# HYDROGEN PRODUCTION BY THERMAL CRACKING OF NATURAL GAS – TEST FACILITY

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*Hydrogen is an energy carrier which makes a decisive contribution for future energy transition. Over 90% of Hydrogen is produced currently from primary fossil fuels with high* $CO_2$*-emissions. Methane cracking is intensively developing, as the storage or using of solid carbon is easier and more attractive than Carbon Capture & Storage (CCS). The process without catalysts is simpler, but requires higher temperatures. Main objective of the test was to show the viability for industrial applications. The test facility consists of two columns (for reversible operation) filled with pebble-bed and a connecting horizontal part. The cracking process takes place at the highest temperature zone, which is the upper pebble-bed and the connecting pipe. The required reaction energy is supplied by adding Oxygen to burn small amount of Hydrogen. Sensible heat of product gas is stored in the pebble-bed and cold gas goes out. The product gas is further cooled and the condensate flows in a drain vessel. The capacity of the facility was 2 - 4* $\frac{m^3_{STP}}{h}$ *of Methane, with corresponding residence time between 0.5 - 2 seconds. To compare the quality of those results, the Hydrogen yield was evaluated. The highest yields have been achieved at temperature above 1500°C, with a maximum value of 94.9%, what is considerably better than results achieved in other test facilities for cracking using catalysts (yield 78% at 1175°C). The comparison shows important advantages of high temperature processes without catalyst. The cracking process at 1500°C is a simpler and more effective way to reach industrialization of that technology.*

Key words: *methane cracking, methane pyrolysis, hydrogen, hydrogen yield, turquoise hydrogen, soot*

## 1. Introduction

Numerous meetings, conferences, discussions and political actions have taken place, discussing and urging measures to reduce greenhouse gas concentration in the atmosphere. It has been always emphasized that utmost urgency is needed as the consequences for climate change will be dire. However, the noticeable effects are missing, as there is no real willingness for changing the paradigm of the energy policy. When the measures for suppression of climate change influence the existing economic interest, everything is forgotten very fast and, with the help of media the old business-asusual prevails. The effects of all those „measures“ from 2005 to 2022 are presented in Figure 1 [1]: no effect! The concentration of $CO_2$ continues to increase steadily from 380 to almost 420 ppm. This equates to 10% increase in the last 17 years!

Such behavior would need to be changed through far-reaching, rationale and good planned measures of energy policies. Short-sighted greed for economic interest, alongside with technology protectionism and fanaticism has to be abandoned. Otherwise, the steady linear increase of $CO_2$ concentration on Figure 1 will inevitably continue.

World-wide usage of renewable energy, not only for electricity generation, nuclear energy and fossil fuels without $CO_2$ emissions would need to replace the present situation. In that context, a very important or even crucial role (it has to be proven through technology openness) will be taken by Hydrogen, as a new energy carrier with some very good characteristics. There are different ways for generating $CO_2$-free Hydrogen, like electrolysis of water, biomass, Methane (and other hydrocarbons) with CCS or cracking.

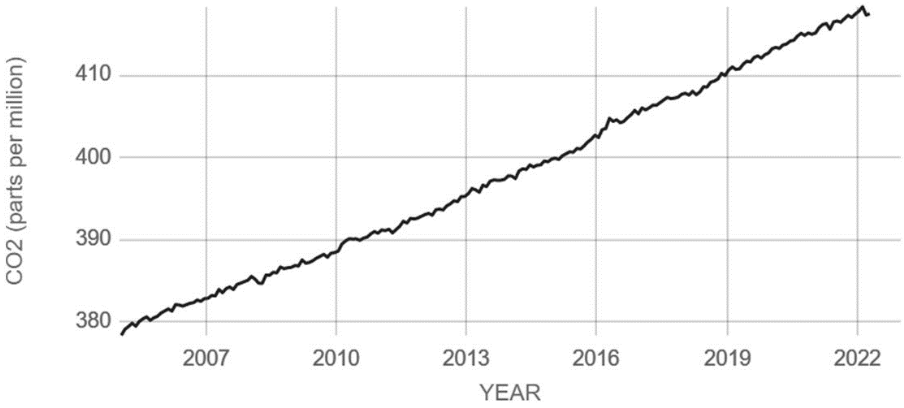

**Figure 1: Increase of the $CO_2$ concentration in the atmosphere [1]**

## 2. Why Hydrogen? Why Cracking?

Hydrogen is a very important energy carrier which can make a decisive contribution to the future energy transition. It may be produced using several technologies, may be stored and transported in several ways. It may be used to cover different energy needs, like transportation, power and heat generation, iron ore reduction etc. However, nowadays well over 90% of existing Hydrogen on the market is “grey”, i.e. obtained from primary fossil fuels with accompanying high $CO_2$ emissions, and as such cannot contribute to the energy transition. It is therefore very important that the produced Hydrogen is $CO_2$-neutral.

