Review

Non-Catalytic Partial Oxidation of Hydrocarbon Gases to Syngas and Hydrogen: A Systematic Review

Iren A. Makaryan [1], Eugene A. Salgansky [1,*], Vladimir S. Arutyunov [1,2] and Igor V. Sedov [1]

1 Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, Ac. Semenov av. 1, 142432 Chernogolovka, Russia
2 N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russia
* Correspondence: sea@icp.ac.ru

Abstract: The review contains a comparative analysis of studies on the production of hydrogen and syngas based on the processes of partial oxidation of natural gas and other types of gas feedstock. The results presented in the literature show the high potential of non-catalytic autothermal processes of partial oxidation of hydrocarbons for the development of gas chemistry and energetics. The partial oxidation of hydrocarbons makes it possible to overcome such serious shortcomings of traditional syngas production technologies as technological complexity and high energy and capital intensity. The features of non-catalytic partial oxidation of hydrocarbon gases, the obtained experimental results and the results of kinetic modeling of various options for the implementation of the process, which confirm the adequacy of the kinetic mechanisms used for the analysis, are considered in detail. Examples of industrial implementation of processes based on partial oxidation and proposed alternative options for its organization are considered. Designs of reactors used to ensure stable conversion of rich mixtures of hydrocarbons with an oxidizer are presented. The possibility of obtaining other chemical products by partial oxidation of hydrocarbons is discussed.

Keywords: non-catalytic partial oxidation; natural gas; methane; conversion; hydrogen; synthesis gas; modeling; reactor

1. Introduction

Modern civilization cannot exist without liquid hydrocarbon fuels and petrochemical products. Due to the decline in world crude oil reserves observed in recent years, these products will inevitably have to be obtained from more common and more accessible gaseous feedstock in the near future. The growing demand for high-quality chemical products has already stimulated an increased interest in the conversion of hydrocarbon gases (natural gas, methane, biogas) into motor fuels and high value-added chemical products, as well as into hydrogen, which is increasingly in demand on the market. First of all, we are talking about the conversion of natural gas and its main component—methane.

Due to the lack of economically justified methods for the direct selective conversion of methane into heavier hydrocarbons, this process is implemented by preliminary oxidative conversion of natural gas or other hydrocarbon gases into syngas (a mixture of CO and H_2 with a different ratio of these gases, depending on the method of its production). The resulting syngas is a raw material for the production of various chemical products, in particular liquid fuels based on the Fischer–Tropsch synthesis (gas-to-liquid technology, GTL). Therefore, the conversion (reforming) of natural gas into syngas and hydrogen is the basis of almost all modern large-tonnage natural gas processing technologies.

The global syngas market was valued at USD 43.6 billion in 2019. According to the forecasts of the analytical company Research and Markets, in the period 2022–2028, the syngas market will develop at a high rate, at the level of 6.6% per year, and will increase from USD 50.1 billion to USD 73.4 billion [1]. The chemical segment is expected to account

for the largest share of syngas consumption in the global market, which will exceed USD 39 billion by 2027, up from USD 25.6 billion in 2019. This is due to the growing demand for environmentally friendly raw materials for the production of many chemical products. Syngas with various H_2/CO ratios is used to produce various petrochemicals, fertilizers, oxygenates and other high value-added products. Syngas also plays a key role in the synthesis of ammonia, the most common petrochemical product on the market, with over 100 years of technology behind it [2].

Syngas is not only a semi-product of the synthesis of more complex organic compounds, but also the main source of hydrogen production. In 2021, the world production of hydrogen amounted to ~90 million tons [3], and world demand for it reached 94 million tons, which is equivalent to approximately 2.5% of world energy consumption [4].

In recent years, the possibility of a transition to low-carbon energy, including through the wider use of hydrogen, has been discussed in the hope that in the long term hydrogen can become a universal environmentally friendly energy carrier [5,6]. The most optimistic forecasts predict that by 2050 hydrogen will account for about 18% of all energy needs in the world and its consumption will grow to 370 million tons per year [7], although there are no real energy and resource prerequisites for this [8,9].

The main difference between H_2 as a fuel and hydrocarbon fuels is a much higher flame speed and wider concentration limit ranges of its propagation, as well as a very low ignition delay time [10]. Therefore, along with the use of H_2 as a fuel, its use as an additive to some fuels, mostly to natural gas, is widely discussed [11].

The emergence of real hydrogen energy and the hydrogen market is impossible without the creation of efficient and safe technologies for its storage and transportation [12,13]. This is a rather difficult task, since the physical properties of hydrogen lead to significantly higher logistics costs compared to other energy carriers.

The most common methods for producing syngas and hydrogen from natural gas/methane are steam reforming, autothermal reforming and partial oxidation (oxidative conversion) [14]. One of the main challenges of these already fairly mature industrial technologies is the need to reduce energy consumption and production costs. The cost of obtaining syngas in the cost of the final product obtained from it can be up to 50–55%, and the share of capital investments in process equipment can be up to 60–65% of the total investment in production. Apart from high capital investments, obtaining various products (hydrogen, ammonia, methanol, GTL products) requires syngas of a specific composition, since the H_2/CO molar ratio plays an important role in subsequent syntheses based on it. For example, the H_2 content of the syngas produced by steam reforming is generally too high for further methanol synthesis. With the partial oxidation of methane, which actually produces syngas with a H_2/CO ratio of less than 2:1 (~1.8), it is too low. Therefore, to obtain liquid GTL products by Fischer–Tropsch synthesis or methanol, a combination of different technologies (combined reforming) is used, as well as adjusting the syngas composition by extracting part of the hydrogen or using the water–gas shift reaction (WGSR).

To overcome the shortcomings of traditional processes, intensive work is underway to modernize them and create fundamentally new technologies for the conversion of gas raw materials. Such technologies should be simple in technological and hardware design, minimize greenhouse gas emissions, reduce energy consumption, optimize the H_2/CO ratio in syngas and increase economic efficiency and commercial attractiveness of the oxidative conversion process as a whole. An important problem remains the need for small-tonnage units for the conversion of syngas into liquid fuels, which could use marginal natural gas sources, since large-tonnage GTL technologies are not applicable to them [15].

Each of the processes listed above, steam reforming, autothermal reforming and partial oxidation, has its own advantages and disadvantages. Partial oxidation of natural gas can be carried out in two versions: catalytic and non-catalytic, the implementation of which in practice has a number of common technological challenges. Among the disadvantages of catalytic partial oxidation are the need to use expensive oxygen, the cost of obtaining which can be up to 50% of the total cost of syngas, high explosiveness, low stability of catalysts

and their destruction due to local overheating in the reactor and intensive soot formation. Therefore, there is growing interest in non-catalytic partial oxidation.

