

Conceptual design of a process for the use of liquid ammonia as hydrogen vector

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Introduction

Chemical energy storage presents a unique feature: flexibility. Chemicals can be moved, stored, and distributed easily, with many of them having a mature market already standing for over decades. Ammonia has been recently presented as a zero-carbon molecule that can provide the required energy storage medium for renewable sources. It can be stored under mild conditions (i.e., refrigerated at $-33\text{ }^{\circ}\text{C}$ at atmospheric pressure or at 0.8–1.0 MPa under atmospheric temperature), thus making it a versatile, easy to store medium. Moreover, liquid ammonia has a greater volumetric hydrogen density than liquid hydrogen itself (i.e., liquid hydrogen at 20 K has approximately 70 kg of H_2/m^3 , while liquid ammonia at 300 K and 1.0 MPa has 106 kg of H_2/m^3), so that the immediate implementation of an “ammonia economy” can support the futuristic “hydrogen economy”.

In this work we present the simulation of a plant for the exploitation of renewable hydrogen with production of renewable ammonia as hydrogen vector and energy storage medium. Data for the simulation of the ammonia synthesis loop were collected from in-house experiments and kinetic modelling on both Fe-base and Ru based catalyst, tested under industrially relevant conditions, up to 100 bar.

Materials and Methods

The simulation and sizing of all unit operations were performed with Aspen Plus® as software. Kinetics was implemented in the simulation routine according to an home-developed kinetic model, adapted to the features of Fe-wustite based and Ru/C catalyst.

Results and Discussion

The Haber-Bosch synthesis of ammonia was carried out at 200 bar and in a temperature range between 300 and 400 $^{\circ}\text{C}$, using two catalysts: Fe (wustite) and Ru/C. Different reactor configurations have been tested, with multi-bed layout, adiabatic operation of the catalyst layer and intercooling. Additional options of feed-split and quenching were compared.

The proposed loop can operate using green hydrogen of different origin, but besides the trivial option to convert electrolytic hydrogen (which however requires careful dehydration, we explored here the possibility to exploit hydrogen from wastes.

Vegetable biomass was used as raw material for hydrogen production, more specifically pine sawdust. The hydrogen production process was based on a gasification reactor operating at high temperature (700–800 $^{\circ}\text{C}$), in the presence of a gasifying agent such as air or steam. At the outlet, a solid residue (ash) and a gas, which mainly contains H_2 , CH_4 ,

CO and some impurities (e.g. sulphur or chlorine compounds) are obtained. After the removal of the sulphur compounds through an absorption column with MEA (to avoid poisoning of the catalyst), 3 reactors are arranged in series: Methane Steam Reforming (MSR), High temperature Water-Gas Shift (HT-WGS), Low temperature Water-Gas Shift (LT-WGS). All the oxygenated compounds must be carefully eliminated: the remaining traces of CO were methanated while CO_2 was removed by a basic scrubbing with MEA (35 wt%) inside an absorption column. In conclusion, from an hourly flow rate of 1000 kg of dry biomass and 600 kg of nitrogen, 550 kg of NH_3 98.8 wt% were obtained, demonstrating the proof of concept of this newly designed process for the production of hydrogen from renewable waste biomass and its transformation into a liquid hydrogen vector to be easily transported and stored. The design of a small-scale ammonia cracker was also added to demonstrate an integrated process for H_2 centralised production and storage and supply to delocalized units.

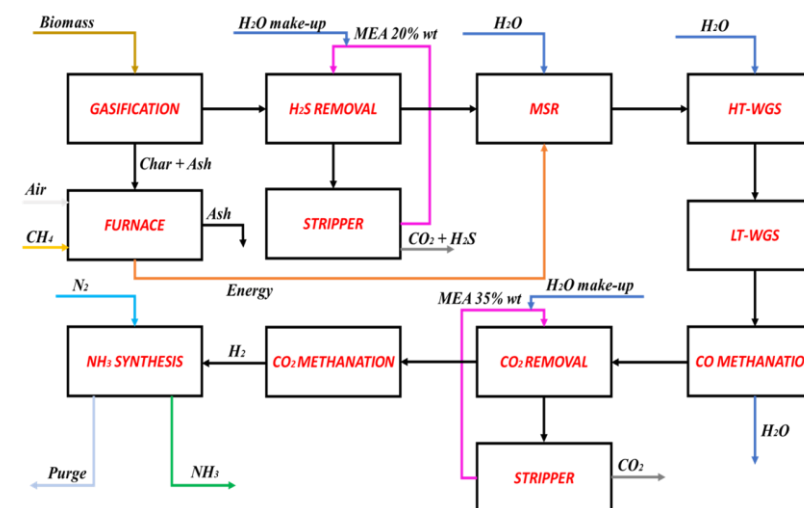


Figure 1. Conceptual design of ammonia production from biomass gasification.

Significance

In this work we demonstrated the proof of concept of a newly designed process for the production of hydrogen from renewable waste biomass and its transformation into a liquid hydrogen vector to be easily transported and stored. As for mass balances, 1000 kg of dry biomass and 600 kg of nitrogen allowed to obtain 550 kg of NH_3 (98.8 wt%). A conceptual scheme was developed of an integrated process, including the delocalized distribution of ammonia to feed H_2 to point users.