The oldest generation of large-scale amounts of Hydrogen is based on coal gasification with water vapor (water gas reaction), through the chemical reaction:

$$C + H_2O \rightleftharpoons CO + H_2 \tag{1}$$

Today, the main process for Hydrogen production is steam reforming, where the Methane from natural gas reacts with the steam:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{2}$$

The yield of hydrogen can be further increased by the water gas shift reaction at lower temperatures:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

One can also use fossil oil to produce hydrogen in a similar process. Hydrogen produced in that way is labelled "grey", as it originates from fossil fuels and its generation is accompanying with high $CO_2$ emissions.

The electrolysis of water is another method to obtain Hydrogen, with very high expectations to become the key technology for the future generation. Today about 4% of the hydrogen produced worldwide is produced by electrolysis. However, such Hydrogen is only "green" if the electricity used is also "green". The problem is that the "green" electricity from solar and wind systems is not always available, what reduces the operation time required for the economical operation. It will be necessary to produce Hydrogen in countries high insolation and to export to other countries. As mentioned, the transport of Hydrogen is possible but expensive and technically not yet realized on a large scale.

Hydrogen can be produced from biomass, as well. Presently, it could be done from bio-methane, or directly from biomass by gasification or steam reforming [2]. Officially, such Hydrogen is labelled as “orange”, as there is a strong resentment against biomass, due to political failures in the near past and its usage in a non-sustainable way. However, the proponents of its usage insist to label it also “green”, like the Hydrogen from electrolysers. It is much easier to control the origin and usage of biomass, than the origin of electricity.

If the carbon dioxide ($CO_2$) produced during the steam reforming of Methane is subsequently separated from the process exhaust gases and stored underground (CCS – carbon capture and storage), such Hydrogen is referred to as “blue” hydrogen. It is also made from fossil fuels, but $CO_2$ emissions are prevented or at least drastically reduced. However, the CCS process is controversial worldwide and still classified as high-risk.

Methane cracking is recently intensively developing and becoming a promising technique. Methane is broken down at high temperatures (in the presence of some catalyst, or without it) into its molecular components, namely Hydrogen and pure carbon. An important factor is that the reaction, which takes place in the absence of Oxygen, does not release any $CO_2$ emissions:

$$CH_4 \rightarrow 2H_2 + C \qquad (4)$$

The reaction heat required for the endothermic reaction is 74.9 kJ/mol. Storing or using of solid carbon is much easier and more attractive than storage of $CO_2$, which speaks in favor of such methods. Hydrogen produced in this way is referred to as "turquoise". However, in case that the Methane is coming from bio-gas, the result is negative $CO_2$ emission, so that the resulting Hydrogen is better than the “green” one!

Hydrogen is an expensive energy carrier, but we have to pay that price in order to protect our environment and to prevent a sudden, catastrophic climate change. In a stable energy market, the cheapest Hydrogen is the “grey” one, from natural gas. But even that solution is more expensive than the usage of fossil natural gas. For the “green” Hydrogen from electrolysis, about 50 to 70 kWh (depending on efficiency) of electricity has to be used to get 1 kg of $H_2$, what makes it also very expensive. In some areas with available waste and residual biomass (like Bavaria in Germany), Hydrogen generated from biomass is a very good solution, especially if there is no sufficient electricity from renewable energy sources. However, the need for Hydrogen is much higher than the amount which can be produced from available biomass.

In such cases the cracking of Methane from natural gas could be an excellent solution, at least an intermediary one. It could enable production of a large amount of Hydrogen at affordable costs in a short-term period, before waist renewable electricity generation is reached, or before big amount of Hydrogen could be imported from other continents. One has to bear in mind that it will not be easy to increase the electricity generation from RES: first to replace all fossil generation and then to increase electricity generation required for mobility, heat-pumps and other, presently non-existing, applications. The same is valid for overseas $H_2$ import and transportation: the time is needed to install the overseas $H_2$ generation capacities, to build new tankers and to install required infrastructure for that. That could significantly reduce the pace of introducing $H_2$ economy.

In case of cracking, the existing pipelines for natural gas transport could be further used, also for gas from LNG terminals. Natural gas may be distributed like nowadays and then locally $H_2$ may be produced by cracking and locally distributed with new $H_2$ network, without a need for $CO_2$ transportation for CCS. That would be a solution for fast and affordable introduction of $H_2$ economy. Finally, the technology could be exported to countries with high reserves of natural gas.

## 3. Conditions for Methane Cracking with high $H_2$-Yield

There is a lot of developments in the area of Methane cracking, i.e. pyrolysis of Methane, especially in the recent years. A comprehensive overview is given in [3]. Some of them are using plasma, the other different catalysts, or pure thermal processes. Big advantage is that there is no emission of $CO_2$, as the carbon is a by-product in a solid form. The decomposition of Methane starts even at 500-600°C, especially in the presence of some catalysts (nickel, iron, carbon...). However, for a more complete reaction, with high $H_2$-yield, considerably higher temperatures are required. Even with catalysts, at least 1200°C is needed [4]. The process without catalysts is simpler, but requires higher temperatures. In the reference [5] it is clearly demonstrated that at 1700K the residence time of 1 second is required for complete decomposition (see Figure 2). That was the motivation and the main design parameter for the development of the test facility presented in this publication.

