

Technology Development for the Pyrolysis of Hydrocarbons in Liquid Metal

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This article describes the development of a new technology based on the application of liquid metal and aims to produce hydrogen by decarbonization (pyrolysis process) of both natural and artificially synthesized hydrocarbons. When biogas with a sufficiently high carbon dioxide content is used as a feedstock, or by the targeted addition of CO₂ to methane, a mixture of hydrogen and carbon monoxide (synthesis gas) can be produced. Furthermore, the paper describes another very interesting application of the technology to create negative emissions. In this scenario, the processes direct air capture, methanation, electrolysis and methane pyrolysis are combined to synthesize solid carbon from atmospheric CO₂. The broad range of process options investigated indicates that, when the technology is scaled up to industrial scale, the result will be a process that is flexible in both the use of reactants and the resulting products.

Keywords: Bubble column, Hydrogen production, Pyrolysis, Liquid metal, Methane

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1 Introduction

Global warming and the resulting abrupt, widespread climate change that has become evident in recent decades have challenged the world community to keep the planet environmentally friendly for human life. At the UN Climate Change Conference in Paris in 2015, almost all countries in the world agreed to unprecedented action to tackle global warming. The main goal of the agreement is to keep the global temperature increase this century below 2 °C and to promote efforts to limit the temperature increase even further, to 1.5 °C above pre-industrial levels [1,2]. The German government, for its part, has set itself the target of increasing the share of renewable energy to 80 % by 2030 and phasing out the use of fossil fuels completely by 2050 [3].

All of these initiatives focus on reducing or eliminating the emission of greenhouse gases into the atmosphere from human activities. However, even this may not be enough to meet the targets that have been set and measures will have to be taken to create what are known as negative emissions, i.e., the removal of CO₂ from the atmosphere.

Hydrogen plays an increasingly important role in the achievement of the goal of energy system transition from fossil fuels to renewable energy sources [4]. It is important to remember that hydrogen is not only the attractive energy carrier of the future, but also a product in high demand in industry today [5]. It is already used in large quantities in the chemical and petrochemical industry, in refineries and in the steel industry. The latter will increase drastically with

the already started transformation from blast furnaces to direct reduction plants.

This article describes the development of a novel technology for the pyrolysis of hydrocarbons in liquid metal (PHLM), its experimental testing in the laboratory and describes potential applications. The aim of this technology is to create an environmentally attractive method of producing hydrogen from hydrocarbon- and primarily methane-containing gases. One specific type of liquid metal-based pyrolysis process is being investigated and the technology advanced at the Liquid Metal Laboratory (KALLA) of the Karlsruhe Institute of Technology, initially in collaboration with the Institute for Advanced Sustainability Studies e. V. (2012–2015) [6] and subsequently with Wintershall DEA AG (2019–2023) [7]. Depending on its implementation, PHLM technology can be used for the direct thermal decomposition of natural and artificially synthesized gaseous hydrocarbons or, in combination with other technologies, can be used to create negative emissions.

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2 Direct Methane Decomposition in a Bubble Column Reactor

2.1 Theoretical Basics

Pyrolysis of hydrocarbons is the process of splitting hydrocarbons at high temperatures (>700 °C) into their elemental components. The pyrolysis of methane is a chain of sequential chemical transformations that ultimately primarily results in the formation of hydrogen gas and solid carbon. Many chemical compounds can act as intermediates, such as ethane, ethylene, acetylene, etc. [8]. The composition of the pyrolysis products in the gas mixture depends on the temperature, pressure and other conditions under which the process is operated. The simplified chemical reaction Eq. (1) reflects only the results of the methane pyrolysis process, excluding a number of important intermediate steps.



The reaction itself is endothermic and the necessary energy can come from a variety of external sources. The reaction takes place without an oxidizing agent, so no CO or CO₂ is produced. In the ideal case, 4 kg of methane are converted to 1 kg of hydrogen and 3 kg of carbon at a conversion rate of 100%. Methane pyrolysis is thermodynamically more energy efficient than other known processes such as steam methane reforming and water electrolysis, as compared in Tab. 1.

Table 1. Standard reaction enthalpies [9].

