



# Investigation of simultaneous removal of ammonia and hydrogen sulphide from producer gas in biomass gasification by titanomagnetite



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## HIGHLIGHTS

- Titanomagnetite can simultaneously remove NH<sub>3</sub> and H<sub>2</sub>S almost completely from an inert gas.
- Temperature has significant effect on the removal of NH<sub>3</sub> and H<sub>2</sub>S.
- Titanomagnetite performance is less effective in a simulated producer gas.

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## ABSTRACT

A novel hot gas cleaning process using titanomagnetite for the simultaneous removal of ammonia (NH<sub>3</sub>) and hydrogen sulphide (H<sub>2</sub>S) from a producer gas in biomass gasification has been developed. In a hot reactor operated at 500–800 °C and under atmospheric pressure, NH<sub>3</sub> is removed by a decomposition reaction to N<sub>2</sub> and H<sub>2</sub>, whereas H<sub>2</sub>S is removed by an adsorption reaction. Titanomagnetite was tested using three different gas streams, namely 2000 ppmv NH<sub>3</sub> in Ar, 2000 ppmv NH<sub>3</sub> and 230 ppmv H<sub>2</sub>S in Ar, and 2000 ppmv NH<sub>3</sub> and 230 ppmv H<sub>2</sub>S in a simulated biomass producer gas. From the experimental results, it was discovered that ferrite (α-Fe) was readily formed by the H<sub>2</sub> reduction of titanomagnetite and that almost complete decomposition of NH<sub>3</sub> (100%) was achieved in Ar gas at 700 and 800 °C. The presence of H<sub>2</sub>S in a gas mixture of NH<sub>3</sub> and Ar slightly reduced the catalytic activity for NH<sub>3</sub> decomposition at 700 and 800 °C (>96%), and H<sub>2</sub>S adsorption of greater than 98% could be achieved in the same temperature range. Under the coexistence of a simulated biomass producer gas, the NH<sub>3</sub> decomposition rate and H<sub>2</sub>S adsorption rate were decreased at 800 °C, which could be due to the high content of H<sub>2</sub> (45 vol%) in the feed gas that favours the reverse reaction of NH<sub>3</sub> decomposition and H<sub>2</sub>S adsorption, the increased surface coverage of the active α-Fe phase by adsorbed hydrogen, and the competition of α-Fe for the reverse water–gas shift reaction. Moreover, it was discovered that temperature significantly affected the removal of NH<sub>3</sub> and H<sub>2</sub>S in the simulated biomass producer gas and thus the operation temperature needs to be optimised.

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## 1. Introduction

Biomass as a clean renewable energy source has gained increased attention worldwide due to a rapid growth in energy consumption and environmental concern. Gasification is a promising and versatile technology for the conversion of various biomass feedstocks into combustible gas or producer gas that can be utilised for production of heat, power, Fischer–Tropsch (FT) liquid fuel and other chemical products. In New Zealand, woody biomass is

widely available as residues from log harvesting and wood processing for use in biomass gasification for energy production.

At the University of Canterbury in New Zealand, a dual fluidised bed (DFB) steam gasifier has been developed, and extensive experiments have been conducted [1–4]. One of the main objectives of application of the DFB steam gasifier is to produce a producer gas with high H<sub>2</sub> and CO contents with an optimum H<sub>2</sub>/CO molar ratio of 2 for FT liquid fuel synthesis, and this has been achieved [1,4]. However, it has become apparent that ammonia (NH<sub>3</sub>) and hydrogen sulphide (H<sub>2</sub>S) present in the producer gas are major obstacles for FT liquid fuel synthesis.