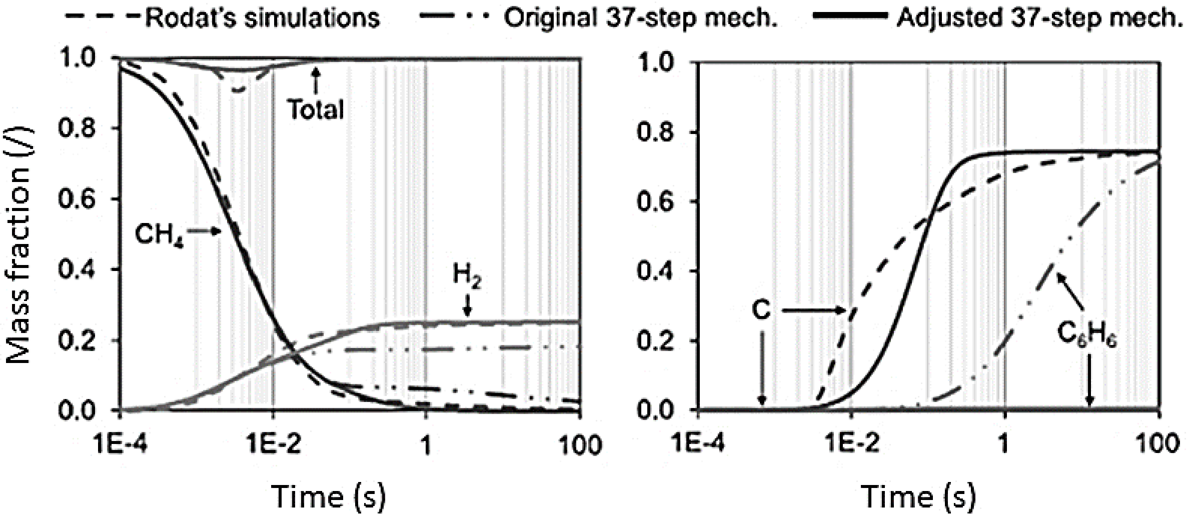

**Figure 2: Thermal decomposition of Methane at 1700 K [5]**

## 4. Development of the Test Facility

The test facility is based on the previous experience with the application of the Pebble-Heater technology for thermal oxidizers [6] and later for tar cracking [7]. As shown in Figures 3 and 4, it consists of two columns filled with pebble-bed and a connecting horizontal part. The upper part of the pebble-beds and the connecting pipe is the highest temperature zone (HTZ) where the cracking process mainly takes place. Its volume is designed in such a way to enable the required residence time. In the middle of connecting part there is a high temperature electrical heater, which role is to preheat the installation.

The PID scheme is presented in Figure 3 [8]. The gas was supplied through standard industrial bottles. Besides CNG (compressed natural gas), pure $CH_4$, oxygen and some compressed air (for initial operation), nitrogen is used for inertization of the atmosphere in the facility.

High pressure of the gas has been reduced to almost ambient pressure through pressure control valves and the flowrates measured by corresponding flow-meters. Temperatures are measured with 7 thermocouples, from position 1 to 7. On positions 1, 6 and 7 thermocouples type K (NiCr-Ni) were used, and in the high temperature zone (position 2, 3, 4 and 5) thermocouples type S (PtRh-Pt) were installed. Two U-tube manometers have measured the pressure drop over the pebble-bed columns.