Name	Reaction enthalpy [kJ mol ⁻¹] (H ₂)
Pyrolysis of methane	37.7
Steam methane reforming	63.4
Water electrolysis	285.8

According to the standard enthalpy of reaction, the pyrolysis of methane requires 37.7 kJ mol⁻¹ to produce one mole of H₂. In steam methane reforming, combined with the water-gas shift reaction and including the heat for water evaporation, this value is 63.4 kJ mol⁻¹. Methane pyrolysis is also a much less energy-intensive process than water electrolysis, which requires 285.8 kJ mol⁻¹ to produce one mole of hydrogen.

2.2 Pyrolysis of Methane in Liquid Metal

The specific feature of the pyrolysis process investigated at KALLA is the use of a bubble column filled with liquid metal as a chemical reactor. The presence of liquid metal in the pyrolysis chemical reaction zone avoids the accumulation of

carbon, which is a product of methane decomposition. This is due to the high density difference between the liquid metal used and the carbon powder produced. It is the deposition of carbon on the reactor wall and catalyst surfaces that was previously the main technical problem in carrying out a continuous methane pyrolysis process. The use of liquid metals in the bubble column not only avoids clogging of the chemical reactor, but also results in a number of other advantages. Thus, the use of a bubble column, where the reagent gas rises from the bottom in the form of numerous bubbles, results in the continuous renewal of the active surface area for the reaction, as the chemical reactions are assumed to take place at the bubble interface and inside of the gas bubble as discussed in publications [8] addressing the formation of different kinds of carbon. In addition, the good thermal conductivity of metals and the hydrodynamics of popping bubbles intensify the heat exchange within the reactor, which also has a beneficial effect on methane pyrolysis.

In order to study the pyrolysis of methane under laboratory conditions, an experimental setup was designed (Fig. 1) and used in several subsequent generations and modifications in recent years. A vertical electric furnace is used as the energy source for the chemical reaction. Inside is a quartz glass reactor tube with a diameter of 40–80 mm and a height of 1.2–1.3 m, depending on the experimental configuration. The reactor is encased by a steel housing for more stability. The reactor is filled with liquid tin with purity of 99.99% to a height of approximately 1 m at 1050 °C. This is equivalent to 8.6–31 kg of tin, depending on the diameter of

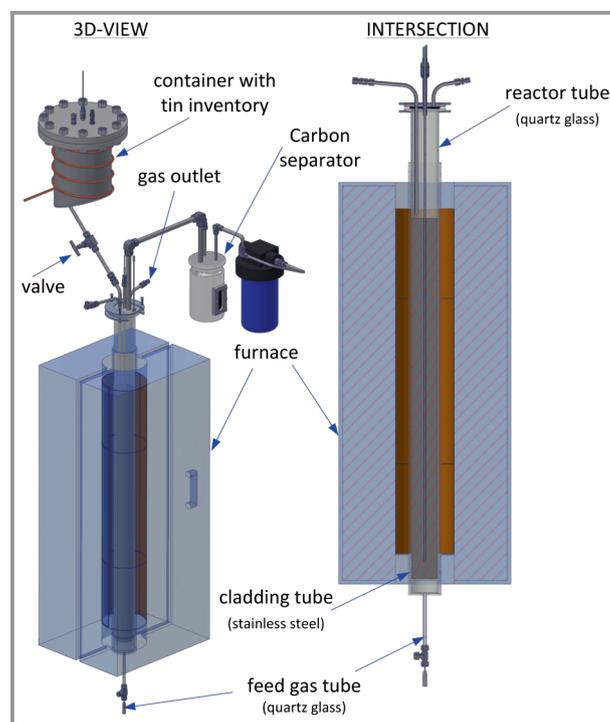


Figure 1. Reactor setup.

the reactor used. The reagent gas is introduced into the reactor through a 0.5 mm orifice in the flat bottom of the reactor. The gas bubbles formed rise to the surface of the liquid metal. The gas inside these bubbles rapidly heats up to the temperature required to start the pyrolysis reaction. The gaseous reaction products (ideally only hydrogen) are exhausted from the reactor through the carbon separator. The composition of the outgoing gases is analysed using a gas chromatograph.

