Experimental study of the process of hydrogen production by methane pyrolysis in a molten tin layer

Evgeniy Kerosirov[1*], *Alexey* Grishin[1], *Alexey* Pashin[1], *Maksim* Popov[2], *Maria* Chudakova[2], *Tatyana* Ilukhina[1], *Timur* Amirov[1], *Victor* Dolgikh[1], and *Igor* Kudinov[1]

[1]Samara State Technical University, Samara, 443100, Russia
[2]Gazpromneft - Industrial Innovations LLC, Saint Petersburg, 197350, Russia

Abstract. The article presents experimental studies on the methane pyrolysis process in a 30 cm layer of molten tin. The experiments were carried out on a specially made setup in the temperature range from 800 °C to 1000 °C, at a pressure of 4.5 atm, and with a gas flow rate of 3 l/h. The dependence of hydrogen concentration, methane, and its derivatives (ethane, ethylene, and acetylene) in the produced mixture of hydrocarbon gases has been obtained.

1 Introduction

According to the International Energy Agency [1], 75% of global production of clean hydrogen comes from natural gas, while 23% comes from coal. However, hydrogen produced from fossil fuels has a relatively high carbon footprint. To reduce it, the implementation of low-carbon hydrogen production technologies is possible, particularly methane pyrolysis technology. The thermal decomposition of methane is considered a promising method for obtaining hydrogen and carbon, and it is the only process completely free from CO_2 emissions.

Hydrogen obtained using low-carbon technologies can be an effective means of decarbonizing industrial sectors that currently consume large amounts of coal or gas as an energy source, or such hydrogen can serve as a low-carbon replacement for the hydrogen already in use [2-6]. Currently, over 95% of the world's hydrogen consumption is attributed to traditional industries, mainly meeting their gas demand through production in specialized facilities directly at the points of consumption.

In the field of thermal power engineering, hydrogen can be used as a carbon-neutral fuel for both centralized and distributed generation. It can also serve as a means of energy storage and be utilized as a secondary energy carrier, accumulating energy produced by renewable energy sources.

Methane pyrolysis belongs to a range of processes that can be divided into several major classes: thermal pyrolysis, catalytic pyrolysis, plasma pyrolysis, and separately, pyrolysis in liquid media.

* Corresponding author: kerosirovv@yandex.ru

2 Experimental research

The laboratory setup for studying the process of hydrocarbon pyrolysis is an installation, the diagram of which is shown in Figure 1, where GDB is the gas distribution block, HB is the heating block, MB is the measuring block, and CS is the control system.

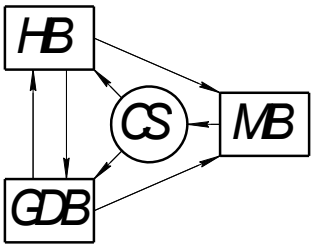

Fig. 1. Flowchart of the experimental setup.

The operation principle of the installation is as follows: the investigated gas enters the gas distribution block. The control system allows setting the desired values of pressure and gas flow. After that, the gas enters the reactor of the heating block. It should be noted that the reactor design for pyrolysis can vary significantly depending on the research objective. In this study, a liquid metal reactor with tin was used, the construction of which is discussed below. The mixture of pyrolysis and residual gases exiting the reactor is cooled, purified from carbon, and supplied to the measurement unit. In this setup, a mini chromatograph is used as the gas concentration measurer.

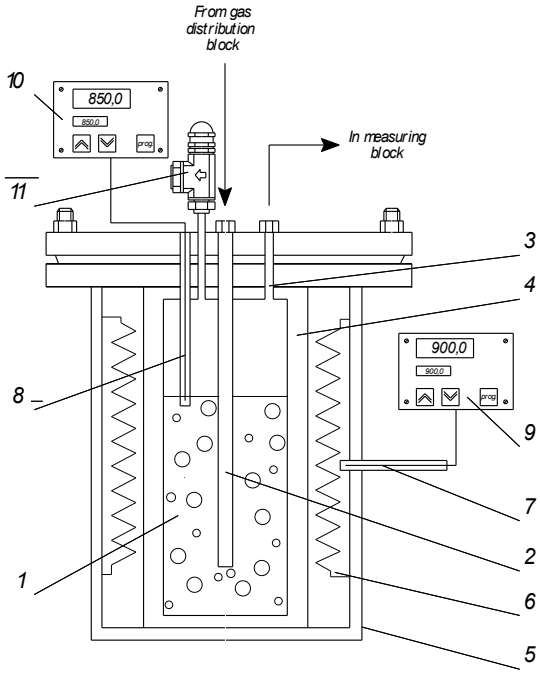

Fig. 2. Heating block. 1 – molten metal; 2 – gas supply tube; 3 – gas extraction tube; 4 – ceramic (corundum) cup; 5 – electric furnace housing; 6 – heating coil; 7, 8 – thermocouple pockets; 9, 10, – microprocessor-based temperature controllers (MTC); 11 – safety valve.

