Methane cracking in molten tin for clean hydrogen and carbon production: an experimental study

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Abstract

Methane cracking is considered a bridge technology between gray and green hydrogen production processes. In this work, an experimental study of methane cracking in molten tin is presented. The influence of the reactor's geometric parameters and the methane injection system is investigated due to their effects on bubble formation, and consequently, gas residence time. The influence of temperature is also studied in the range of 950–1070 °C. Carbon morphology was analyzed using scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET) surface area analysis. The results showed that the reactor diameter affects methane conversion, with larger reactors leading to higher conversions. The diameter of the injection capillary also influences conversion: smaller capillary diameters produce smaller bubbles and slightly increase residence time within a narrow range. The resulting carbon exhibits sheet-like structures and results more ordered when produced at higher temperatures.

Introduction

Currently, hydrogen is mainly produced from fossil fuels by steam methane reforming technology, responsible for about 3% of the global CO_2 emissions in the industrial sector with approximately 7 kg of CO_2 emitted per kg of H_2 produced. The development of sustainable and efficient processes for the production of CO_2-free H_2 is therefore mandatory [1]. A viable alternative for clean hydrogen production may be represented by methane pyrolysis. Methane pyrolysis is in fact considered a bridge technology between grey and green hydrogen production. The global reaction of methane degradation can be briefly described by the following:

$$CH_{4(g)} = C_{(s)} + 2H_{2(g)} \quad \Delta H_{25°C} = 74.85\ kJ \cdot mol_{CH_4}^{-1}$$

where methane CH_4(g) is cracked at high temperatures into solid carbon C(s) and hydrogen H_2(g). The production of solid carbon as by-products represents one of the main interesting features of the process and at the same time one of the main issues. The co-production of carbon with valuable chemical and physical characteristics is a crucial parameter for the economic feasibility and the global environmental performance of the process. When catalyst is used carbon immediately deactivated it and furthermore, the production of carbonaceous material creates serious problems of reactor clogging, so that the process is generally forced to be discontinuous. One of the most attractive solutions to catalyst deactivation and reactor clogging consists

in the use of molten metals as medium for the reaction. Many molten metals have been used in the process with different performances, in this work the use of molten tin will be investigated and the influence of temperature and reactor geometry on CH_4 conversion and carbon production examined.

Experimental section

A simplified scheme of the experimental set-up adopted in this work is presented in Fig. 1. Experimental tests have been conducted in quartz tubular reactors having different internal diameters (i.d = 1.5, 2 and 6 cm) and length L = 40 cm. The reactors are heated by an electrical furnace for 20 cm height and the temperature of the reactor is continuously measured by K thermocouple. The temperatures were varied between 950 and 1070 °C. The methane with a flowrate of 20 $mL \cdot min^{-1}$ has been injected from the bottom of the reactor by capillaries with i.d. varying between 0.1 to 0.53 mm. Smaller capillary diameter can produce smaller bubbles which lead increased residence time, following the equation reported in [2] in this system bubbles diameter decreased from 3.1 to 2.4 mm and the residence time increased from 1 to 1.2 s.
The details about experimental set-up are reported in author's previous article [3].

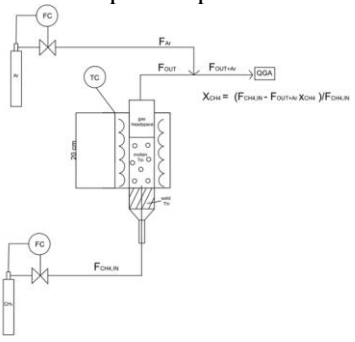

Figure 1. Experimental set-up.

The morphology of the recovered carbon product was analyzed using a high-resolution AURIGA Zeiss scanning electron microscope equipped with an energy dispersive X-ray analyzer (EDS) for elemental analysis. Raman spectra of the carbon were acquired by a micro- Raman dispersive spectrometer (SENTERRA, Bruker Optics) Elemental analysis was performed with EUROVECTOR EA3000 in order to examinate C/H ratios and tin content in the different carbon samples.

Results

In Fig. 2 the results of the methane conversion with different reactor diameter are reported, as the reactor diameter increased the conversion is higher since the bubble when the reactor is smaller tends to flow on the reactor wall with higher velocity. The capillary diameter also has an influence as reported in Fig 2b, smaller diameters of the bubble lead to slightly higher conversion and also some differences can be seen in the carbon morphology (Fig.3).

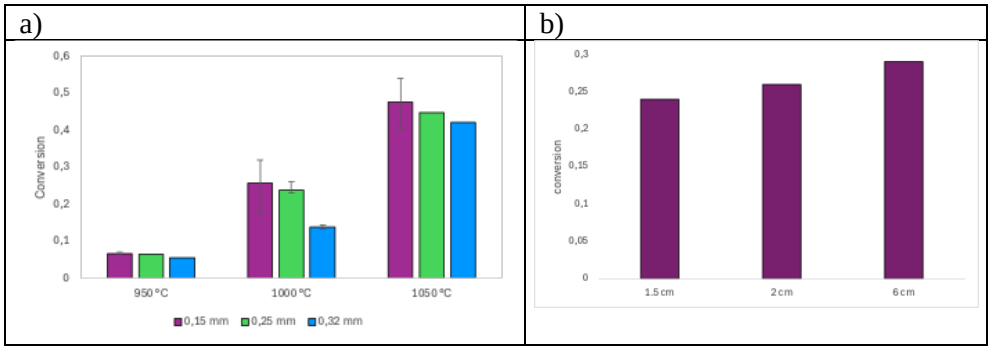

Figure 2. Methane conversion as a function of capillary dimension (a) and reactor dimeter, tests at 1000 °C (b).

In Figure 3 the SEM images of the carbon produced are reported, the carbon has a sheet like morphology due to the reaction occurring at the bubble surface. When lower capillary diameter is used the carbon is more ordered from Raman analysis, in fact ID/IG bands are 0.7 when capillary diameter is 0.15mm and 0.74 for 0.32 mm.

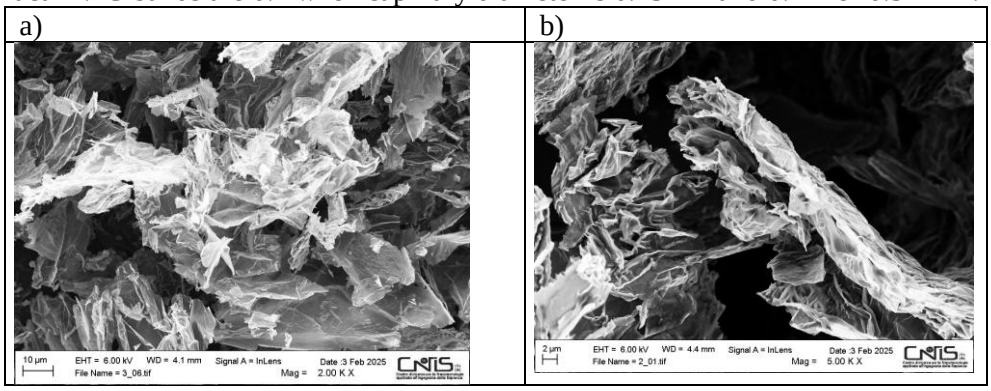

Figure 3. SEM pf carbon for 0.15 mm capillary (a) and 0.32 mm capillary (b)

Conclusions

The results demonstrated that the process is feasible and that the geometric parameters have a great influence on the process and on the carbon which is a target product.

References

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