The use of liquid tin as the working fluid in a bubble column reactor was based on the following criteria: inertness to reaction gases, high thermal conductivity and high density compared to carbon, non-toxicity and long chemical stability. In recent years, extensive comparative experimental studies have been carried out in the KALLA laboratory on the pyrolysis of pure methane and natural gas, as well as on the addition of individual components typically found in natural gas to methane. One important result of these studies is shown in Fig. 2 [10]. The methane to hydrogen yield in experiments using pure methane and high caloric natural gas (molar fraction: 98.2 % methane, 1.71 % ethane, 0.07 % propane, another components 0.02 %) as a process feedstock is compared in the diagram for otherwise similar process conditions. It is evident, that at low temperatures the hydrogen yield of pure methane is several percent lower than that of methane in natural gas. The difference decreases as the temperature increases. At temperatures above 1350 K, this effect is no longer significant. This is due to the presence of ethane in natural gas. This effect and potential reasons are described and discussed in more detail in [10]. This experimental result demonstrates that a successful transition from laboratory to industrial scale is possible without reducing the efficiency of the process being developed.

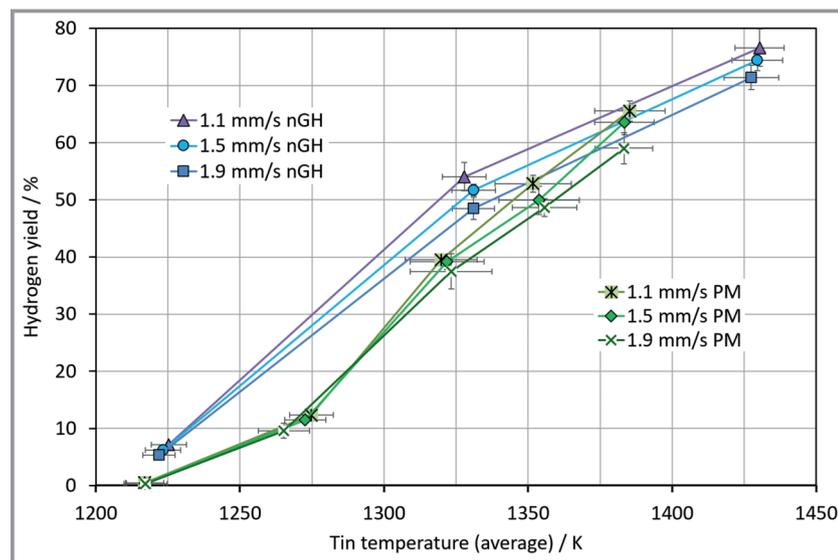


Figure 2. Temperature-dependent methane to hydrogen yield for pure methane (PM) compared to natural gas (nGH) as reactants at different superficial gas velocities (SGV) [10].

If successfully scaled up, PHLM technology will be a candidate process to replace or compete with steam methane reforming (SRM), currently the most prevalent chemical process used in the industrial hydrogen production plants. This alone will reduce CO₂ emissions from the global industrial sector by approximately 3 % [11]. Depending on the achievable quality, the carbon powder produced at PHLM as a by-product of hydrogen might be favourable compared to CO₂. It is more compact, stable, easier to handle and might be usable as a valuable product in many industries. Elemental carbon in several modifications is a major commodity already today, produced almost solely from fossil sources along with significant direct CO₂ emissions.

2.3 Use of Renewable Energy

Although the direct thermal pyrolysis of methane does not produce CO₂ as a product, the use of PHLM technology can only be made environmentally viable if the energy required for a continuous process is obtained from renewable or emission free sources.

As part of the development of the PHLM technology, various scenarios are being considered for the possible use of solar or wind energy to power the pyrolysis process. Fig. 3 illustrates several possible scenarios for coupling solar energy to the methane pyrolysis reactor. The main difference is the type of solar radiation used: PV harvests solar energy by transforming it into electricity, while CSP converts it into (high temperature) heat. PV systems are specifically designed to capture global horizontal irradiance (GHI), which represents the total solar radiation received on a horizontal surface, including both direct and indirect radiation.