The conversion of natural gas into hydrogen and syngas is still the most complex and costly stage of modern gas chemical processes, the low efficiency of which hinders the development of modern gas chemistry. Therefore, over the past two decades, many works have appeared on the study of the possibility of efficient production of syngas and hydrogen by non-catalytic partial oxidation as an alternative to steam and autothermal reforming, as well as catalytic partial oxidation.

The aim of this review is to analyze research in the field of development and improvement of processes for non-catalytic partial oxidation of hydrocarbon gases (natural gas, methane, biogas, refinery, coke, furnace and other carbon-containing gases) in order to create effective technologies for producing syngas and hydrogen on their basis.

2. The Main Processes for Obtaining Syngas and Hydrogen

Currently, there are several main processes for the conversion of natural gas/methane to syngas:

- steam methane reforming (SMR);
- autothermal reforming (ATR);
- partial oxidation (POX);
- catalytic partial oxidation (CPOX);
- dry methane reforming (DMR);
- combined methane reforming (CMR);
- tri-reforming of methane (TRM);
- reforming using membrane reactors.

Each of these processes has certain advantages and disadvantages. While SMR, ATR, POX and CMR are used on an industrial scale (SMR is by far the leader), the rest of the processes remain under development and are the subject of research into the prospects for their application to reduce greenhouse gas emissions, minimize energy consumption and increase reforming productivity. CPOX, due to its relative simplicity and compactness, is often used in pilot and small-scale installations.

Brief information about the three most common processes for producing syngas and hydrogen is given in Table 1.

Table 1. Comparative characteristics of the three most common methods for producing syngas and hydrogen [16].

Production Method	Temperature (°C)	Pressure (atm)	Molar Ratio H_2/CO
SMR	750–900	15–40	3–5
ATR	850–1000	20–40	1.6–2.65
POX	1200–1500	20–150	1.6–1.8

SMR has been widely introduced on an industrial scale since the 1960s, when natural gas was used instead of coal as a feedstock for producing syngas.

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad \Delta H_{298} = +226 \text{ kJ/mol} \qquad (1)$$
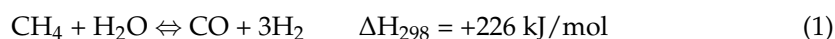
This process is also the most popular and cheapest way to produce hydrogen, as compared to the electrolysis of water per unit of energy expended, it allows the acquisition of 5–6 times more H_2 [8].

Usually, the SMR process is carried out on nickel catalysts at temperatures of 750–900 °C, pressures above 1.5 MPa and a high (to reduce catalyst coking) ratio of H_2O/CH_4 of 2.5–3.0 and higher. When implementing industrial steam reforming processes, the most serious problems are associated with hydrogen sulfide poisoning of catalysts, coke formation and significant sizes of apparatuses. Steam reforming natural gas reformers typically use

externally heated reaction tubes containing a relatively inexpensive nickel catalyst. The two most important parameters of the SMR process are the H_2O/C ratio and the reaction temperature. Low values of these parameters are preferred to increase energy efficiency, however, this increases the risk of carbon deposits on the catalyst and its poisoning [16].

The ATR autothermal reformer was developed by Haldor Topsoe (the ATR process is currently marketed under the name Autothermal Reformer Process TOPSOE™'s Syn-COR™ [17]). ATR is a combination of partial oxidation and steam reforming processes, which allows reducing the total enthalpy of the process to almost zero [18,19]. A consequence of this is that the H_2/CO ratio obtained in the ATR process is intermediate between the values obtained in SMR and POX (Table 1). It takes place in two zones: a partial oxidation zone, which generates the heat required for the subsequent endothermic steam reforming stage, and a catalytic steam reforming zone, in which the final composition of the syngas is reached. Operating temperatures of the process range from 850–1500 °C with a sharp increase in temperature in the oxidation zone and a uniform decrease in the zone of endothermic catalytic transformations, and the operating pressure of the process is more than 2 MPa.

An industrial process for the oxidative conversion of methane to syngas was developed in the early 1950s [20]. As a rule, the process is carried out at a pressure of 30–100 atm using oxygen, which is supplied in a slight excess compared to the reaction stoichiometry. This makes it possible to reach the temperature required for process stability and high methane conversion. However, this leads to the formation of a certain amount of deep oxidation products (CO_2 and H_2O). In addition to methane, raw materials such as oil residues, biogas, etc. can be used to produce syngas by partial oxidation.

Nickel or rhodium catalysts are usually used to carry out catalytic partial oxidation, most often on ZSM-5 zeolites. At the same time, the process proceeds under relatively mild conditions (800–900 °C, 2.5–3.5 MPa), which makes it possible to implement it on a small scale. The process can proceed according to two mechanisms: (a) a sequential mechanism (through deep oxidation of some of the methane to CO_2 and H_2O and subsequent steam and carbon dioxide conversion of the remaining methane), which is promoted by high temperatures, short contact times and catalysts reduced to a metallic state; (b) a direct mechanism (through the complete dissociation of $CH_4 \rightarrow C_{ads} + 4H_{ads}$ and $O_2 \rightarrow 2O_{ads}$ on the catalyst surface with subsequent formation of final products $C_{ads} + O_{ads} \rightarrow CO$ and $2H_{ads} \rightarrow H_2$), which is observed at low temperatures and long contact times on oxidized catalyst surfaces.

The industrial implementation of catalytic partial oxidation is associated with great technical difficulties. These include a high probability of self-ignition of the reaction mixture before contact with the catalyst, a sharp temperature profile and a high probability of the formation of hot spots in the catalyst, which contribute to its sintering, deactivation and metal carryover. This negatively affects the stability and safety of the CPOX process, making it unlikely to be used for large-scale production. Until now, we have been talking about the implementation of the CPOX process only at demonstration and pilot plants, in the development of catalysts for which Exxon is the leader [21]. Demonstration units using Conoco Phillips technologies were also built (closed due to rapid catalyst deactivation) [22] and also Dason CPOX.

The largest developers and licensors of non-catalytic processes for the partial oxidation of various types of hydrocarbon feedstock into syngas are Shell, Texaco and Lurgi. [23]. Of the commercialized POX technologies, Shell's Shell Gasification Process (SGP) technology, implemented at the plant in Bintulu (Malaysia) and the world's largest natural gas conversion plant Pearl GTL in Qatar [24]; Texaco Syngas Generation Process (TSGP) technology [25]; the High Pressure POX (HP POX) process by Lurgi in Freiberg (Germany) [26]; and the Gas POX process by Air Liquide Engineering & Construction [27] are the most well-known. It is worth noting that Shell SGP's POX gasification process is a flexible process for producing syngas for the production of high-pressure high-purity H_2, methanol, ammonia, fuel gas, domestic gas or reducing gas [28].