HB (Figure 2) consists of a vertical electric furnace with a power of 6 kW and a reactor directly connected to it. The control system, using a universal measuring and regulating device, allows programming the heating rate and the holding time of the desired temperature in the reactor, ranging from room temperature to 1050 °C with an accuracy of ±15 °C. The working space of the electric furnace is formed by an 80 mm diameter corundum ceramic tube. The vertical orientation of the furnace is necessary for conducting experiments with liquid metals and salts. And for the convenience of maintenance, the furnace is designed to be tilted relative to the horizontal axis.

The investigated gas enters the medium of molten metal 1 through the gas supply tube 2 and bubbles through it. The molten metal is contained in a ceramic cup 4 and heated by an electric furnace, consisting of a housing 5 and a heating coil 6. The temperature in the furnace and reactor is monitored by thermocouples 7 and 8, which are connected to microprocessor-based temperature controllers (MTC) 9 and 10. To prevent excessive pressure in the system, a safety valve 11 is provided.

GDB (Figure 3) consists of a reactor gas delivery system, as well as a filtration and reaction product release system. The design of the GDB allows for experiments to be conducted with gas flow rates ranging from 2 to 1800 l/h and pressures from 1 to 10 bar. To ensure safe operation of the setup, the gas inlet and outlet systems are equipped with back-flow valves and safety valves. For pressurizing connections and removing oxygen from the reactor prior to GDB testing, the system has the capability to supply inert gas, typically nitrogen or argon, into the system.

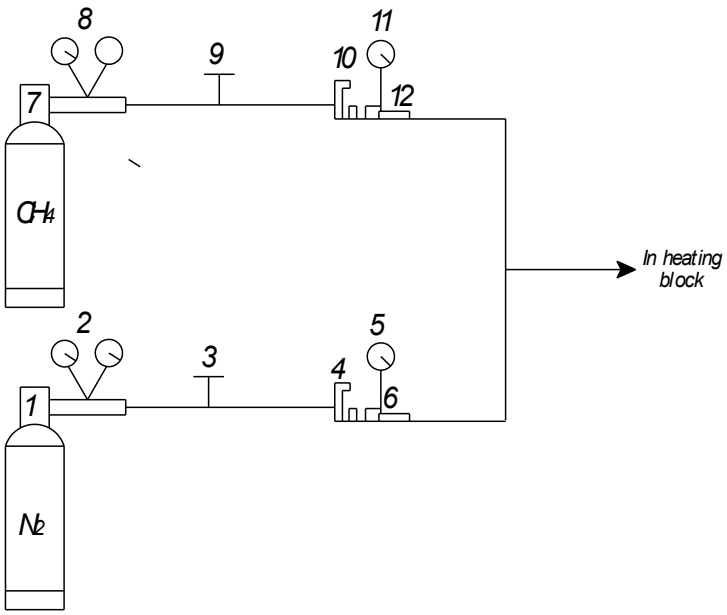

Fig. 3. Gas distribution block. 1 – nitrogen gas cylinder; 2, 8 – pressure reducing valves; 3,9 – needle valves; 4, 10 – gas flow regulator; 5, 11 – manometers; 6, 12 – back-flow valves; 7 – methane gas cylinder.

To prevent the exothermic reaction of hydrogen and oxygen, it is necessary to remove oxygen from the system by purging it with an inert gas - nitrogen. Nitrogen is supplied from cylinder 1, and the delivery pressure is regulated by pressure reducing valve 2. Needle valve 3 is used to completely stop the gas supply in case of emergency and for more precise pressure regulation. During each experiment, it is necessary to set the exact gas flow rate.

For this purpose, a gas flow regulator 4 is installed in the system. A manometer 5 is also installed to monitor the pressure in the gas system, and a back-flow valve 6 is included to prevent backflow of gas. After removing oxygen from the system, methane is supplied. The methane gas distribution system consists of cylinder 7, pressure reducing valve 8, needle valve 9, gas flow regulator 10, manometer 11, and back-flow valve 12, and it operates on a similar principle as the nitrogen gas distribution system.