In contrast, CSP systems require direct sunlight and are optimized to capture direct normal irradiance (DNI), which refers to the solar radiation received on a surface perpendicular to the sun's rays. PV systems produce electricity, while CSP systems have the advantage of generating heat directly, which can be employed to heat the reactor or converted into electricity to power an electric furnace. Both PV and CSP systems can leverage energy storage systems to maximize their benefits. Energy storage allows surplus energy generated during peak periods to be stored and utilized when energy demand is high or when sunlight is insufficient. PV systems commonly employ battery storage. In contrast, CSP systems can utilize both battery storage and thermal energy storage techniques.

Another option for achieving emission free operation is to use some of the

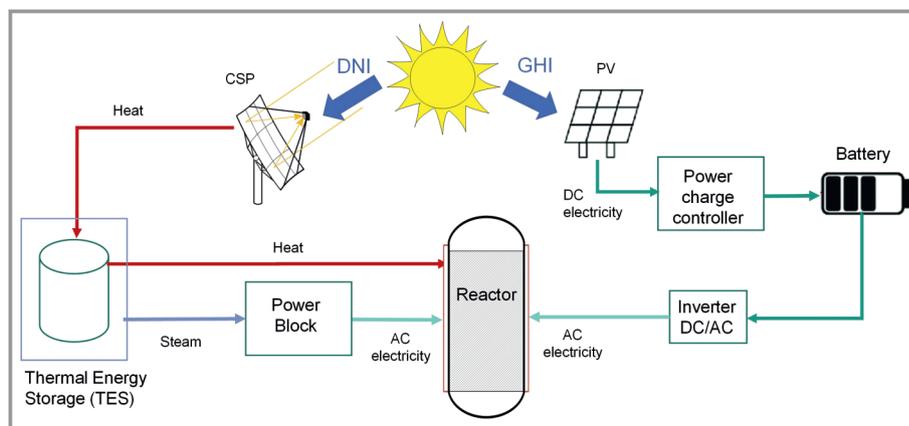


Figure 3. Possible renewable energy scenarios for the methane pyrolysis process.

hydrogen produced as an energy source. Postels et al. [12] estimates that this will require about 23–25 % of the hydrogen produced. In this case, only the start-up phase of the plant requires external energy. Of course, if hydrogen is the target product, supplying the energy needed for the pyrolysis reaction from another source, like renewable heat or electricity, will be the preferred option. Still, all the scenarios considered are technically realistic. The efficiency of each scenario is determined by the size and the specific design of the plant, as well as by the natural and landscape conditions of its specific location.

3 NECOC Project

This section of the paper describes the application of methane pyrolysis technology as part of a modular plant for the decomposition of CO_2 extracted from the air. The purpose of this development is to connect negative greenhouse gas emissions with producing a value product (carbon). The main idea is to combine tested and well-proved technologies in such a way that ambient air is used as a feedstock to reduce the currently too high concentration of CO_2 to produce air depleted in CO_2 , oxygen gas and solid carbon powder as products. According to the latest IPCC report, carbon dioxide removal technologies are necessary to limit global warming to 1.5°C by reducing the atmospheric CO_2 concentration. Depending on the subsequent utilization, the production of solid carbon offers the perspective to combine long-term storage and utilization, in contrast to, e.g., synthetic fuels. In addition to CO_2 from ambient air, also industrial off-gases with higher CO_2 concentrations should be considered as alternative CO_2 sources for the described process in future studies. In total, four technologies are involved in the proposed process: CO_2 capture, methanation, electrolysis und pyrolysis (see Fig. 4) [13]. In the first stage (CO_2 capture), a cyclic sorption process captures CO_2 . The purified air is released back into the atmosphere. The concentrated CO_2 is subsequently used for methanation, which is the second process step. The methanation process also requires hydrogen, which is circulated between the processes without leaving the

overall system. The products of the methanation process are methane and water.