Numerous reviews, including [29–32], are devoted to the analysis of industrial methods for producing hydrogen. The most common of them is carried out in three steps: (a) preliminary conversion of natural gas into syngas, which is implemented in one of three ways: steam, carbon dioxide and oxidative conversion; (b) steam reforming of formed CO (water–gas shift reaction, WGSR); (c) CO_2 removal.

From the point of view of greenhouse gas emissions during its production, the resulting hydrogen is usually divided into the following categories: (a) "gray" hydrogen, obtained from coal, oil and gas, (b) "blue", obtained at combined cycle power plants using the technology of capturing and storing carbon dioxide capture and storage (CCS) or, at nuclear power plants, (c) "green" hydrogen obtained from renewable energy sources (solar, wind, etc.) and water electrolysis. Unlike well-established SMR hydrogen production processes, carbon dioxide capture and storage technologies are still far from full-scale commercialization. Companies are using CCS technology to extract CO_2 from industrial emissions and then pump the CO_2 underground. In 2022, 61 new CCS projects were announced, bringing the total number of commercial plants under development to 196, of which 30 are currently in operation, 11 are under construction and the remainder are under development [33]. After the completion of the implementation of all the above projects, a total of 244 million tons of carbon dioxide per year will be captured in the world. However, according to the feasibility study given in [34], in the case of introducing CCS into the technological scheme of the hydrogen production process using steam reforming technology, capital costs (CAPEX) increase by 87%, and operating costs (OPEX) by 33%. Therefore, the present value of the produced hydrogen in this case increases one and a half times (up to 1.8 euros per kg), and the price of carbon dioxide utilization is EUR 70 per ton of CO_2.

Currently, more and more energy companies are declaring their intention to take an active part in the transition to carbon-neutral energy. Shell has developed a new highly efficient process for producing "blue" hydrogen without a carbon footprint—Shell Blue Hydrogen Process (SBHP). SBHP combines two of the company's successful technologies—SGP gas partial oxidation technology to convert steam cracking residues into syngas and ADIP ULTRA absorption technology to capture CO_2 from high-pressure POX processes [35].

For separation of pure hydrogen from the products of the oxidative conversion of hydrocarbon gases, one of three methods is usually used: membrane separation, pressure swing adsorption and cryogenic separation [36]. Membrane systems can separate hydrogen from impurities, but are not able to provide high purity of the resulting hydrogen. Pressure swing adsorption systems can produce ultra-high-purity hydrogen (up to 99.999%). They operate at elevated pressures, require complex control systems and high capital and operating costs. Cryogenic separation is a much more capital- and energy-intensive and complex process compared to the two above, so it is used only for very large-scale hydrogen production or very high purity requirements.

Comparative data on the efficiency of H_2 production in processes of various degrees of commercial readiness are presented in Table 2.

Table 2. Comparative data on the efficiency of hydrogen production methods [29].

Process	Feedstock	Thermal Efficiency
Steam reforming	Hydrocarbons	70–85%
Partial oxidation	Hydrocarbons	60–75%
Autothermal reforming	Hydrocarbons	60–75%
Plasma reforming	Hydrocarbons	9–85%
Electrolysis	H_2O + electricity	50–70%

3. Results of Studies of Non-Catalytic Partial Oxidation of Hydrocarbon Gases

The partial oxidation of methane to syngas is a slightly exothermic reaction.

$$CH_4 + {}^1\!/_2 O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298} = -36 \text{ kJ/mol} \qquad (2)$$
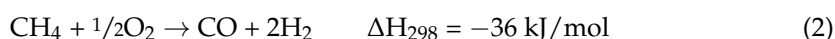
Under normal conditions, it is always accompanied to some extent by the reaction of deep oxidation of methane, which provides the necessary amount of energy for the actual autothermal process to proceed.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -891 \text{ kJ/mol} \tag{3}$$
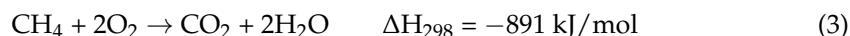
Due to the exothermic nature, partial oxidation does not require external energy supply to the process itself and energy to steam production, therefore it is considered a more economical process than steam reforming.

An important factor affecting the composition of the syngas is the composition of the initial hydrocarbon mixture. However, under real conditions, with homogeneous oxidation of very rich gas mixtures, it is difficult to achieve an equilibrium chemical composition of the products. In addition, for the efficient implementation of subsequent processes based on syngas, it is necessary to obtain it at high pressure. However, increasing pressure reduces methane conversion and syngas yield. The unfavorable influence of pressure is compensated by increasing the process temperature.

Interest in non-catalytic partial oxidation of methane resumed in the 1990s and early 2000s. The reaction was studied in a wide temperature range using flow reactors [37], and its thermodynamic [38] and kinetic analysis was carried out to identify the effect of the composition of the initial mixture, temperature and pressure on the yield of syngas [39].

Typically, the partial oxidation of hydrocarbon gases occurs in the medium temperature range from 300 to 1200 °C, which is much lower than the temperatures typical for gas-phase combustion of hydrocarbons. The paper [40] notes a fundamental difference between combustion and partial oxidation processes, associated not only with the difference in temperatures, but in the mechanisms of these processes. A distinctive feature of the mechanism of partial oxidation of alkanes is the large role of radicals and peroxide compounds in it. In the low-temperature interval, these are the ROO• radicals and the ROOH and R1OOR2 molecules (for CH_4, respectively, $CH_3OO•$ and CH_3OOH), and in the high-temperature interval the HOO• radicals and the HOOH molecules. At the same time, the role of O, CH_2, CH, C_2 particles, as well as excited molecules and radicals actively participating in combustion processes, is insignificant in POX. That is, in different parts of the specified temperature range, different products predominate. At the same time, in the shift to the higher temperatures, products thermodynamically stable under these conditions begin to predominate more and more, and their maximum yield increases (for syngas, it becomes almost 100%). An important feature of this range is also the fact that at such temperatures, processes occurring both on a solid surface (heterogeneous catalysts and reactor walls) and in the gas phase successfully compete with each other [41]. Therefore, regardless of whether the process is carried out as a catalytic or as a homogeneous process, it is necessary to take into account the role of reactions involving another phase. Sometimes the average temperature range of 300–1200 °C is divided into three subregions: (a) predominant formation of oxygenates (300–600 °C), (b) oxidative condensation of methane with predominant formation of C_2 hydrocarbons (600–900 °C), (c) predominant formation of syngas (>900 °C). POX processes are modeled using various Chemkin packages with detailed oxidation mechanisms, such as GRI-Mech, AramcoMech, NUI GALWAY and others.