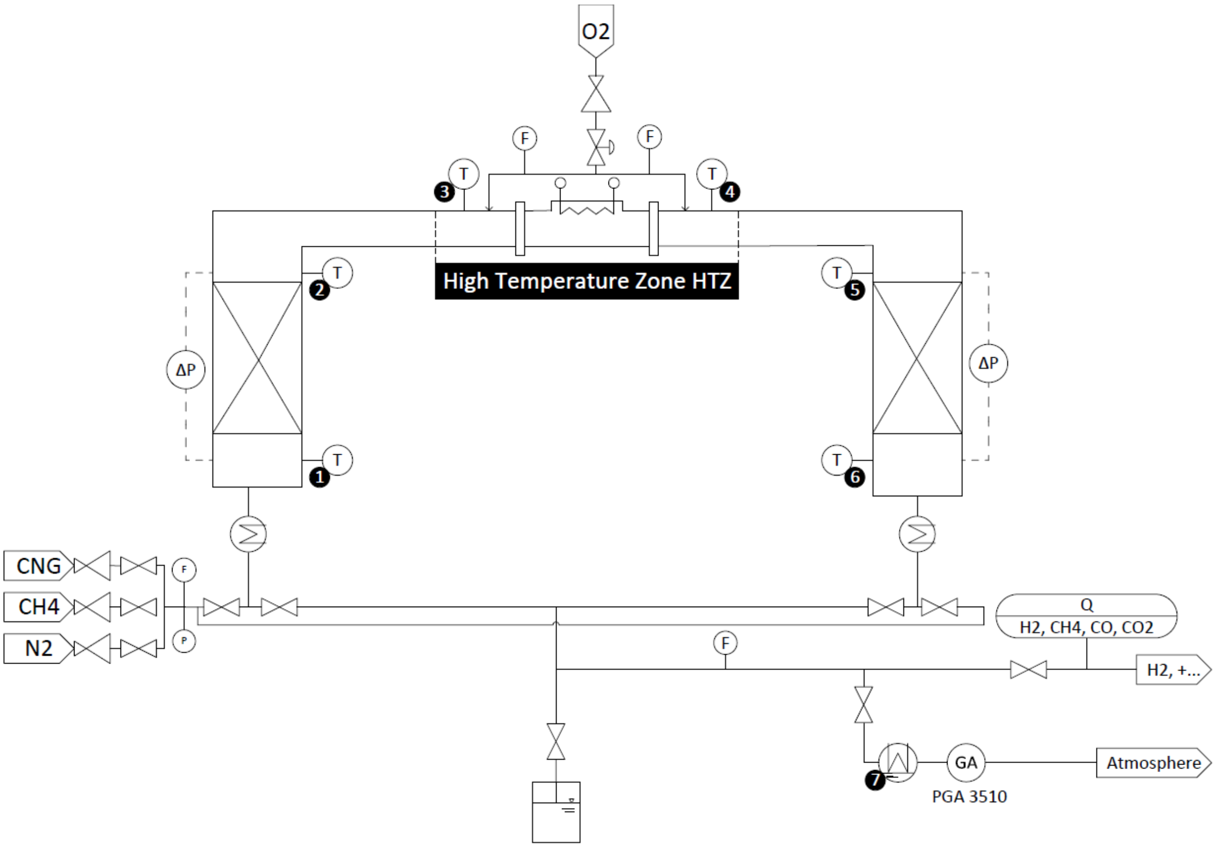

**Figure 3: PID scheme of the test facility [8]**

At the outlet from the pebble-bed columns the gas was cooled in order to protect sensitive cells for $H_2$, $CH_4$, CO and $CO_2$ in the gas analyzer. Condensate that occurred during that gas cooling was collected in a separate drain vessel. The gas by-pass direction gas analyzer was additionally cooled to max. 5°C and dried in a silica-gel column.

In one pebble-bed the inlet Methane is preheated to cracking temperature. In the high temperature zone (HTZ), the cracking process is very intensive and the required reaction energy is supplied by adding some oxygen to burn small amount of Hydrogen. In that way, the temperature of the product gas has the same temperature at the inlet to the second pebble-bed. Sensible heat of product gas is stored there and cold gas goes out. In a condenser under each column, the product gas is further cooled, and the occurred condensate flows in a drain vessel. After some time, by switching corresponding valves, the flow direction is changed, so that Methane enters the second pebble-bed and the product gas goes out through the first pebble-bed.

To start the process, the electrical heaters heat up the HTZ to at least 1000°C. That temperature is high enough to enable a smooth ignition of the Methane with added Oxygen (or compressed air). Further preheating of the facility takes place by the combustion of Methane. When the required temperature (e.g. 1500°C) is achieved, the amount of Oxygen is reduced, so that partial combustion goes over to cracking. The Oxygen is added on both sides of the electrical heating system. The electrical system may be switched off at that phase of process.

The capacity of the test facility was 2 – 4 $\frac{\mathrm{m}^3_{\mathrm{STP}}}{\mathrm{h}}$ of Methane, with corresponding residence time in the range 0.5 to 2 seconds in different sections or in the whole HTZ.

The photo of the test facility is given in Figure 4 [8]. Two columns with pebble-beds may be seen (with outside insulation), as well as the connecting pipe with electrical heater. Under the pebble-bed columns there are coolers/condensers (grey).

In the meantime, the process and corresponding facility have been applied for a patent [9].

**Figure 4: Photo of the test facility**

## 5. Test Campaign

As described above, before each test the facility had to be preheated by electrical heater to at least 1000°C in the HTZ. This process usually took more than 10 hours, some days the heater was turn on over the entire night. Then the flow of CNG was started, in the range 2 – 4 $\frac{m_{STP}^3}{h}$, immediately the compressed air has been added and the combustion, mostly partial, started. The amount of added air was controlled through the temperature measurement, in order to avoid temperatures above 1500°C.

When the required temperature has been reached, the air was gradually replaced with oxygen and the flow rates of gas and oxygen had to be adjusted to maintain the required temperature. After these preparations the test could start.