MB (Figure 4) allows monitoring the following parameters:

- Temperature in the furnace and reactor (there is one thermocouple in the furnace, the number of thermocouples in the reactor depends on its design).
- Power consumption (instantaneous, over a specific time interval, throughout the experiment).
- Gas flow rate and pressure at the reactor's inlet and outlet.
- Concentration of reaction products.

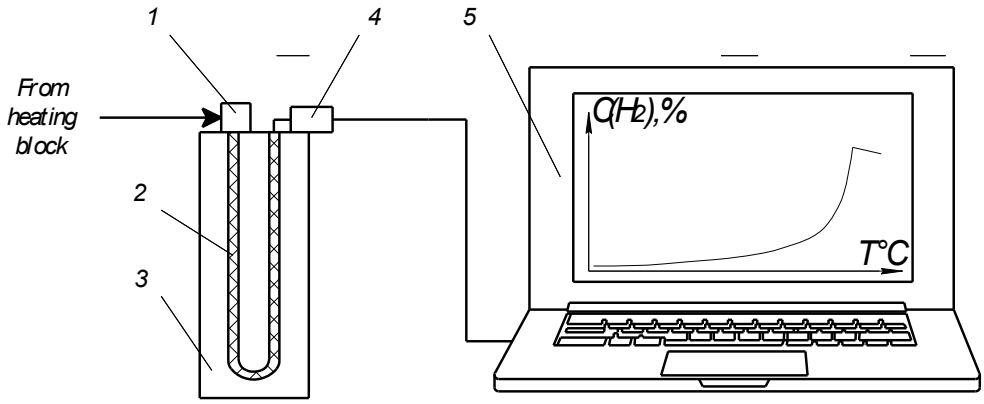

Fig. 4. Measuring block. 1 – sample injector; 2 – chromatographic column; 3 – thermostat; 4 – detector; 5 – personal computer.

The produced gas mixture is fed into the chromatograph through a sample injector 1, then analyzed on chromatographic column 2, the temperature of which is maintained using thermostat 3. At the chromatograph's outlet, there is a detector 4 that converts the signal and transfers the information for analysis to a personal computer 5.

The versatility of this stand allows for testing various types of reactors: for thermal pyrolysis, for catalytic pyrolysis, reactors for studying the influence of plasma on pyrolysis, and pyrolysis in condensed media. This work presents the results of experiments in a reactor with liquid tin.

3 Results and Discussion

The experiment was conducted with a constant methane flow rate of 3 l/h and a pressure of 4.5 atm in the reaction zone (Table 1). The experiment lasted for 2 hours and 20 minutes. Significant methane conversion starts at temperatures above 800°C, which is attributed to the tall height of the reaction zone (35 cm) and the catalytic action of tin on the pyrolysis process. The amount of hydrogen in the product gas increased from 8.9% to 65.5% when the temperature of the reaction zone was raised from 800°C to 1000°C (Figure 5).

Table 1. Thermal decomposition of methane in tin.

No. sample	Temperature of the reactor, °C	Flow rate, l/h	Pressure in the reactor, atm	Sampling time	CH_4, %	N_2, %	H_2, %
1	800	3	4.5	00:30	77.3	0.76	9.3
2	850	3	4.5	00:50	71.8	1.00	23.8
3	900	3	4.5	01:20	40.5	0.40	55.6
4	950	3	4.5	01:50	31.1	0.50	61.2
5	1000	3	4.5	02:20	24.0	0.40	67.8

