

Ammonia yield from gasification of biomass and coal in fluidized bed reactor



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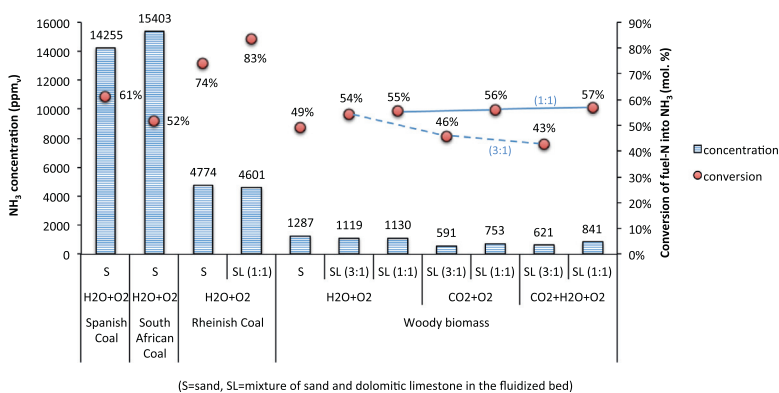
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HIGHLIGHTS

- We investigated the conversion rate of fuel-N into ammonia.
- We adjusted ammonia sampling and analysis procedure.
- We measured the effect of limestone and CO₂ addition.

GRAPHICAL ABSTRACT



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ABSTRACT

Gas from the gasification of coal and biomass can be used for combined production of heat and power or for the synthesis of alternative fuels. In both cases, ammonia, which is created by the conversion of fuel-bound nitrogen, can cause technological difficulties. Therefore, ammonia concentration in the produced gas has to be monitored, or, at least, estimated to take appropriate measures for its abatement.

In this paper, we report in detail the analysis of ammonia content in the produced gas as well as results of several experiments of fluidized-bed gasification of Spanish coal, South African coal, Rheinisch coal and woody biomass. We focused on the evaluation and comparison of ammonia yield based on the following variables: (1) different fuels, (2) the addition of dolomitic limestone into the fluidized bed and (3) the use of carbon dioxide instead of steam in the gasifying agent.

The conversion rate of fuel nitrogen into gas was surprisingly high for the less-reactive coals and within presumed levels for Rheinisch coal and biomass. The presence of dolomitic limestone in the fluidized bed substantially increased the conversion rate of fuel-nitrogen into ammonia. The use of different gasifying agents had an ambiguous effect on ammonia yield.

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Abbreviations: CEM, controlled evaporation and mixing system; ER, equivalence ratio; IC, ion chromatography; LHV, lower heating value; MFC, mass flow controller; PTFE, polytetrafluoroethylene (Teflon).

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1. Introduction

Biomass and coal can be processed into gaseous fuel via gasification in a fluidized bed reactor. The produced gas can be used as fuel for gas engines with internal combustion – in this case it can be called ‘producer gas’ – or as a raw material for synthesis of

various chemical products, such as methanol or Fischer-Tropsch fuels – in this case it may be referred to as ‘synthesis gas’.

Gaseous nitrogenous compounds are regarded as an unwanted component of the gas. In the case of producer gas, they reduce the operating lifetime of oil in the internal combustion engine [1] and they can act as precursors of formation of nitrogen oxides [2,3]. For example, trials with 300–1120 ppmv NH_3 showed that, during gas turbine combustion, 20–50% of ammonia is converted into NO_x [4]. However, the conversion rate can vary in a relatively broad range according to experimental conditions [3]. In synthesis gas applications (such as methanol production or Fischer-Tropsch synthesis) ammonia can contribute to the formation of amines on the synthesis catalyst or it can poison the catalyst itself. The presence of amines in the final products (methanol, liquid fuels) is not permitted in the internationally accepted specifications and their removal is possible only with an ion exchanger [5]. Moreover, where chlorine is present (typically when gasifying coal) ammonia will combine with chlorides to form ammonium chloride at about 250–280 °C, which can form deposits on gas coolers or gas filters [5]. Thus, the concentration of nitrogen compounds in both the producer gas and synthesis gas has to be monitored and minimized.

However, the nitrogenous-compounds-content is not usually the main issue regarding gas purity. Tar and soot removal, desulfurization and dehalogenation take priority over the removal of N-compounds; thus, the reduction of nitrogenous compounds is usually a by-product of some other means applied; for example, oil or water quench for tar removal, in which the nitrogenous compounds are absorbed into water phase [1,6]. Consequently, the nitrogenous compounds are usually not fully removed from the producer gas. Their more efficient removal can be achieved through installing another gas cleaning unit, but this may render smaller plants uneconomic [1]. Lower emissions can also be achieved by adjusting the operating parameters of the gasifier or of the gas cleaning devices. For this purpose, both theoretical and empirical knowledge of the behavior of nitrogenous compounds during gasification and gas cleaning stages is required.

