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Hydrogen Production by Thermal Cracking of Methane – Investigation of Reaction Conditions

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1 Introduction

The solar-thermal decomposition of methane represents a process, which allows the combined production of hydrogen and particulate carbon without generating CO₂-emissions. Solar radiation provides the heat necessary to run the cracking reactions. Different reactors have been used for solar operation (cf. e.g. [1], [2], [3]). The knowledge of reaction kinetics is essential for the design of reactors and plant operations. Although a lot of research has already been done in this field, a coherent and comprehensive characterization has not been reported in literature, yet. In order to learn more about the dependencies of the dissociation on the reaction conditions, numerous kinetic experiments have been carried out in the laboratories of DLR employing a tubular alumina reactor.

2 Experiments without Seeding

The nominal temperature of the electric tube furnace, which was used to heat the reactor, ranged from 1200 °C to 1600 °C, while the gas mixture fed into the reactor comprised a molar fraction of methane (in argon) between 2 % and 10 %. The full spectrum of conversion of methane and yield of hydrogen at a total pressure close to 1 bar was considered by variation of the residence time as shown in Figure 1 a and b. Different initial molar fractions of methane result in a moderate diversity of values for the conversion and the yield regarding similar reaction condition. The residence time is here defined as the time needed by the entering molar flow to pass through the heated volume of the reactor, characterized by the inner diameter of the reactor and the heated length of the tube furnace. For the calculation of the residence time it is assumed, that the heated volume holds the nominal temperature of the tube furnace and that the pressure equals the pressure measured at the inlet of the reactor. Beside the desired products, hydrogen and carbon, intermediates could be found at the reactor outlet, predominantly the C₂-hydrocarbons ethane, ethene, and ethyne. Maximum yields of 0.972 % for ethane, 4.71 % for ethene, and 59.5 % for ethyne were observed.

The sum of the molar fractions of argon, methane, hydrogen, and the C₂-hydrocarbons satisfies approximately 100 % taking the range of uncertainty of the measurands into account. Besides roughly all hydrogen atoms inserted to the system in form of the methane flow can be found in the considered compounds of the product flow.

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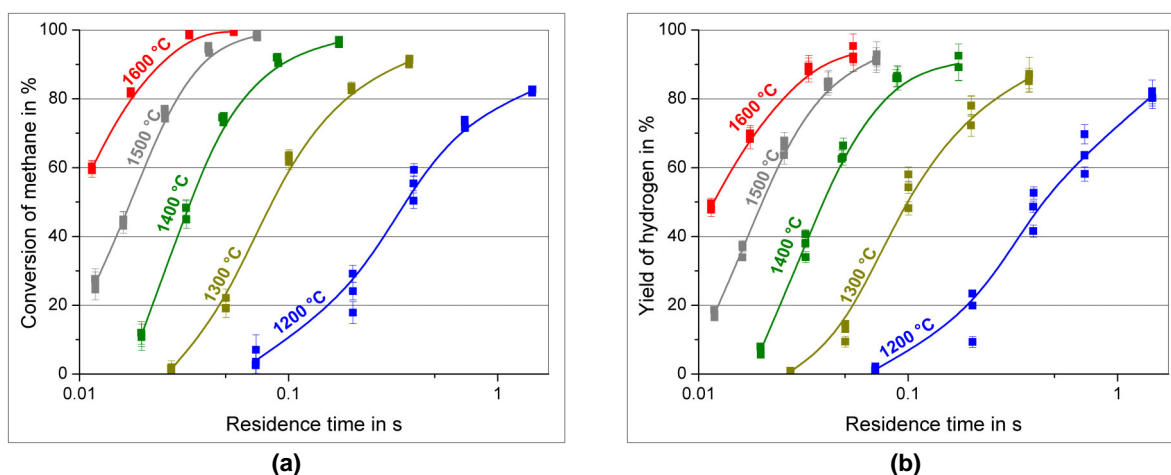


Figure 1: Conversion of methane (a) and yield of hydrogen (b) as a function of the residence time and the nominal furnace temperature, dilution gas: argon, initial molar fraction of methane: between 2 % and 10 %.