3.1. POX Process Thermodynamic and Kinetic Modeling

Theoretical studies of POX processes were mostly associated with thermodynamic calculations, which are still the focus of researchers' attention. The equilibrium composition of the products of partial oxidation and steam and carbon dioxide reforming of hydrocarbons in the temperature range of 1100–1500 °C is analyzed [42]. An important role is shown in approaching the equilibrium composition of the products of the water–gas shift reaction (WGSR), the equilibrium between the components of which is established already at the intermediate stages of the process, long before reaching complete equilibrium in the system. For these processes, critical temperatures have been established, at which, at various molar

ratios of O_2:CH_4 and CO_2:CH_4, an appreciable (0.01 mol%) amount of solid carbon appears in the equilibrium products. It has been established that steam reforming of methane at H_2O:$CH_4 \geq 1$ proceeds without soot formation.

Based on thermodynamic calculations, estimation was made of the regimes of non-catalytic natural gas conversion with the production of syngas [43]. The authors considered various types of conversion, including air and steam–air, with increased oxygen content or initial temperature. The results of the analysis for mixtures with the combustion temperature of at least 700 °C (at lower temperatures unreacted methane is contained in the products) showed that when air is used as an oxidizer, the maximum content of carbon monoxide and hydrogen in gaseous products can be 13.2 and 28.3 vol.%, respectively. At the value of the equivalence ratio $\varphi = 2.6$, the maximum yield of H_2 and CO from one mol of CH_4 is 1.65 and 0.77 mol, respectively. An increase in the mixture's initial temperature leads to an increase in the combustion temperature and the yield of CO, as well as to a decrease in the concentration of H_2 in the products.

However, thermodynamic calculations do not provide real information about the composition of natural gas partial oxidation products, but only about the potentially achievable composition of products. For a deeper understanding of the kinetics of the processes of non-catalytic partial oxidation of natural gas, experimental data on the kinetics of these processes under various conditions, as well as their detailed kinetic analysis, are required.

A kinetic analysis of the partial oxidation of methane to syngas using various detailed oxidation mechanisms was carried out in [44]. The existence of two reaction zones has been established, namely the fast oxidation zone and the slow conversion zone. In the oxidation zone, both complete and partial oxidations are observed, as well as hydrogen combustion. The conversion zone is dominated by methane steam reforming, WGSR and acetylene steam reforming. Temperature significantly affects the duration of the process.

The mechanism of the reaction of non-catalytic partial oxidation of methane with the production of syngas in a flow reactor was modeled and compared with experimental data in [45]. The experiments were carried out with a premixed gas (0.2% methane and 0.1% oxygen were diluted with argon 99.7%), which reduced the exothermic effect of the reaction at temperatures from 950 to 1250 °C under pressure. As an initial step in the simulation, the values of the reaction rate constants were taken from a NIST database. The rate constants for the reactions $O + OH = O_2 + H$, $CH_3 + O_2 = CH_3O + O$ and $C_2H_2 + O_2 = HCCO + OH$ were taken from other works. This optimization made it possible to reduce the mean square prediction error from 6.70 to 1.18.

The process of non-catalytic partial oxidation of methane was modeled in a wide temperature range from 550 to 1260 °C in [46]. For comparison, the experimental results obtained in two flow tube reactors in which highly diluted $CH_4/O_2/N_2$ mixtures interacted at a pressure of 1.2 atm and a residence time from 1 to 164 s were used. It has been established that with a short interaction time, the overall rate of the POX process is determined by three reactions: chain branching $H + O_2 = OH + O$, recombination $CH_3 + CH_3 (+M) = C_2H_6 (+M)$ and oxidation of the methyl radical $CH_3 + O_2 = CH_2O + OH$. With a longer contact time, a strong influence of heterogeneous reactions occurring on the walls of the reactors begins to have an effect, which leads to inhibition of the oxidation process.

Kinetic modeling of non-catalytic partial oxidation of an $NG/O_2/H_2O$ mixture into syngas at elevated pressures based on detailed mechanisms of methane oxidation was carried out in the work [47]. The dependence of the reaction time on the temperature at the reactor inlet, the pressure in the reaction system and O_2/CH_4 ratio were studied. It was predicted that the conversion of methane to syngas at a pressure of more than 30 atm and a temperature of 1150 °C should be completed within less than 0.1 ms. It has been established that for the complete conversion of methane under conditions typical of industrial reforming processes, an O_2/CH_4 ratio of at least 0.64 is required. The results of calculations of the effect of the O_2/H_2O ratio in the initial gas showed that the addition of H_2O can be an effective tool to control the H_2/CO ratio in the product, as well as to adjust

the flame temperature. The formation of C_{2+} hydrocarbons and soot was not analyzed in this work.

The most detailed kinetic analysis of the gas-phase partial oxidation of methane and other gas-phase alkanes to syngas was carried out in a series of works [42,48–50]. The presence of three consecutive reaction zones was found: a fast oxidative conversion zone, a subsequent slower post-flame thermal conversion zone and a final zone in which the equilibrium composition of the products is slowly reached. In the oxidizing zone, partial and deep oxidations of hydrocarbons, as well as the resulting hydrogen, proceed. The subsequent post-flame zone is dominated by the pyrolysis of the remaining hydrocarbons, steam reforming of methane, the WGSR and steam reforming of acetylene. It was shown that, in the temperature range of 1100–1500 °C, the initial stage of the non-catalytic conversion of methane in the post-flame zone is its thermal pyrolysis to acetylene, which is weakly affected by the presence of H_2O and CO_2 in the reaction medium. As a result, in this zone there is a rapid accumulation of acetylene as an intermediate product of the process. Subsequently, steam and carbon dioxide conversion of acetylene proceeds, which leads to a significant increase in the yield of H_2 and CO. In this case, equilibrium is quickly established in the WGSR. At the third, slowest stage, the content of conversion products slowly approaches the equilibrium values. An increase in temperature leads to a reduction in the length (duration) of all reaction zones.

Shifting from the catalytic CPOX process to non-catalytic POX is proposed as a solution to the problem of converting to syngas the oven gas, which consists mainly of hydrogen (58%) and methane (26%) and is contaminated with solid impurities and a high content of organic sulfur [51]. Thermodynamic analysis of the characteristics of the oxidation process, taking into account the dynamics of reaction flows, showed that in a non-catalytic gas generator there are three flow regions (a jet-flow region, a recirculation-flow region and a tube-flow region) and three reaction zones corresponding to them. The combustion of oven gas takes place mainly in the jet-flow region, while its conversion takes place in the two other regions. It has been established that during the decomposition of methane at temperatures above 1200 °C, no soot is formed due to the very low content of C_{2+} hydrocarbons in the oven gas. To simulate the POX process, an integrated gasifier model with in-line gasification was used. Calculations showed that the optimal ratio of oxygen to oven gas at various pressures is 0.22–0.28.

