Hydrogen Production and Carbon Capture by Pyrolysis of Methane and Biogas: From Reaction Engineering to Techno-Economic Studies

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Highlights

- Techno-economic study of pyrolysis processes coupled with experimental studies
- Competitive hydrogen prices compared to steam reforming and water electrolysis
- Carbon utilization is key factor for industrially feasible syngas production from biogas

1. Introduction

The pyrolysis of methane (CH_4) allows to produce hydrogen (H_2) without direct carbon dioxide (CO_2) emissions [1,2]. If the CH_4 originates from fermentation of biomass, the GHG emissions are even negative as the CH_4/CO_2 mixture in the biogas is converted to syngas [3]. This study presents a comprehensive exploration of the development of a competitive process for hydrogen or syngas production using methane sources such as natural gas, flaring gas, or biogas. Experimental data on gas phase species concentrations and resulting carbon, obtained at a high-temperature setup, facilitate process optimization for each methane source from both techno-economic and ecological perspectives.

2. Methods

Pyrolysis experiments were conducted in a high-temperature setup [2,3] operated between 1000 and 1600 °C and with residence times between 1 and 7 s at atmospheric pressure. Mass spectrometry (end-of-pipe) and gas chromatography (spatially resolved data along the reactor) were used to analyze gaseous products. Solid carbonaceous species formed during the reaction were characterized with regard to morphology, surface, structure, and particle size (TEM, BET, DLS, XDS, Raman) for potential industrial applications. Species boiling at high temperatures, for instance polyaromatic hydrocarbons (PAH), were characterized via gas chromatography. Aspen Plus was employed for process development, considering techno-economic aspects through the calculation of both mass and energy balances.

3. Results and discussion

First, the thermal pyrolysis as well as the thermo-catalytic pyrolysis with carbonaceous materials of methane, synthetic natural gas (SNG), and biogas is investigated in a high-temperature setup, whereby the influence of process parameters – temperature, residence time, pressure, and H_2 dilution – is clarified for each feed gas stream. Herein, industrially relevant CH_4 conversions (>80%), CO_2 conversions (>97%) and H_2 selectivities (>97%) can be achieved at temperatures above 1400 °C and residence times above 5 s while simultaneously fixing over 90% (for CH_4 and SNG) or 70% (for biogas), respectively, of the elemental carbon as solid product. The presence of a carbonaceous fixed bed accelerates heterogeneous reactions during carbon deposition, which increases both CH_4 and CO_2 conversion and suppresses the formation of undesired by-products such as C_2 species or benzene.

In addition to the aforementioned parameter studies, mechanistic aspects must be considered as well. For all feeds, a strong inhibiting effect of the dilution gas H_2 can be observed, which can reduce the CH_4 conversion by up to 50% compared to an inert gas dilution, but also prevents by-product formation in the gas phase. The formation of propylene is particularly critical, as it does not act as an intermediate for solid formation but can rather be regarded as a dead-end in the reaction system and thus impedes the complete decomposition to carbon and H_2. Furthermore, for SNG as feed, a positive influence of the additional hydrocarbons in the feed on CH_4 conversion and H_2 selectivity can be observed. Most likely this is due to the faster decomposition of higher hydrocarbons compared to methane, with radicals formed from the first accelerating subsequent dehydrogenation steps. For biogas as feed, further reactions such as dry reforming, Boudouard equilibrium, and the water-gas shift reaction must be considered. Since syngas (H_2/CO mixture) is the primary product when biogas is used as feed, various biogas compositions and their corresponding biomass feedstocks were studied to achieve a H_2:CO ratio of 2:1 in the product gas stream, commonly used in syntheses processes relying on syngas. Using a CH_4:CO_2 feed gas ratio of 1:1, e.g. as typically obtained from the fermentation of cattle slurry or corn silage, led to the optimal syngas ratio mentioned above. The mechanistic investigations were supported by spatially resolved measurements of the gas phase composition in a flow reactor, which allowed conclusions to be drawn about the formation of any intermediates and by-products.

In combination with the results of the carbon and PAH characterization, the kinetic tests are the basis for a techno-economic study. Herein, all data were fed into Aspen Plus simulations in order to design industrially feasible processes for hydrogen and syngas production from natural gas or biogas. Results from energy and mass balances were used to evaluate overall energy consumption, operating costs, and capital costs as functions of both process and external parameters. This study determined a hydrogen price of approximately 2 €/kg and a syngas price between 1 and 1.5 €/kg. A graphical overview of the conducted work is provided in Figure 1.

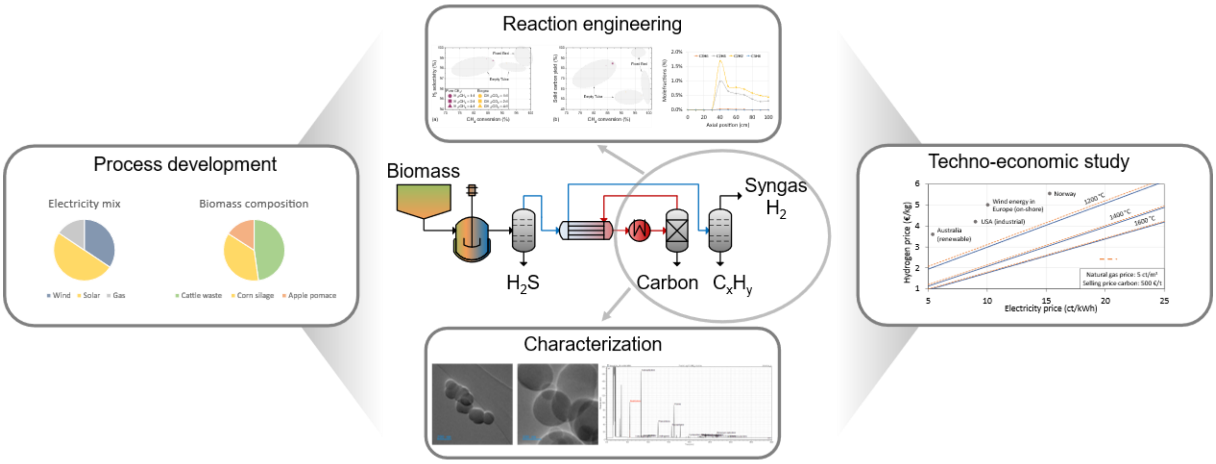

Figure 1. Overview of the present work.

4. Conclusions

Our work comprises a process development for the production of climate-friendly hydrogen or syngas from pyrolysis processes with variable feedstock. Based on experimental parameter studies on various methane sources – pure CH_4, natural gas, flaring gas, biogas – as well as a comprehensive characterization of the resulting carbon and any high-boiling products, extensive overall processes were developed. Herein, H_2 prices of approx. 2 €/kg and syngas prices of 1 to 1.5 €/kg can be realized. Compared to conventional processes, the pyrolysis of methane or natural gas and flaring gas is quite competitive, whereas syngas production from biogas calls for further process optimization. Notably, the competitiveness for each process is highly dependent on the carbon price. Suitable applications, e.g. carbon use in rubber or tire production, can result in significantly higher carbon prices compared to the values assumed in this study, which would make also syngas production from biogas appealing.

References

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Keywords

Clean hydrogen and syngas production, pyrolysis processes, renewable feedstocks, techno-economic study