The water separated from the permanent gases goes to the electrolyser (the third process unit) where hydrogen and oxygen are separated. At this stage, the oxygen, as the final product, leaves the overall system and the hydrogen is returned to the methanation unit. Methane, produced among water in the methanation process, is the feedstock for pyrolysis (the fourth process step). The products of the pyrolysis

process are hydrogen, which is recycled in the process, and carbon powder, which leaves the system at this stage. Thus, by combining the four processes, it is possible to remove CO_2 from atmospheric air and separate it into gaseous oxygen and solid carbon. The NECOC project (2019–2023) [14], funded by the Bundesministerium für Wirtschaft und Klimaschutz, was initiated by KIT in cooperation with INERATEC GmbH and Climeworks Deutschland GmbH in order to experimentally test the idea described above. In this project, all parts of the technology, with the exception of the electrolysis, have been assembled and combined to form an integrated system. As a result, carbon was successfully produced from atmospheric CO_2 for the first time in late 2022 [15]. This experiment demonstrated the possibility of combining negative emissions by using atmospheric CO_2 with the production of the potential value product carbon. The process is currently under investigation and the results including the selectivity of the entire process will be published in detail in a separate publication in the near future. The hydrogen selectivity of the methane pyrolysis process at various process parameters has also been considered in [8, 10]. In general, only small amounts of by-products (ethane, ethene) have been detected in the product gas in previous studies. After the experimental study and optimization phase of the NECOC process is completed, the results

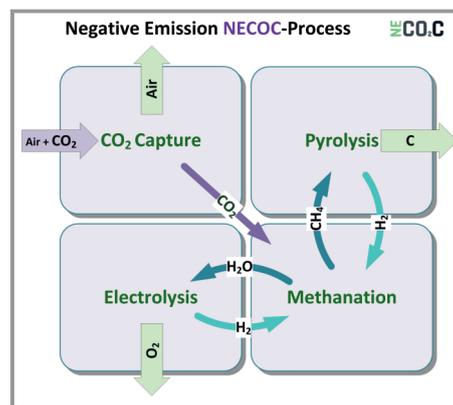


Figure 4. NECOC process diagram.

obtained will also be used to assess the potential for practical heat exchange between all process units and the energy balance of the entire process.

4 Biogas

One promising potential application of the PHLM technology under development is the pyrolysis of biogas, also known as Dry Reforming of Biogas. Currently, 90 % of biogas is mainly used to produce heat and electricity [16]. This is done by burning the biogas in combustion systems such as boilers, turbines and fuel cells. This process inevitably produces CO₂. Although this is regarded as emission-neutral due to the nature of the biogas source, it is still an undesirable re-emission of CO₂ already removed from the atmosphere by natural photosynthesis. Furthermore, the combustion of biogas is not very energy efficient due to the high CO₂ content. The main idea of pyrolysis of biogas, which will be explored in future studies, is to use it to produce the essentially valuable chemical product syngas (H₂ + CO), accompanied by certain amounts of carbon, water, etc. At the same time, negative emissions could also be produced, provided of course, the products made using the syngas will not be transformed again into CO₂.

The biogas pyrolysis process is carried out in a similar way to the methane pyrolysis process in an identical reactor filled with liquid metal. Instead of methane, biogas is used as the feed gas, which is injected into the reactor through an injector. The biogas consists mainly of methane (45–70 %) and carbon dioxide (30–45 %), the nitrogen content varies between 5–15 % [17]. The inclusion of CO₂ to the process adds complexity compared to the pyrolysis of pure methane, as it leads to additional chemical reactions. If the presence of further minor components in the biogas is neglected, the most important four reactions are given in Tab. 2.

The crucial difference between dry reforming of methane (DRM) and standard reforming technologies, such as steam methane reforming (SRM), is that DRM consumes CO₂ as part of the feedstock, whereas other reforming reactions produce CO₂. To limit the effects of climate change caused by CO₂ emissions, technologies that consume CO₂ should be developed further to replace standard ones that emit CO₂. The standard approach for DRM is to use a catalytic fixed bed. However, these approaches face the challenge of catalyst deactivation due to coking and/or sintering. It should be noted that carbon formation should be minimized to maximize the syngas yield. However, research on DRM shows that carbon formation is one of the major problems in this context, though. A typical strategy to regenerate catalysts after coking is to burn off the carbon, i.e., to convert it back into CO₂. By using the presented LM technology, it is possible

Table 2. Main chemical reactions for drr Reforming of biogas [17].

Name	Reaction
Pyrolysis of methane	$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$
Dry reforming of methane	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$
Boudouard reaction	$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$
Reverse water gas shift	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$

to deal with coking without having to interrupt the DRM process for catalyst regeneration. Furthermore, the carbon produced as a by-product of syngas in a LM bubble column reactor does not need to be burned but can be recovered as a solid product.