3 Modeling the Reactor

Reactions in the test reactor were simulated employing a flow model and a kinetic model in order to extract kinetic parameters, which are the activation energy, the pre-exponential factor, and the reaction order for the four reactions. One of the main influencing factors concerning the kinetics is the temperature. For every combination of furnace temperature and residence time axial temperature profiles were measured using a thermocouple type S, which was stepwise moved through the reactor operated with a pure argon stream. The gained information was used to determine profiles for the wall temperature. With temperature profiles of the wall and velocity profiles at the entrance of the reactor temperature inside the whole reactor as well as flow lines were calculated utilizing the software COMSOL Multiphysics. A nested tube reactor model was chosen to approximate the laminar flow conditions inside the reactor. Reaction rates and finally leaving molar flows were obtained for discretized parts of the nested tube reactors. Each reaction step was followed by an ideal diffusion step in radial direction, equalizing molar fractions of the different species at the outlet of the considered discretized part. The kinetic model comprised the dehydrogenation reactions of methane, ethane, ethene, and ethyne (cp. [4]) and followed



Employing best fit kinetic parameters found by an optimization tool fairly good agreement for the conversion of methane and the yield of hydrogen between experimental results and output of the simplified model could be achieved. However the performance of the model offers potential for improvement. The dissociation of the species is not only the result of homogeneous reactions, but a combination of homogeneous and heterogeneous effects.

Thus an implementation of heterogeneous reactions will enhance the quality of a model of the thermal decomposition of methane. Heterogeneous effects occur on generated carbon particles – literature indicates rate-increasing effects of carbon-based catalysts (cp. e.g. [5], [6], [7]) – as well as on the surface of the reactor, which in operation is partly covered by carbon deposition. Additional experiments have been carried out, in order to learn about heterogeneous effects.

4 C-balance and Characterization of Samples

The latest experiments repeating selected reaction conditions, allow the balance of the amount of C-atoms. In contrast to the H-balance, the C-balance shows that about 25 %, and up to 50 %, of carbon atoms are contained in compounds of the product gas, which have not been considered in this work. As a result the presence of a low amount of substances with high C/H-ratios is probable. Without the consideration of further C-rich fractions the amount of particulate carbon is overestimated and, consequently, likewise the surface area provided for reactions. For the C-balance samples of carbon were obtained by removing carbon deposition from the inner wall of the reactor and from the filter element. In most carbon samples from the reactor not only black particulate carbon was found but also thin layers of shiny gray pyrocarbon (see Figure 2 a), which have the curved shape of the inner reactor wall. Some samples of carbon located in the filter show a slightly yellow color, which confirm the presence of high molecular by-products (see Figure 2 b). The BET-surface of particles found in the reactor range between $6.9 \text{ m}^2/\text{g}$ and $56.4 \text{ m}^2/\text{g}$, whereas the range for particles found in the filter is characterized by higher values between $22.3 \text{ m}^2/\text{g}$ and $139.1 \text{ m}^2/\text{g}$. Some samples show very similar specific surface areas to commercial carbon blacks.

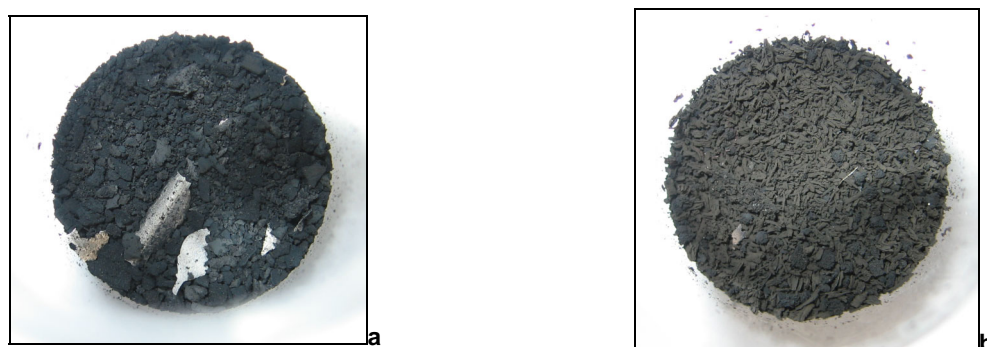


Figure 2: Examples of carbon samples: removed from the reactor wall (a) and removed from the filter (b).

5 Experiments with Particle Seeding

Experiments with carbon particle seeding of the inlet gas were carried out employing a recently developed apparatus, in order to expand data regarding heterogeneous effects. The material used for seeding was “Super P”, a commercial carbon black produced by Timcal, featuring a typical particle size of 40 nm and a specific surface area of $62 \text{ m}^2/\text{g}$ (BET) (cp. [8]). The specific surface area of “Super P” has the same order of magnitude as most values for extracted samples from the reactor and the filter. The chosen reaction conditions were a

nominal furnace temperature of 1400 °C and a total volume flow of 3800 sccm (referring to standard conditions 0 °C and 1.01325 bar) consisting of 5 % methane in argon. The reference case without seeding corresponds to a calculated conversion of 48.2 % and 38.0 % yield of hydrogen. By adding a mass flow of about 5.24 g/h “Super P” the conversion of methane and the yield of hydrogen could be increased by 18 % and 33 %, respectively, compared to the reference case without seeding. The yields of ethane and ethene decreased by 40 % and 25 %, respectively, whereas the yield of ethyne rose slightly by about 4 % (see Figure 3 a). The related yields of hydrogen and C₂-hydrocarbons increased from 1.38 to 1.81. Thus obviously carbon particle seeding effects the dissociation of methane promoting the formation of the desired product hydrogen. Seeding influences the conditions inside the reactor in different ways, providing additional surface area for heterogeneous reactions and improving the heat transport between the reactor wall and the flow through the reactor.