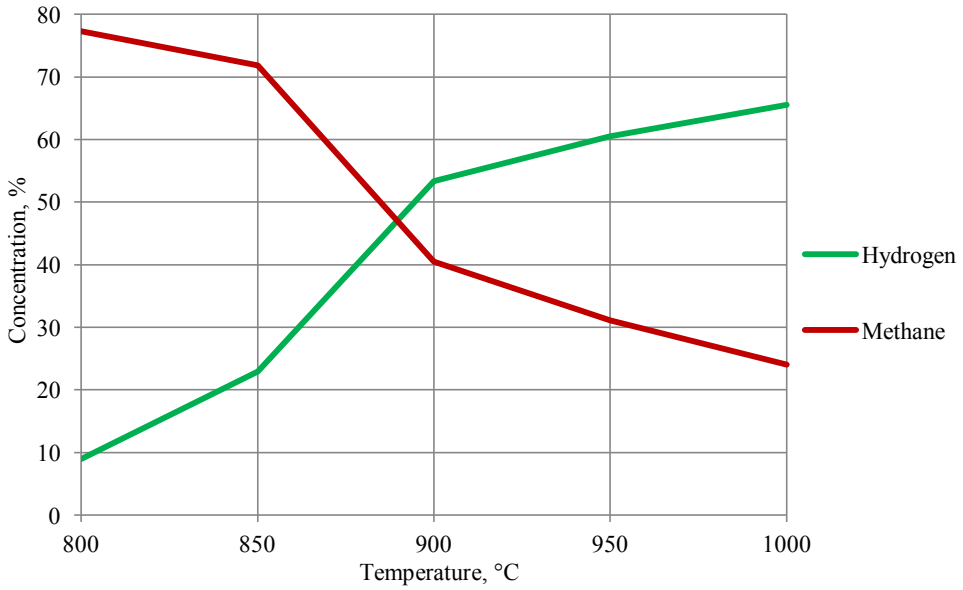

Fig. 5. The concentration of methane and hydrogen at the reactor outlet.

Thus, the conducted experiment has demonstrated the fundamental possibility of obtaining hydrogen by introducing methane into a layer of molten tin, 35 cm in height, in this setup. The results of the experiment (characteristics of the technological process) are consistent with the findings of other authors [7-9], namely, the hydrogen yield increases with temperature and exceeds 60% at temperatures above 900°C.

Increasing the height of the liquid column leads to an increase in the amount of hydrogen in the generated gas. For instance, in [10], it was shown that at a height of 10 cm for the liquid tin column, the amount of hydrogen at 1000 °C is only 12%, while in the present study, the amount of generated hydrogen reached 67.8%.

A large amount of carbon particles has been found on the surface of tin, which can be removed, for example, by blowing. As the flow rate of the generated gas increases, the amount of carbon particles also increases. Examination of carbon material samples using scanning and transmission electron microscopy revealed the presence of carbon nanoparticles ranging in size from 10 nm to 100 nm.

4 Conclusions

An experimental methane pyrolysis setup has been developed in a condensed media, consisting of a control system, a heating block, a gas distribution block, and a measuring

block. Experimental investigations have been conducted on this setup, and data on the concentration of the target product (hydrogen) in the produced gas have been obtained.

Based on the results of the performed work, it can be concluded that tin has a catalytic effect in the methane pyrolysis reaction. The concentration of hydrogen in the gas mixture reached 67.8% at a reaction temperature of 1000 °C.

Acknowledgement

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (theme No. FSSE-2023-0003) as part of the state task of the Samara State Technical University.

References

1. International Energy Agency. CO_2 Emissions in 2022, IEA, Paris, https://www.iea.org/reports/co2-emissions-in-2022
2. Y. Pleshivtseva, M. Derevyanov, A. Pimenov, A. Rapoport, Comprehensive review of low carbon hydrogen projects towards the decarbonization pathway, International Journal of Hydrogen Energy, **48**, 3703-3724 (2023)
3. V.E. Parfenov, Methane pyrolysis for hydrogen production: Specific features of using molten metals, Russian Journal of Applied Chemistry, **93**, 625-632 (2020)
4. I.V. Kudinov, A.A. Pimenov, G.V. Mikheeva, Modeling of the Thermal Decomposition of Methane and the Formation of Solid Carbon Particles, Petroleum Chemistry, **60**, **11**, 1239–1243 (2020)
5. V.D. Dolgikh, *Experimental research of the process of methane pyrolysis in a layer of liquid tin aiming to get hydrogen*, IOP Conference Series: Earth and Environmental Science. – IOP Publishing, **1070**, **1**, 6 (2022)
6. Y. Pleshivtseva, M. Derevyanov, A. Pimenov, A. Rapoport, Comparative analysis of global trends in low carbon hydrogen production towards the decarbonization pathway, International Journal of Hydrogen Energy, **48** (2023)
7. S. Abanades, G. Flamant, High-temperature solar chemical reactors for hydrogen production from natural gas cracking, Chem. Eng. Commun, 195, 1159–1175 (2008)
8. J. Zeng, M. Tarazkar, T. Pennebaker, M.J. Gordon, H. Metiu, E.W. McFarland, Catalytic Methane Pyrolysis with Liquid and Vapor Phase Tellurium, ACS Catal., **10**, 8223–8230 (2020)
9. W. Yan, S.K. Hoekman, Production of CO_2-free hydrogen from methane dissociation: A review, Environmental Progress & Sustainable Energy, **33**, **1**, 213–219 (2014)
10. I.V. Kudinov, A theoretical and experimental study on hydrodynamics, heat exchange and diffusion during methane pyrolysis in a layer of molten tin, International journal of hydrogen energy, **46**, **17**, 10183-10190 (2021)