Unfortunately, it was very difficult to perform the planned schedules. The rotameters for the flow measurement and corresponding regulation valves were not sufficiently accurate to control the test conditions. That is the point that has to be improved on the next pilot facility, in the form of coupled control loop temperature - flow rate.

Furthermore, the flow rate was too low (typical for small test facilities) and the leakage rate was relatively high. Consequently, a precise mass and energy balance was not possible to estimate. The injection and flushing with Nitrogen was not done automatically after and before each test. When performing tests, in one occasion it was left out and a small deflagration occurred. On a facility with such a small capacity it was a minor incident, but on a bigger facility it would need to be prevented.

There were some other "teething" problems. For instance, the ceramic tubes for Oxygen injection were not correctly centered. At very high temperatures the flame destroyed locally some part of alumina refractory. Additionally, it was not possible to control separately the Oxygen flow rate at each injection point, what is crucial for preventing generation of CO and $CO_2$.

However, the biggest problems, which influenced the time-table of the entire tests campaign, were with the electrical heaters. On the other hand, the lessons learned will be very useful for the pilot facility. Test with thick Kanthal-A wire were done, as well as with SiC-heaters. The second solution was very good for high temperatures and simple for operation (no need for a transformer), so that it could be placed directly in the gas flow. However, when the cracking of Methane started, the heater braids were blocked with generated soot, what caused the short circuit and the heaters were destroyed. A good working solution was found to be the use of Kanthal wire coupled with a precise temperature controller.

In spite of those problems very good tests were done, which confirmed the intended process of solely thermal cracking, without any catalyst.

As example, the results of Test 2.2 are presented in Figure 5. Temperature T4 on the end of HTZ in the flow direction was in the range 900-1500°C. That was still a preheating phase of the whole facility, therefore the Hydrogen production was low at the beginning. Only since that temperature reached 1500°C (due to partial combustion of 4.8 $\frac{m_{STP}^3}{h}$ CNG with 2.1 $\frac{m_{STP}^3}{h}$ $O_2$), a significant concentration of $H_2$ was registered. That was a sign of intensive cracking, which on the other hand influenced the temperature T4 to drop. The maximal value of Hydrogen was 48.3%, what caused a very favorable ratio between $H_2$ and $CH_4$. That was a partial combustion, as the oxygen was injected before the cracking started. Therefore, a significant amount of CO (together with some $CO_2$) occurred. Due to further temperature drop, the whole process lost on intensity soon. One can notice a time delay between the measured temperature and described gas fractions, due to considerably longer time constant of the gas analyzer.

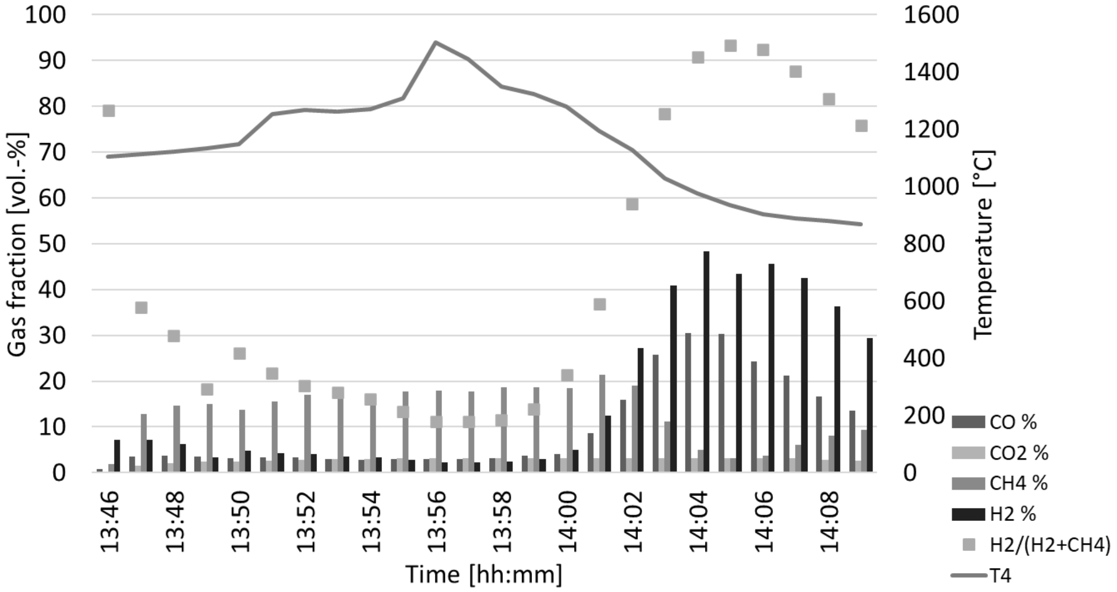

**Figure 5: Gas composition after $CH_4$ cracking dependent on temperature, Test V2.2**

Test V3.3 is a good example how the cracking process runs when the whole facility is well on the temperature. Very high $H_2$-ratio is reached anytime when the temperature T4 is high enough. At above 1450°C, the $H_2$-ratio was always above 90%. On the other hand, it drops significantly when the temperature is 1200°C or lower. That is an excellent proof of temperature importance for the cracking process in absence of metallic catalyst, as clearly presented in Figure 6.