The proposed idea of biogas to syngas conversion needs to be more thoroughly studied and experimentally investigated. As with methane pyrolysis, the production of a carbon powder remains a challenge for dry reforming of biogas. Further research seems well justified, in particular as producing synthetic methane from green hydrogen and carbon dioxide also results in a mixture of CH₄ and CO₂.

5 Summary

This paper describes the development of a new promising method of direct methane pyrolysis, which is based on the application of liquid metal technology. The proposed method is quite versatile and can be applied both individually and in combination with other technologies. This opens up the possibility of a diverse and flexible practical application of the PHLM technology (Fig. 5) and allows to cover a wide range of possible technical solutions to achieve the goals of

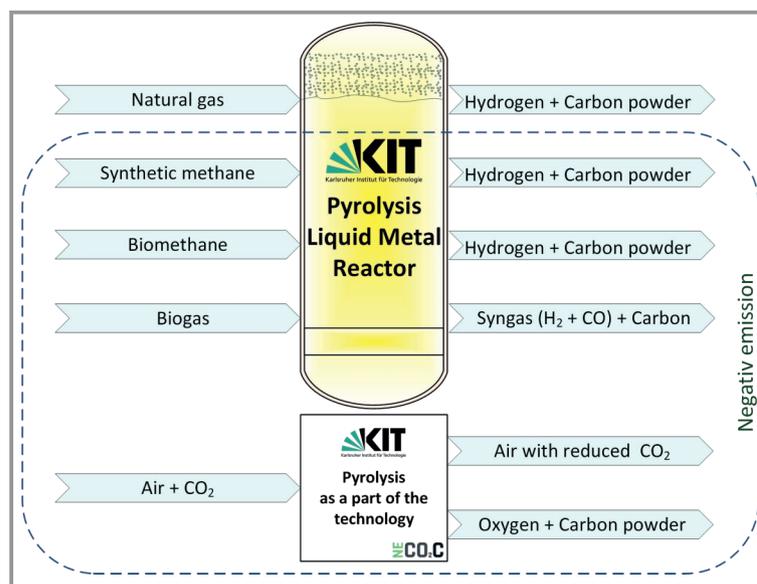


Figure 5. Potential pathways for the pyrolysis of hydrocarbons in liquid metal.

industrial decarbonisation and climate change prevention goals.

Using natural gas, synthetic methane or biomethane as feedstock, the process products are hydrogen and carbon powder. PHLM technology also allows biogas to be used directly as the feedstock without the need for preliminary methane separation. In this case, the product is syngas, a mixture of hydrogen and carbon monoxide that is a valuable reagent for the synthesis of methanol and other industrial chemicals and fuels. Combined with DAC, electrolysis and methanation (as in the NECOC process), PHLM technology enables the utilisation of CO₂ from the atmosphere, cleaning the ambient air and decomposing the CO₂ into oxygen and carbon powder.

If only renewable energy sources are used for the technological process itself, negative emissions would be achieved in all the potential pathways described. The only exception is the pyrolysis of natural gas, where emission neutrality can be achieved, but no net negative emissions.

At the heart of all these approaches is HPLM technology, adapted to the specific application. The variety of solutions on offer enables flexible decentralisation and scalability of individual solutions, increasing the range of available options of the transition to renewable energy.

The technology is not yet fully developed and not all process issues have been thoroughly investigated and optimized for industrial use. The current technology readiness level is TRL 4. Challenges include finding the optimum combination of reactor design and reactor fabrication materials to ensure a continuous, long-term process, heat integration and efficiency optimization in general, as well as process optimisation to achieve the highest possible product purity (hydrogen and carbon powder or syngas) depending on its future use.

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Abbreviations

nGH	high-caloric natural gas
PHLM	pyrolysis of hydrocarbons in liquid metal
PM	pure methane
SGV	superficial gas velocity (mm s ⁻¹)

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Research Article: This paper describes the pyrolysis process for the decarbonization of gaseous hydrocarbons. Possible applications of the developed technology for effective reduction of carbon dioxide emissions or generation of negative emissions are briefly presented. Experimental results and experience show the technical feasibility of such systems. ■