The effect of hydrogen additions on the non-catalytic partial oxidation of a natural gas/oxygen mixture in a flow reactor with increased thermal intensity was studied in [52]. The simulation results showed that the addition of hydrogen ($CH_4/H_2 = 3$) to a fuel-rich natural gas/O_2 mixture with an excess oxidizer ratio $\alpha = 0.34$ leads to an increase in the yield of H_2 and CO and the ratio of H_2/CO, as well as to a decrease in the yield of CO_2, H_2O, C_2H_4, C_2H_2 and soot formation.

The features of the non-catalytic partial oxidation of methane with the formation of syngas in an adiabatic POX reactor operating in a non-isothermal plug flow mode have been studied [53]. The determination of the functional features and characteristics of the POX reactor was carried out according to equations that were modeled using Simulink 7.5 and solved using MATLAB. The calculated optimal values of the parameters were used to design a hypothetical reactor capable of processing about 600 million m^3 of natural gas per day into syngas. The simulation results showed that parameters such as residence time and product yield increase with increasing methane conversion, while volume velocity and selectivity decrease. Operation at high pressure (60–70 atm) increases the syngas yield and volume velocity and reduces the residence time and reactor length required to achieve high methane conversion (0.95–0.99).

Numerical studies of the partial oxidation of a CO_2/CH_4 mixture were carried out using a two-layer reactor with an inert filler with different porosities based on a two-temperature two-dimensional model with different oxidation mechanisms (GRI-Mech 1.2, DRM 19 and GRI-Mech 3.0) [54]. Particular attention is paid to the influence of the choice of a particular mechanism on the prediction of the temperature distribution inside the burner, the chemical

structure and the efficiency of the process of producing syngas. The equivalence ratio had a fixed value of 1.5, while the CO_2:CH_4 volume ratio varied from 0 to 1. The available experimental data and predicted results were compared. It was found that, with the exception of the exothermic zone, the mechanisms used in the calculations have little effect on the resulting temperature distribution in the burner. Good agreement between experimental and calculated values was obtained using the GRI-Mech 1.2 and GRI-Mech 3.0 mechanisms, which showed the same accuracy in predicting the yield of CO, H_2 and CO_2. Calculations based on DRM 19 underestimated the molar ratio of CO and H_2. A strong influence on the process of obtaining syngas was found from the thermal conductivity of the porous medium. As it decreased, the oxidation temperature increased and the yield of hydrogen increased.

It is shown that non-catalytic partial oxidation of methane under the conditions of the operation of matrix converters opens up the possibility of efficient production of hydrogen directly at the places of its consumption, including from local bioresources and unconventional fossil hydrocarbons [49]. Kinetic modeling showed that the process proceeds in two stages: in the combustion zone in the presence of O_2, along with H_2, CO, H_2O and CO_2, products of the oxidative conversion of methane are formed. Then, in the zone following the flame zone, in the absence of oxygen at a temperature of 1100–1300 °C, slow pyrolysis and steam reforming of the obtained products are carried out. Moreover, the pyrolysis of CH_4 to acetylene and the subsequent steam reforming of the latter proceed much faster than the interaction of CH_4 with H_2O, which leads to a decrease in the concentration of methane and acetylene and an increase in the concentration of H_2 and CO. Optimization of conditions in the post-flame zone makes it possible to increase the yield of hydrogen and reduce the yield of acetylene.

3.2. POX Process CFD Modeling

The parameters of the process of partial oxidation of natural gas at high pressures and temperatures in real reaction apparatuses are affected by many physical factors, including the often occurring turbulence of reaction flows. Modeling of reactors operating at high pressures and temperatures is possible both on the basis of one-dimensional models [47] and on multidimensional CFD models [55–57]. Numerical computational fluid dynamics (CFD) modeling of reaction dynamics can provide detailed information about the multidimensionality of the flow, the distribution of various types of flows, as well as temperatures. This requires information about the reactor system used, a detailed description of the design of the reactor and burner, data on the material and energy balance, etc. The results of numerical CFD modeling of non-catalytic partial oxidation of natural gas at high pressures and temperatures have been successfully collected on a semi-industrial HP POX high-pressure pilot plant at TU-Freiberg (Saxony, Germany) of Lurgi [58,59]. The plant, operating at pressures up to 100 atm, is capable of processing 500 Nm^3/h of natural gas or 500 kg/h of liquid hydrocarbon feedstock into syngas with a capacity of up to 1500 Nm^3/h.

Based on the results from this HP POX high-pressure pilot plant, a numerical simulation of non-catalytic natural gas reforming was performed using a simulation in Virtuhcon Benchmark [60]. The composition of the gas phase and the temperature of the walls throughout the reactor were experimentally studied for temperatures from 1200 to 1400 °C and pressures from 50 to 70 atm. The length and width of the flame zone were estimated by optical methods. The well-known eddy dissipation concept model and the improved flamelet/progress variable-based approximation developed for POX processes were used to evaluate chemical interactions under turbulent conditions. In contradistinction to standard approaches to describing ignition, the proposed improved model can adequately describe both the reaction zone and relatively slow chemical processes in the post-combustion zone. On the basis of experimental data, the applicability of various numerical models to the description of the POX process was tested. In contrast to the models presented in a number of literature sources, the model used was based on the analysis of the optical characteristics of the flame, which made it possible to predict the local effects of reaction flows in indus-

trial reactors for POX processes under high-pressure and high-temperature conditions. The results showed that both applied approaches make it possible to reliably predict the composition of the resulting syngas, as well as the length and width of the flame.

