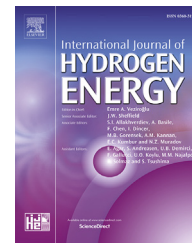




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Towards autothermal hydrogen production by sorption-enhanced water gas shift and methanol reforming: A thermodynamic analysis

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ABSTRACT

Hydrogen production by the water gas shift reaction (WGS) is equilibrium limited. In the current study, we demonstrate that the overall efficiency of the WGS can be improved by co-feeding methanol and removing CO₂ in situ. The thermodynamics of the water gas shift and methanol reforming/WGS (methanol-to-shift, MtoS) reactions for H₂ production alone and with simultaneous CO₂ adsorption (sorption-enhanced, SEWGS and SEMtoS) were studied using a non-stoichiometric approach based on the minimisation of the Gibbs free energy. A typical composition of the effluent from a steam methane reformer was used for the shift section. The effects of temperature (450–750 K), pressure (5–30 barg), steam and methanol addition, fraction of CO₂ adsorption (0–95%) and energy efficiency of the shift systems have been investigated. Adding methanol to the feed facilitates autothermal operation of the shift unit, with and without CO₂ removal, and enhances significantly the amount of H₂ produced. For a set methanol and CO input, the MtoS and SEMtoS systems show a maximum productivity of H₂ between 523 and 593 K due to the increasing limitation of the exothermic shift reaction while the endothermic methanol steam reforming is no longer limited above 593 K. The heat of adsorption of CO₂ was found to make only a small difference to the H₂ production or the autothermal conditions.

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Introduction

During the last decades the continuous increase in the demand of energy and environmental concerns have promoted interest in the use of hydrogen as energy carrier for stationary and mobile applications, since no carbon emissions would be generated by the end users. Hydrogen can be produced from a variety of sources and routes although the cheapest is steam reforming of methane and other hydrocarbons, [Reaction 1](#). The process consists of a syngas

generator (i.e. reformer or gasifier) followed by a water gas shift (WGS) section, [Reaction 2](#). A simplified scheme of a hydrogen manufacturing facility is shown in [Fig. 1](#). Typically, the shift stage consists of two consecutive steps: 1) a high temperature shift (HTS) carried out between 573 K and 773 K to benefit from high reaction rates, and 2) a thermodynamically favourable low temperature shift (LTS) that takes place between 483 K and 543 K.



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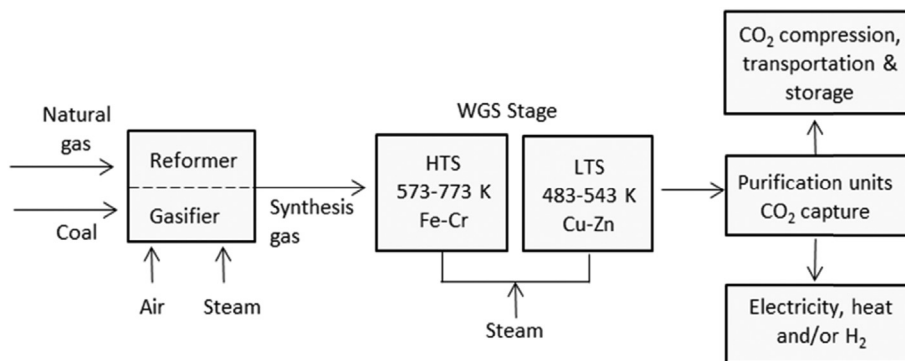


Fig. 1 – Typical stages of the process of hydrogen production from natural gas (reforming) or coal (gasification).



The energy efficiency of the syngas generators has increased significantly in recent years. However, there has been little progress on improving the efficiency of the shift stage. The temperature of the effluent of the reformer/gasifier is significantly higher (1123 K–1373 K) than that specified for the WGS catalyst, so cooling is needed before the shift reactor. Many manufacturers cannot export the steam produced in these heat exchangers and therefore it is desirable to reduce this waste. One of the few attempts to enhance the performance of the WGS section is the methanol-to-shift (MtoS) process developed by Haldor Topsøe, which aims to minimise the energy losses while boosting the hydrogen productivity, Fig. 2 [1]. In the MtoS process, methanol and syngas are co-fed to a reactor where water gas shift occurs alongside methanol decomposition (Reaction 3) and steam reforming of methanol (Reaction 4). Thus, the heat that needs to be removed downstream of the syngas generator is transferred as sensible and latent heat to the methanol stream. Additionally, the energy released by the exothermic WGS can compensate the heat used in situ by the endothermic steam reforming of methanol, resulting in the autothermal operation of the shift reactor. The reforming of methanol also contributes to the formation of hydrogen and it has been reported that the MtoS process can increase the H_2 productivity up to 25% [1]. The Cu/ZnO/Al₂O₃ based catalyst used in this process is reported to be very selective to both reactions and to tolerate higher temperatures than conventional shift catalysts [1,2]. The Topsøe Methanol-to-Shift Technology was developed to meet the increased

demand for extra hydrogen from refineries and other users. In principle, the process is applicable to a hydrogen plant on any scale. An advantage of using methanol as energy carrier in the process is that methanol is produced in very large scale at places where natural gas is cheap, and in the future is expected to serve as a vector for renewable hydrogen [3,4].



Other significant costs involved in the production of hydrogen are related to the purification of H_2 and to the capture of the associated CO_2 to meet environmental regulations. The removal of CO_2 from the effluent of the WGS reactor is usually conducted at medium pressures in pressure-swing adsorption (PSA) columns. An alternative approach is the in situ sequestration of CO_2 as it is formed in the WGS reactor by means of solid adsorbents. The so-called sorption enhancement process is very appealing as it would also favour the shift reaction thermodynamically, rendering higher yields of H_2 . Instead of having two shift reactors in series operating at high and low temperatures, sorption-enhanced water gas shift (SEWGS) requires only one reactor at intermediate temperature, where fast kinetics assisted by adsorption potentially result in smaller units [5]. Although the concept of sorption enhancement has been claimed to be useful for various reactions, it has been shown to be more suitable for the WGS [6]. The CO_2 adsorption requirements for the WGS

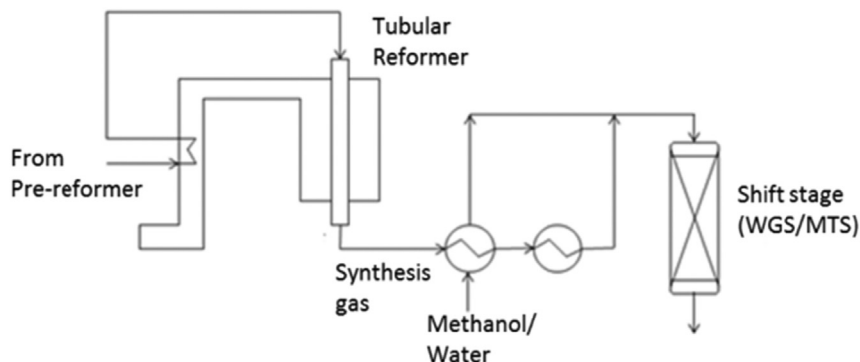


Fig. 2 – Simplified methanol-to-shift process based on Nielsen et al. [1].

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