In FT liquid fuel synthesis, NH<sub>3</sub> and H<sub>2</sub>S are poisonous to employed catalysts including cobalt (Co) and iron (Fe)-based catalysts [5]; thus, they must be removed from the biomass producer

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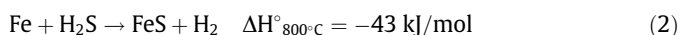
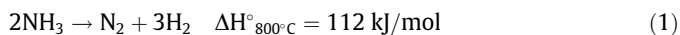
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gas to an acceptable level for FT liquid fuel synthesis. In the biomass gasification process,  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gases are formed from nitrogen (N) and sulphur (S) in biomass feedstock under reducing gasification conditions at high temperatures [5–7]. In the producer gas from the gasification of woody biomass, which commonly has a N content below 0.5 wt%, the  $\text{NH}_3$  concentration ranges from 100 to 2000 ppmv [8], whereas the  $\text{H}_2\text{S}$  concentration varies from 20 to 230 ppmv [9].

The removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  from the biomass producer gas can be performed by a cold or hot gas cleaning process. In cold gas cleaning, a wet scrubber with water or acid solutions is used to remove  $\text{NH}_3$  [5,10], whereas a wet scrubber with basic solutions is used to scrub  $\text{H}_2\text{S}$  [11]. In hot gas cleaning,  $\text{NH}_3$  is removed by a decomposition reaction with catalysts and  $\text{H}_2\text{S}$  is adsorbed into the adsorbents [6,12]. However, in the experiments performed at the integrated biomass gasification and FT liquid fuel synthesis, cold gas cleaning was used for  $\text{NH}_3$  removal, whereas hot gas cleaning was used for  $\text{H}_2\text{S}$  removal [5]. If the simultaneous removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  can be achieved in one reactor, both the capital and the operating costs involved in the cleaning process could be reduced.

For the hot gas cleaning process, many studies on the downstream catalytic decomposition of  $\text{NH}_3$  have been conducted and a review on these studies has recently been published [8]. However, a few reported studies focusing on the simultaneous removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  in the hot gas cleaning process have been found [13,14]. From the review paper by Hongrapipat et al. [8], the iron (Fe)-based catalysts have shown a complete  $\text{NH}_3$  decomposition (100%) in an inert gas and a high  $\text{NH}_3$  decomposition rate (>80%) in a real producer gas from the air gasification of peat produced in a pressurised updraft gasifier. Moreover, use of limonite iron ore ( $\alpha\text{-FeOOH}$ ) following reduction with  $\text{H}_2$  achieved almost complete decomposition of 2000 ppm  $\text{NH}_3$  in He gas at 500, 750, 850 and 950 °C [15–17]. Although the reduced limonite ( $\alpha\text{-Fe}$ ) was reported to have a high tolerance to  $\text{H}_2\text{S}$  with respect to  $\text{NH}_3$  decomposition in He gas [15], the specific removal of  $\text{H}_2\text{S}$  was not reported. Furthermore, in the presence of a simulated producer gas, the activity of the reduced limonite for  $\text{NH}_3$  decomposition was drastically reduced to 45% at 750 °C [17].

In this study, the simultaneous removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  from an inert gas using a naturally available Fe-based material, namely titanomagnetite, in a hot gas cleaning reactor is investigated. The impact of producer gas species ( $\text{H}_2$ , CO,  $\text{CO}_2$  and  $\text{CH}_4$ ) on the removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  is subsequently established. The titanomagnetite was tested for its activity in regard to the  $\text{NH}_3$  decomposition reaction and the  $\text{H}_2\text{S}$  adsorption reaction as described in Eqs. (1) and (2), respectively [15].



Based on Eqs. (1) and (2), titanomagnetite with a high Fe content was expected to be a promising catalytic and adsorbing precursor for the simultaneous removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  from producer gas in the biomass gasification process.