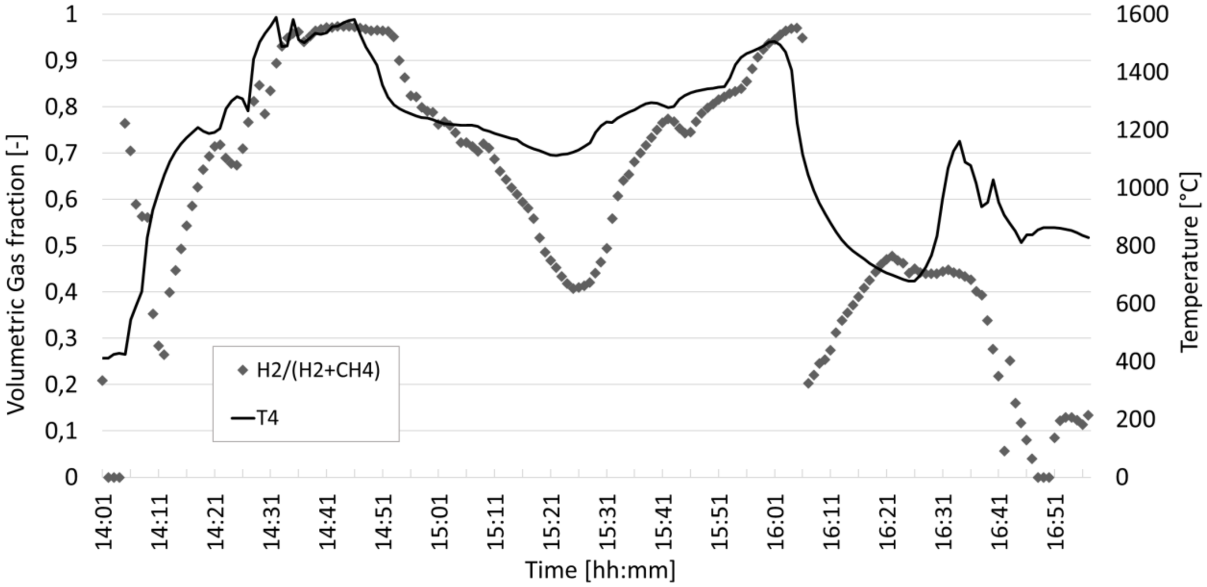

**Figure 6: Ratio of $H_2$ to ($H_2$+$CH_4$) dependent on temperature, Test V3.3**

More detailed evaluation of the test results may be found in [8].

Especially in the last test, a considerable amount of condensate was created, proving the oxidation of some part of Hydrogen and energy supply through that process. Soot was mainly found as deposition in the pebble-bed columns, but some amount was found in the synthesis gas and consequently in the condensate.

## 6. Analysis of the Test Results

In order to compare the quality of the achieved results, the yield of Hydrogen from Methane decomposition $Y_{\mathrm{H_2,CH_4}}$ was evaluated for the best test conditions (required temperature and flow-rates), with the same methodology as in [4]. For syngas without the presence of the diluting gases like Nitrogen, Carbon monoxide and/or Carbon dioxide, the Hydrogen yield could be calculated with:

$$Y_{\mathrm{H_2,CH_4}} = \frac{y_{\mathrm{H_2}}\left(1 + X_{\mathrm{CH_4}}\right)}{2} \tag{5}$$

whereas $y_{\mathrm{H_2}}$ represents the volume (molar) fraction of Hydrogen in the syngas and $X_{\mathrm{CH_4}}$ the Methane conversion:

$$X_{\mathrm{CH_4}} = \frac{1 - y_{\mathrm{CH_4}}}{1 + y_{\mathrm{CH_4}}} \tag{6}$$

with $y_{\mathrm{CH_4}}$ as molar fraction of rest Methane in syngas. On that way (with $y_{\mathrm{H_2}} + y_{\mathrm{CH_4}} = 1$), the final expression for the Hydrogen yield is:

$$Y_{\mathrm{H_2,CH_4}} = \frac{y_{\mathrm{H_2}}}{2 - y_{\mathrm{H_2}}} \tag{7}$$

Using that formula, the results are plotted in Figure 7. The highest yields have been achieved at temperature above 1500°C, with a maximum value of 94.9% at 1560°C.