During gasification, fuel nitrogen is liberated mainly in the form of ammonia, cyanides, thiocyanates, molecular nitrogen, nitrogen oxides and various aromatic compounds, while a smaller part of the nitrogen is retained in solid char [7]. The yield of these compounds and their ratios depend on various parameters of the gasification process; such as, the type of gasifier, temperature, equivalence ratio (ER) and catalysts. In fluidized bed reactors, longer gas-char contact time results in higher NH_3/HCN ratio [7]; consequently, NH_3 is a vastly predominant nitrogenous compound in the resulting gas [8].

The yield of ammonia is influenced by the gasification process parameters whose effects are summarized in the literature [9–11]. In this study, we want to contribute to the knowledge base of nitrogen behavior during gasification by presenting the data obtained during fluidized-bed gasification of coal and biomass at 850 °C at atmospheric pressure. We focused on evaluating and comparing the ammonia yield based on the three following variables: (1) different fuels, (2) the addition of dolomitic limestone into the fluidized bed and (3) the use of different gasifying agent mixtures ($\text{H}_2\text{O} + \text{O}_2$, $\text{CO}_2 + \text{O}_2$, $\text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$).

1.1. Ammonia yield from gasification of different types of coal and biomass

The yield of nitrogenous compounds during gasification is dependent on the nitrogen forms in the fuel. Leppälathi and Koljonen [7] published a comprehensive review about the forms of nitrogen in coal, peat and wood. It is generally assumed that the majority of nitrogen in coals is in pyrrolic and pyridinic form, and, on the other hand, nitrogen in living organic tissues is bound

mainly in proteins, aminoacids and alkaloids. Consequently, in peat and wood gasification, most of fuel nitrogen is liberated during the pyrolysis stage and, in coal gasification at low temperatures (<1200 K), most of the nitrogen is retained in char after pyrolysis and released during the char gasification stage.

Leppälathi and Koljonen also report the rate of fuel-N to NH_3 conversion for different fuels during fluidized bed gasification of lignite, sub-bituminous and bituminous coals and wood by oxygen and steam. During the gasification of lignite and sub-bituminous coal at high pressures (0.8 and 1.5 MPa), approximately 60% of fuel-N was converted into NH_3 . Even, a conversion of 93% was observed with a highly volatile coal. With bituminous coal, the ammonia conversion was significantly lower (0.6%–19%). In wood gasification, the NH_3 conversion was 72%–97% (at pressure 0.4–1.0 MPa). However, lower gasification pressure can lead to a significantly lower NH_3 yield. [7] In allothermal steam gasification of wood in the Guessing (FICFB) plant, up to 70% of the fuel nitrogen was found as NH_3 in the producer gas [1]. The concentration of nitrogen in fuel can also affect its conversion into gas; with the increase of concentration of chemically bound nitrogen in fuel, its conversion rate decreased [3]. The innovation of this study is the comparison of the yield of ammonia during atmospheric fluidized-bed gasification of less reactive Spanish coal and South African coal, reactive Rheinisch coal and woody biomass. To our best knowledge, such a comparison is missing in the available literature.

1.2. Dolomitic limestone in the fluidized bed

The use of catalytically active dolomitic limestone during gasification promotes char conversion, changes product gas composition, and reduces tar yield [12]. Inevitably, it will also affect the yield of ammonia.

The presence of a catalyst can affect both the creation of ammonia and its decomposition. The decomposition of ammonia into H_2 and N_2 occurs over a reforming catalyst at high temperatures (~1073 K) [13]. For example, Simmel et al. [14] report a 100% conversion rate on a nickel catalyst and a 53% conversion rate on dolomite in a laboratory-scale fixed-bed tube reactor at temperature of 900–910 °C, residence time 0.2–0.3 s and pressure 1 bar (in simulated synthesis gas). On the other hand, Leppälähti et al. [15] stated that the limestone and dolomite did not have any catalytic effect in the decomposition of ammonia, but they reduced the nitrogen cyanide content in the producer gas [15].

Pinto et al. [11] tested the use of dolomite directly in fluidized bed. They report that dolomite did not change the concentration of NH_3 in the producer gas from coal gasification, but it increased the conversion of fuel-N into NH_3 (this discrepancy is caused by the increase of overall producer gas yield on dolomite) [11]. This indicates that a directly used catalyst enhances the formation of NH_3 from fuel, probably by increasing the conversion rate of char and by increasing the concentration of hydrogen in the system. This enhancement probably prevails over ammonia-decomposition effect.

In this article, we compare the yield of ammonia from the gasification of reactive Rheinisch coal or biomass either on sand in the fluidized bed or on the mixture(s) of sand and dolomitic limestone in the fluidized bed. To our best knowledge, such a comparison of ammonia yield on different mixtures of sand and dolomitic limestone has not been published.

1.3. The use of different gasifying agents

Gasification in steam generates large amounts of H radicals as an intermediate between the reactions of steam with char, drastically enhancing the formation of NH_3 [16]. The use of CO_2 as

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