## 2. Materials and methods

### 2.1. Sand materials and preparation

Titanomagnetite ( $\text{Fe}_{2.9}\text{Ti}_{0.1}\text{O}_4$ ) deposits in the western coast of the North Island of New Zealand are among the largest deposits in the world, containing a total identified reserve of concentrate titanomagnetite of over 850 Mt [18]. There is a limited extent of similar magnetite-bearing sand deposits that have been mined

for iron ore in Japan, Philippines and Indonesia [18]. In this research, this Fe-based material was used as a catalytic and adsorbing precursor for the removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$ . The hot gas reactor was operated in a bubbling fluidised bed (BFB) regime. Titanomagnetite was chosen due to its high Fe content (60.3 wt%) and its abundance locally in New Zealand. In addition, another type of natural iron sand containing ilmenite ( $\text{FeTiO}_3$ ) and natural silica sand were also tested in the first stage with 2000 ppmv  $\text{NH}_3$  in Ar gas for comparison. Iron sand containing ilmenite is denoted as ilmenite sand in this study. These three natural sands are readily available in New Zealand. All of the sands were first sieved to specified particle sizes and pre-dried in an oven at 105 °C for 2 h before filling into the reactor. The iron sands containing titanomagnetite and ilmenite were reduced in the reactor with 36.5 vol%  $\text{H}_2$  in Ar gas at 800 °C until the  $\text{H}_2$  reduction process was completed, which was identified when no change was observed between the inlet and outlet  $\text{H}_2$  concentrations of the reactor by an Agilent 3000 micro-gas chromatography (micro-GC). In the reduction process, a total flow rate of 36.5 vol%  $\text{H}_2$  in Ar gas was controlled to be 3.7 l/min. The time required for the complete reduction of the titanomagnetite and ilmenite was approximately 6 h and 3 h, respectively.

### 2.2. Sand material characterisation

An X-ray fluorescence (XRF) analysis of all three sands was conducted using a Phillips PW2400 sequential wavelength dispersive X-ray fluorescence spectrometer to determine their composition. For titanomagnetite,  $\text{N}_2$  physisorption isotherms were determined at the liquid nitrogen temperature (−195 °C) using a Micromeritics Tristar 3000 instrument. The samples were degassed at 100 °C under  $\text{N}_2$  for 1 h prior to the  $\text{N}_2$  adsorption measurements. The specific surface area was calculated based on the Brunauer–Emmett–Teller (BET) method from the  $\text{N}_2$  adsorption data. The cumulative pore volume and average pore diameter were calculated from the adsorption isotherms by the Barrett–Joyner–Halenda (BJH) method. Finally, the X-ray powder diffraction (XRD) analysis of the titanomagnetite samples was conducted with a Philips PW1700 series diffractometer using  $\text{Co K}\alpha_1$  radiation at an X-ray wavelength of 1.78896 Å.

### 2.3. Equipment setup

The hot gas cleaning reactor was a vertical cylindrical fused quartz reactor with an internal diameter of 40 mm, an outer diameter of 46 mm and a length of 1020 mm. The reactor was operated in the BFB regime due to its uniform temperature profile along the radius and axis of the bed, and the uniform mixing of gas and fluidised material, which provided a high contact surface area between the gas and the fluidised material. The BFB reactor was operated isothermally between 500 and 800 °C at atmospheric pressure. The sand was supported on a porous fused quartz distributor located 380 mm from the bottom of the reactor. The inlet gas was fed from the bottom of the reactor to fluidise the sand. The heat to the reactor was supplied by a three-heating-zone ceramic tube furnace and the operation temperature was controlled by the electric current to the furnace. Two sets of K-type thermocouples were installed at two different radial and height positions of the BFB bed. The gas temperature differences between the two thermocouples in the fluidised bed during testing were approximately  $\pm 2$  °C, indicating a relatively uniform temperature profile within the fluidised bed. All parts of the reactor system that were in contact with the  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gases were made of inert materials such as fused quartz and perfluoroalkoxy (PFA) to avoid  $\text{NH}_3$  decomposition and  $\text{H}_2\text{S}$  adsorption at the inner surface of the equipment and parts.

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