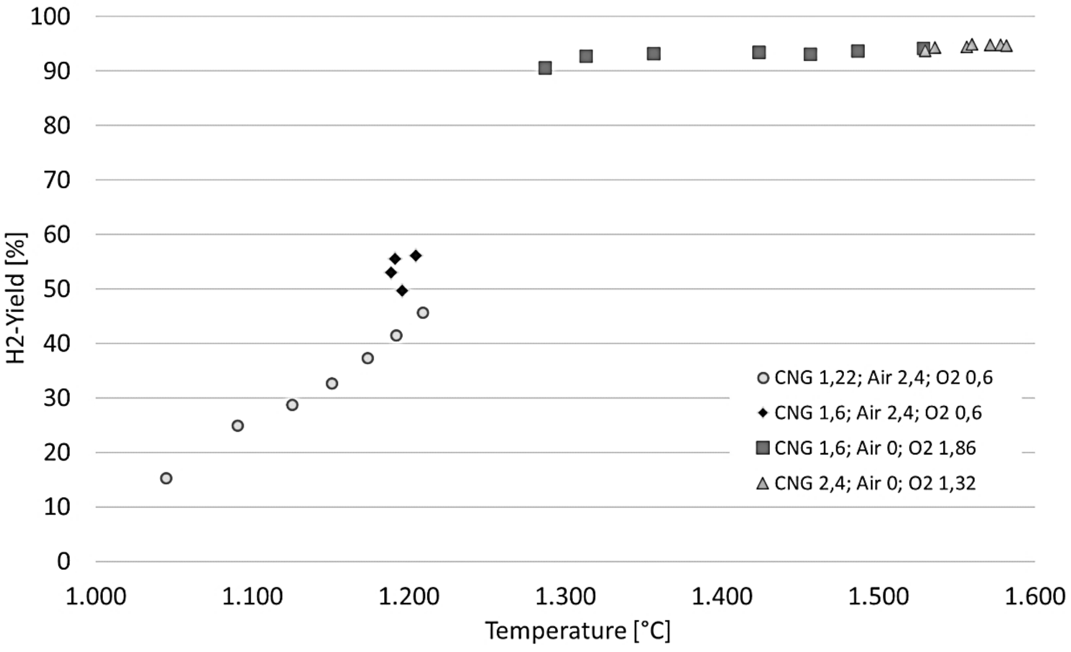

**Figure 7: Hydrogen yield as a function of temperature (CNG/Air/$O_2$ in $\frac{\mathrm{m^3_{STP}}}{\mathrm{h}}$) [8]**

Those results are considerably better than achieved in the facility of KIT [4], presented in Figure 8. The capacity there was very small, 50 and 200 ml/min (3 and 12 l/h), and with liquid tin as catalyst. The highest yield was 78% at 1175°C.

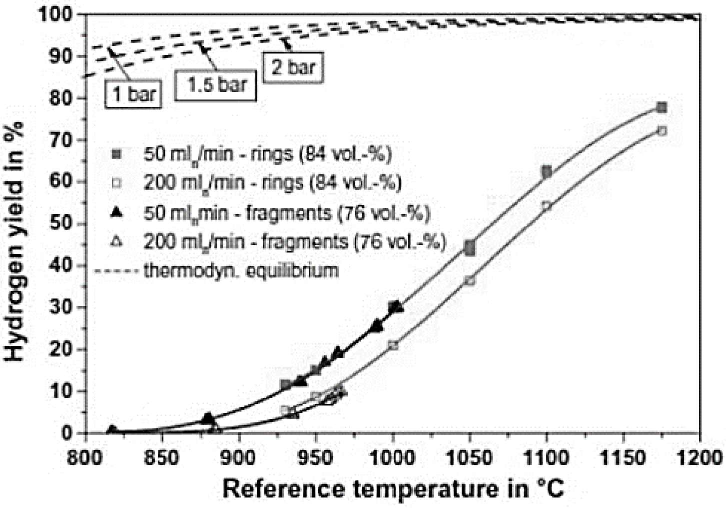

Figure 8: Hydrogen yield of the Methane pyrolysis process of KIT [4]

That comparison shows important advantages of the high temperature process without catalyst. If one has the experience and technology for high temperatures (1500°C and more) that is a simpler and more effective way to reach industrialization of cracking technology.

