control and measurement systems, which have been described previously [9]. The scheme for the experimental system is illustrated in Fig. 1. During each test, the air flow rate was adjusted to the designated value by the valve of the air supply. The steam flow rate was adjusted by the frequency controller of the water pump. The biomass feed rate was adjusted to the desired value by the screw feeder of the biomass feeder. When the reactor had reached a steady-state (i.e. the temperatures in the partial oxidation zone and the reduction zone were almost stable, and the temperature of the throat was 700–800 °C) after around 70 min, the sulfur species began to be sampled and analyzed. Besides, the temperature distribution of the reactor at five points was recorded simultaneously. The bed temperature distribution is not identical all the time, due to the internal heating gasification system. According to the previous study [9], the temperature measured at T3 point in the partial oxidation zone was always the highest. Therefore, we only presented the temperature of T3 point in the present study. During the whole test, the equivalence ratio was varied by changing the air flow rate to the feed rate of biomass, while the steam to biomass mass ratio was varied by changing the steam flow rate to the feed rate of biomass.

2.4. Sulfur species measurements

Sulfur in non-woody feedstock is released mainly in two principal chemical forms, including gaseous compounds in the fuel gas produced and bounded to the ash during the gasification process. In terms of the sampling of gaseous sulfides, the raw gas was continuously extracted from the gas outlet of the cyclone. Then a condensation system removed dust, water and tar in the raw gas. The system is composed of a primary condenser and a secondary condenser surrounded by ice. Afterwards, the cooled gas was filtered by glass wool and then dried with silica gel. The purified gas sample was collected in bags to analyze the sulfur species by a micro gas chromatograph (Micro-GC 3000A, Agilent Technologies, Santa Clara, CA) equipped with a PFPD (pulsed flame photometric detector). Helium was selected as the carrier gas in all analyses.

In respect to the measurement of sulfur species bounded to the ash during the gasification, the ash hopper 1 located at the bottom of the gasifier was used to collect the bottom ash whilst the ash