The proposed reduced order model (ROM) describes the process of non-catalytic partial oxidation of natural gas at high pressure and high temperature, the reactants of which are introduced into the reactor using a multichannel burner, as shown in Figure 1. Three streams of reactants were taken into account—natural gas as a fuel, steam as a process phlegmatizer and oxygen (previously mixed with steam) as an oxidizer. After entering the reactor, these flows are mixed with each other, which starts the oxidation process. The reactions continue until one of the reactants is completely consumed.
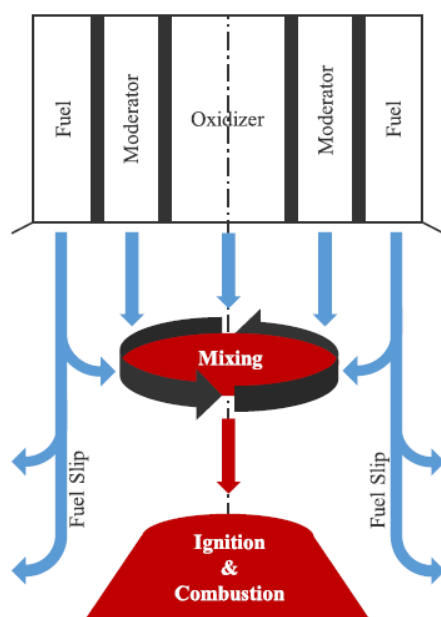

Figure 1. Reactant mixing diagram for the concentric oxygen burner nozzle design used in the POX reactor [60].

To identify the reactor zones, streamlines were modeled from the results of CFD modeling to visualize fluid trajectories (Figure 2). Gas recirculation occurs in the reactor, while streamlines indicate that the recirculation zone is described by complete fluid circulation, and the zero axial velocity boundaries divide this zone into two regions. Based on the analysis of the flow lines, the zero axial velocity boundaries and the flow function, the reactor was divided into the following five zones: combustion, bypass, plug-flow, recirculation and outlet zones (to simplify calculations, each zone was considered cylindrical).

The proposed ROM was also confirmed by comparing the calculated parameters of a large-scale process and experimental data [61]. In fact, a later version of the ROM used a network of perfectly mixed reactors, each of which described a separate reactor zone and the corresponding natural gas conversion steps. This model is able to predict the main operating characteristics of the reactor and the structure of the reaction streams, which makes it possible to optimize the geometrical parameters of the reactor. In addition, the model can be used to predict POX processes.

When creating mathematical models for describing turbulent combustion during the partial oxidation of natural gas, an approach based on the probability density function (PDF) or multienvironment PDF (MEPDF) approach is often used. For example, such a method was used in [62] for the numerical study of POX processes with moderate and low oxygen content in order to calculate turbulence–chemical interactions in complex turbulent flames [63]. Micromixing was taken into account using the interaction by exchange with the mean (IEM) model, and detailed kinetics was modeled using the GRI-Mech 3.0 oxidation mechanism. Based on the numerical results, the possibilities of flame stabilization, its struc-

ture and the conditions of the self-ignition process were clarified based on the recirculation rate, the distribution of the Damkohler turbulence number, the scalar dissipation rate, the average temperature and the molar ratio of CH_2O and OH.
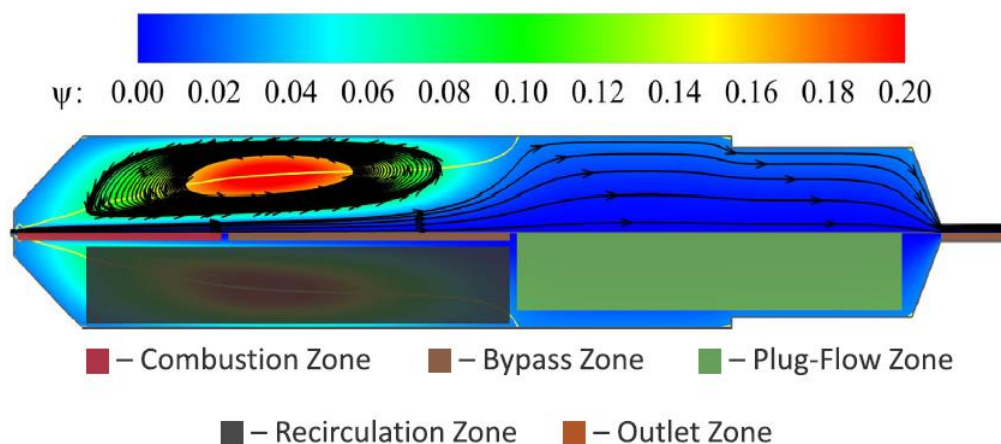

Figure 2. Flow function in a typical Virtuhcon Benchmark reactor derived from 2D axisymmetric CFD simulation [60]: the upper part of the figure reflects the flow function ψ and the flow direction; the yellow curve in the middle part indicates the limit of zero axial velocity; the lower part reflects the different zones of the conversion.

In [64], the MEPDF approach was applied, while varying the volumetric flow rate, to numerically study a series of turbulent pre-mixed flames in a pilot jet burner. The MEPDF approach, together with micromixing models (IEM, EIEM) and the GRI-Mech 3.0 oxidation mechanism, qualitatively predicted ignition, local quenching and re-ignition processes at the three volumetric flow rates studied.

A 2D model of a reformer for non-catalytic partial oxidation of natural gas (NG) was studied [55]. The simplified GRI-Mech 3.0 oxidation mechanism was used to calculate the reaction rates, and the modified eddy dissipation concept (EDC) model and the PDF model were used to calculate chemical interactions, taking turbulence into account. Using the EDC model, the effect of pressure and O_2/NG and steam/NG molar ratios on reformer performance was studied. The calculated values are in good agreement with the performance of the industrial reformer. It has been shown that the increase in pressure promotes methane conversion, therefore, for operation in industrial conditions, it was proposed to use pressures above 3 MPa. With an increase in the O_2/NG molar ratio, the oxidation temperature increases, and the CH_4 concentration in the syngas decreases. With an increase in the steam/NG molar ratio, a decrease in the flame temperature in the reformer and an increase in the H_2/CO molar ratio were observed.
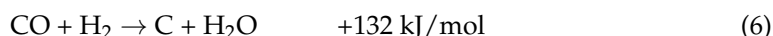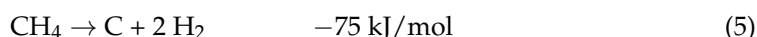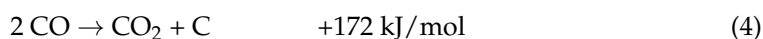
Not only natural gas or methane, but also other carbon-containing gases, can be used as feedstock for the production of syngas and hydrogen by POX methods. It is possible to use biogas, the main components of which are methane and CO_2, which are obtained in the processes of biomass fermentation. There is some interest in the production of carbonaceous fuels and chemicals from biomass due to the drive towards decarbonization. A mini-review [65] discusses in detail the state of research on the conversion of biomass into liquid fuels that are in demand on the market, progress in the creation of new electrically heated reformer reactors, as well as the complexities and prospects for the development of biomass-based processes. Several possible technologies for syngas production from biomass are analyzed: POX, CPOX, ATR, SMR, CSMR and MR. It is noted that despite the problems with energy efficiency and the need for improvement, traditional processes for reforming various feedstocks (SMR, POX, ATR) are technologically mature. The transition to biomass reforming processes will require addressing both the existing shortcomings of traditional processes and addressing new problems arising from the use of new fuels.