The theoretical mass flow of generated carbon particles equals about 1.3 g/h for the reference case. In contrast to this calculation regarding the considered reaction condition without seeding the fraction of carbon atoms in not identified compounds of the product flow equals more than 20 %, leading to a practically negligible mass flow of generated particles. Therefore it is admissible to state, that major part of particles present in the reactor was contributed by particles, which were seeded. The surface area of added particles in the heated volume of the reactor can be approximated employing the mass flow, the residence time and the specific surface area (BET) of “Super P”. The theoretical surface area inside the reactor arises from the sum of the surface area of added particles and the geometrical surface area of the reactor, which equals about 0.0063 m². In Figure 3 b conversion and yields of the considered components of the product flow are depicted as a function of the theoretical surface area inside the reactor.

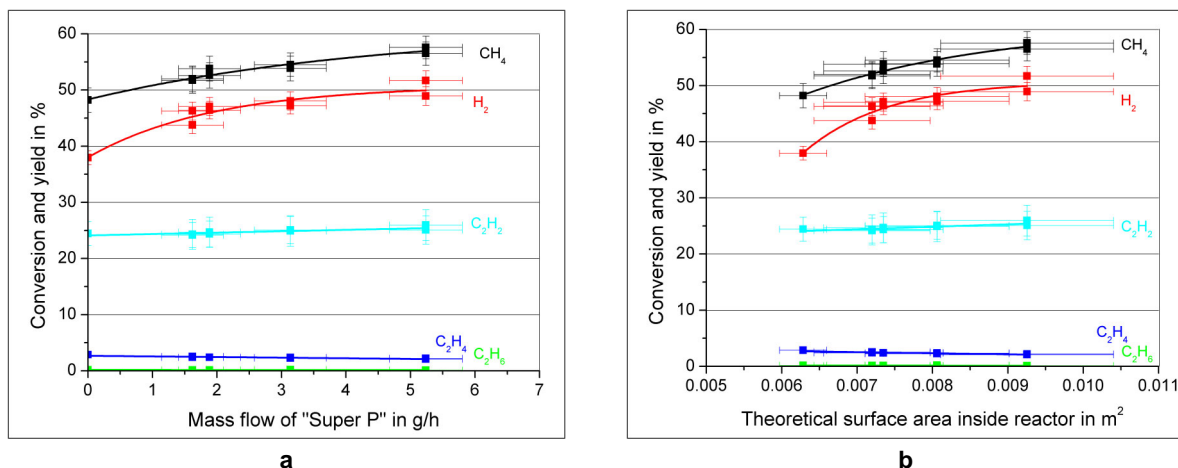


Figure 3: Conversion of methane and yield of hydrogen, ethane, ethene, and ethyne as a function of the mass flow of added carbon black (a) and the theoretical surface area inside the reactor (b), nominal furnace temperature: 1400 °C, dilution gas: argon, initial total standard volume flow: 3800 sccm, initial molar fraction of methane: 5 %, pressure approximately 1.02 bar.

The diagram suggests that the surface area provided for reactions strongly affects the reaction rates, even though the influence of particle seeding is partly based on an improved heat transfer. Since the reactor wall provides surface area in the same order of magnitude as added particles, the wall should be considered as a preferred location for reactions. The specific surface area of carbon deposition found in the reactor and the filter is often similar (or even higher) compared to figures of "Super P", indicating that also the surface of generated particles serves as reaction sites.

6 Summary and Conclusions

The thermal dissociation of methane comprises the presence not only of the final products hydrogen and carbon, but also of intermediates such as the C₂-hydrocarbons. A kinetic model considering the stepwise dehydrogenation from methane to finally hydrogen and carbon with the intermediates ethane, ethene and ethyne leads to fairly good agreement between results of the experiments and simulations concerning the conversion of methane and the yield of hydrogen. In order to learn about heterogeneous effects and to identify ways to improve the performance of the model for the thermal dissociation of methane further experiments were carried out. It was realized that remarkable fraction of C-atoms were located in compounds of the product flow with high C/H-ratios, which have not been considered in this work. Seeding of the inlet gas with carbon black results in an increase of both, conversion of methane and yield of hydrogen. It is suggested that the surface of the reactor as well as the surface of particles serve as reaction sites.

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