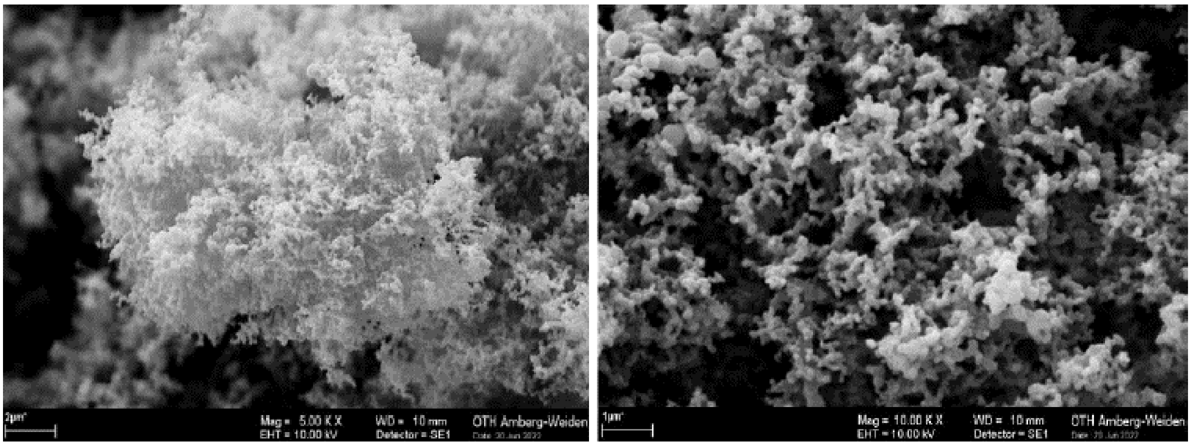

Figure 9: REM photos of soot, with 5.000 and 10.000 enlargement [8]

The analysis of the extracted soot was limited only to making different photos, like the example presented in Figure 9. The most important conclusion is that the soot has a form of small balls, which stick to each other, forming a very porous structure. Therefore, the pressure drop is small, and the bulk density is extremely low. That is important for the further development.

The extracted condensate was examined as well. It was blurry due to entrained soot particles, pH values in the range 4-5 and the total hardness <1.8 mol/m$^3$ (very soft). As the condensate comes from pure reaction steam, the hardness originates from minerals contained in refractory materials. Anyhow, for further usage a pretreatment will be necessary.

## 7. Further Work

A further step in developing this technology will be to design, build and test a pilot facility. It is foreseen that its capacity should be in the range of 100 $m^3_{STP}/h$, i.e. the scale-up factor 25 – 50. In such a way the follow up step towards full industrialization will be considerably easier.

Hydrogen generation will be up to 18 kg/h and almost 54 kg/h carbon black. Again, the high temperature electrical heaters will be used, but not only for preheating the installation. The possibility to use solely electrical energy for cracking process will be tested. For that, the electrical power of about 100 kW will be needed. Thus, the formation of CO and $CO_2$ will be completely inhibited. The formation of steam/condensate will be also repressed. However, the other possibility to use $O_2$ for energy supply through the oxidation of one part of formed Hydrogen, will be also further developed. The position and redistribution of injected Oxygen will be optimized in order to minimize the formation of CO and $CO_2$.

The main development will be to find a simple and effective way for soot collection and removal from the facility. The solution will be based on the experience with previous projects, as well as on the results of an ongoing project with extremely high dust loads at high temperature. The further usage of extracted soot will be also analyzed.

## 8. Conclusion

The results of the test facility have demonstrated the simplicity and effectiveness of the cracking process when only high temperature is used, without any metal catalyst. The achieved Hydrogen yield of 94% is the best value reported on similar facilities. Further development has to include the increase of capacity and automatic removal of collected soot.

The possibility to use electricity and/or Oxygen for supplying required reaction heat is very favorable. In some parts of Europe, it could be opted between the two, according to the market conditions and availability of green electricity. If the electrolysis for Hydrogen generation increases as planned, there will be a lot of Oxygen available for this process.

In case of countries with high insolation and high natural gas reserves, this technology could be exported and used in different modi during the day and night.

## References

[1] ***, National Aeronautics and Space Administration, https://climate.nasa.gov

[2] D. Stevanović, Method and Device for producing Hydrogen (in German language), *DPMA Deutsches Patent- und Markenamt*, DE 10 2021 129 804.0, Nov. 16, 2021

[3] S. Schneider et al., State of the Art of Hydrogen Production via Pyrolysis of Natural Gas (in German language), *Chemie Ingenieur Technik*, *vol. 92*, *Nr. 8*, pp. 1023–1032, June 2020

[4] T. Geißler et al., Hydrogen production via methane pyrolysis in a liquid metal bubble column reactor with a packed bed, *Chemical Engineering Journal*, *vol. 299*, pp. 192–200, September 2016

[5] T. Keipi et al., Methane thermal decomposition in regenerative heat exchanger reactor: Experimental and modeling study, *Energy*, *vol. 135*, pp. 823–832, June 2017

[6] D. Stevanović, H.-G. Faßbinder, Regenerative Thermal Oxidizers based on the Pebble-Heater technology, in *Proc. INFUB 2000 – 5th European Conference on Industrial Furnaces and Boilers, Vol. II*, 11-14 April 2000, Espinho-Porto, Portugal

[7] D. Stevanović and Th. Oehmichen, Device and Method for Cracking Gas (in German language), *DPMA Deutsches Patent- und Markenamt*, DE 10 2012 111 900, Dec. 6, 2012

[8] J. Schimmel, Evaluation of the Hydrogen yield and potential by-products resulting from the Thermal Cracking of Methane (in German language), B. Eng. thesis, University of Applied Sciences, Hof, Germany, 2022

[9] D. Stevanović, Thermal Cracking of Methane or Natural Gas (in German language), *DPMA Deutsches Patent- und Markenamt*, DE 10 2022 118 858.2, Aug. 1, 2022

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