Thermodynamic calculations of biogas conversion with the production of hydrogen and synthesis gas have been carried out in [66]. The modes of conversion by atmospheric air of the initial and dried biogas, and conversion at increased content of O_2 in the air, were studied. Model compositions of low-calorific (25 vol.% of CH_4) and high-calorific (50 vol.% of CH_4) biogas are considered. Calculations were carried out for mixtures with the combustion temperature of at least 700 °C. It is shown that with air reforming of low-calorific dry biogas, the maximum content of carbon monoxide and hydrogen in gaseous products can be 20.8 and 22.3 vol.%, respectively, and for high-calorific biogas, these contents can be 16.3 and 26.0 vol.%, respectively. At an oxygen content of 41 vol.%, the conversion of low-calorific dry biogas provides gas with a content of 31.0 vol.% H_2 and 28.3 vol.% CO, and in the case of high-calorific biogas, that with a content of 39.0 vol.% and 25.0 vol.%, respectively.

3.3. Experimental Studies and Apparatus for the Implementation of POX Processes

In addition to the conditions, the efficiency of the processes of non-catalytic partial oxidation of hydrocarbon gases largely depends on the design of the reaction apparatus in which they are implemented.

By improving and modernizing the designs of reaction apparatus, one of the main tasks in the implementation of POX processes related to the soot formation control can be successfully solved. High temperatures in the oxidation reactors contribute to the destruction of hydrocarbons, leading to the formation of soot as a result of reactions that can occur under conditions of turbulent combustion:

$$2\,CO \rightarrow CO_2 + C \qquad +172\ kJ/mol \qquad (4)$$

$$CH_4 \rightarrow C + 2\,H_2 \qquad -75\ kJ/mol \qquad (5)$$

$$CO + H_2 \rightarrow C + H_2O \qquad +132\ kJ/mol \qquad (6)$$

In [67], the effect of saturation of CH_4 with water vapor on the formation of soot was studied in various conversions of methane to syngas. Experiments on the production of syngas were carried out at a test facility for high-temperature non-catalytic partial oxidation of methane in a reactor with a capacity of 8 Nm^3/h. As a result, a stable mode of POX was provided with the ratio H_2/CO = 1.87 in the resulting syngas. The relationship between the syngas composition and the input H_2O/CH_4 ratio was revealed, as well as the quantitative and qualitative dependence of the formation of soot agglomerates on the degree of saturation of CH_4 or natural gas with water vapor. Structural features of soot and its formed samples were studied using scanning and transmission electron microscopy and X-ray diffraction analysis.

The partial oxidation of hydrocarbon gases is traditionally carried out in flow reactors [68]. Figure 3 shows a traditional POX reactor. Pre-heated natural gas and oxygen are fed into the burner, where they react in a turbulent-diffusion flame mode. The reactor has a refractory lining to operate at high (1400 °C) temperatures.

According to [69], the POX reactor consists of two zones. The first zone is the flame zone, where hydrocarbons and oxygen react in the presence of a small amount of steam. The second zone is the heat exchange zone, in which the processes proceed due to the released heat of the oxidation reaction. Under real conditions, when rich mixtures of methane and oxygen interact, temperatures of 1500 °C and higher are reached. Taking into account the formation of CO_2, the H_2:CO ratio is usually close to 1.7–1.8. To increase the conversion of methane, the proportion of oxygen is increased, which contributes to the formation of a significant amount of CO_2. Although POX technology is more energy efficient than steam reforming, an additional air separation unit is required, which increases capital and operating costs, as well as increases CO_2 emissions.
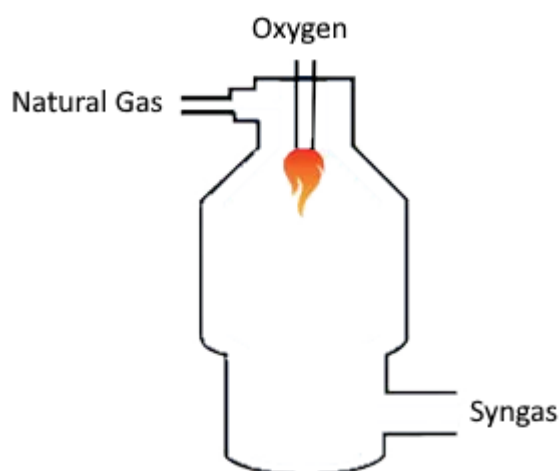
Figure 3. Traditional POX reactor.

Shell, the largest developer of POX technology, uses a reaction apparatus with a burner system to implement its process. Natural gas at a temperature of 400 and oxygen at a temperature of 2500 °C are separately supplied to the burner or burner system, while the oxygen supply rate significantly exceeds the gas supply rate (V_{CH_4}/V_{O_2} velocity ratio is in the range of 0.25–0.6) [70]. In the upper part of the burner device, partitions are installed that separate the flows of gas and oxygen. The uppermost part of the burner is made of ceramic materials, and sometimes even of precious metals or their alloys, which possibly act as a catalyst that starts the oxidation process. Shell's burner layout for the POX process is shown in Figure 4.
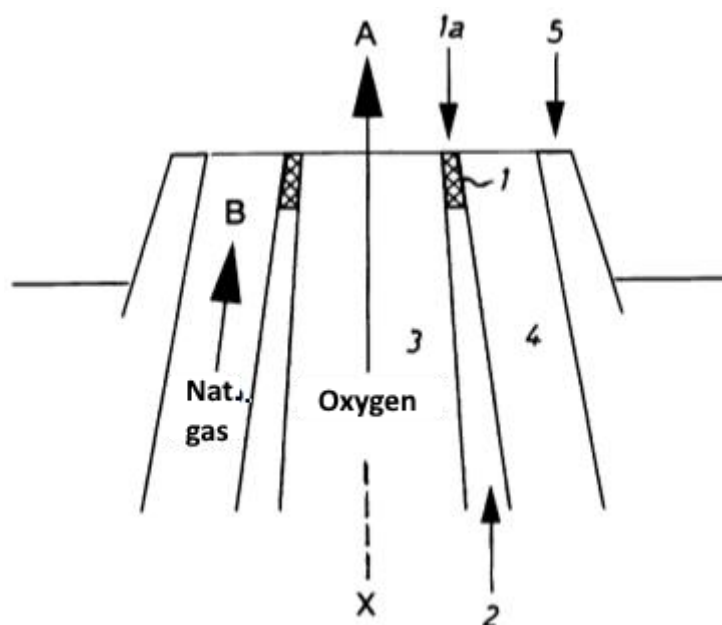

Figure 4. Schematic diagram of a Shell burner for the high-pressure POX process [70]: 1—the upper part of the partition separating the channels, 1a—the outer part of the partition separating the channels, 2—the partition separating the channels, 3—central channel for supplying oxidant, 4—external channel for supplying natural gas, 5—outer wall of the burner.

A POX reactor system using indirect induction heating of a flow tubular reactor has been created and tested [71]. This type of heating has proven to be very effective due to the response to the sharp temperature changes that normally accompany ignition reactions in POX. Experiments were carried out both on dilute and undiluted mixtures. In dilute mixtures, the influence of temperature was studied (1000–1500 °C). For the

conditions of concentrated mixtures, the process time, temperature regimes (1490–1590 °C), ratio of reagents (CH_4/O_2) (1.59–1.74) and flow rates were studied. Later, the authors continued their research using a flow gas reactor with indirect induction heating [72]. When carrying out experiments on the partial oxidation of methane diluted with nitrogen, the effect of temperature (1000–1500 °C), the ratio of reagents ($CH_4/O_2 = 1$–2) and the addition of hydrogen were studied. It has been established that the dominant method of heat transfer during the movement of reaction flows is thermal radiation. To correct the temperature profiles, computer modeling of CFD hydrodynamics based on simplified oxidation mechanisms was used. Kinetic modeling of the experiments was carried out using the well-known GRI-Mech 3.0 and Glarborg mechanisms [73]. In both cases, the calculated compositions of the gas phase at the reactor outlet coincided with the experimental data. However, it was found that the Glarborg mechanism is more accurate in predicting the selectivity of C_2 hydrocarbons, in particular acetylene, since it contains more variations in the conversion of C_2H_2 to polycyclic aromatic hydrocarbons.

The optimal construction of a flow chemical reactor with an increased thermal value during the partial oxidation of natural gas with O_2 was determined experimentally with the oxidizer excess factor in the range $0.27 < \alpha < 0.4$ [74]. It is shown that a reactor with a supercritical pressure drop at the outlet of the combustion chamber and a chamber for additional turbulent mixing of reagents can provide a combustion mode as an oxidation process in a plug-flow reactor. An increase in the strength of thermal processes in the reactor combustion chamber as a result of a decrease in its size led to complete conversion of the initial reagents and a decrease in soot formation. A decrease in the size of the combustion chamber was accompanied by an increase in heat density in it, which led to a change in the structure of the combustion and mixing zones. This made it possible to determine the optimal volume of the combustion chamber.

When obtaining syngas by partial oxidation, a two-pronged problem must be solved. On the one hand, to initiate the endothermic stages, it is necessary to supply energy to the reaction mixture; on the other hand, it is necessary to utilize the heat of the formed products. This problem can be solved by carrying out the process under conditions of filtration of the reaction gas mixture through an inert porous medium (filtration combustion mode) with a combination of oxidative and steam reforming of methane [75,76]. For this, reactors of various designs are offered, for example, with separate input of reagents in an upstream filtration combustion reactor with a moving bed of an inert coolant, shown in Figure 5 [77,78]. A distinctive feature of such reactors is the presence of a heat exchange device (Figure 5b), which allows more efficient use of the heat of an inert coolant due to air pre-heating, and also involves a variety of options for introducing an oxidizer into the system.

The process of hydrogen production by the POX method is proposed to be carried out in a layer of solid porous media, when the flame speed is 10–30 times higher than the laminar flame speed, which improves the performance of the process and expands the combustion limits (Figure 6) [79].

Two other methods of organizing the process in porous systems, carried out in stationary and dynamic modes, are more efficient. In the first case, which is widely used in radiant burners and heaters based on surface combustion, the combustion zone is stabilized within a certain position in the porous matrix. In the case of transient regimes, the conversion occurs in a propagating combustion wave, which alternately moves in one direction or the other in a porous medium.
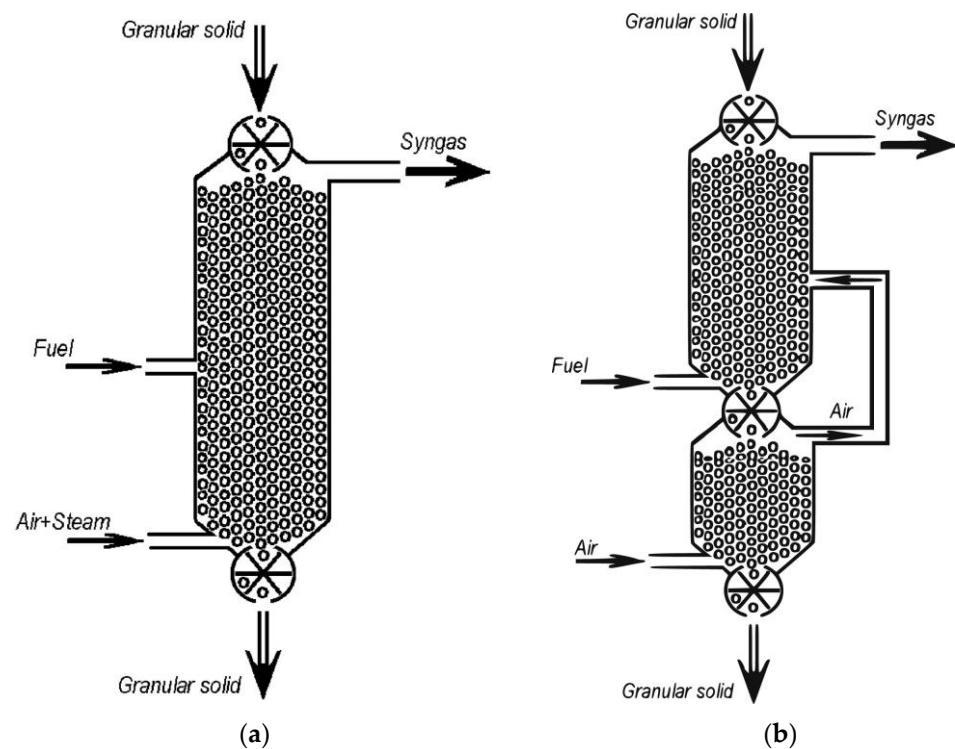
Figure 5. Counterflow filtration combustion reactors with a moving bed of inert coolant: (**a**) without a heat exchanger with lateral fuel inlet [77] (copyright with permission from [77], Elsevier, 2019); (**b**) with a heat exchanger with lateral pre-heated air inlet [78] (copyright with permission from [78], Elsevier, 2019).
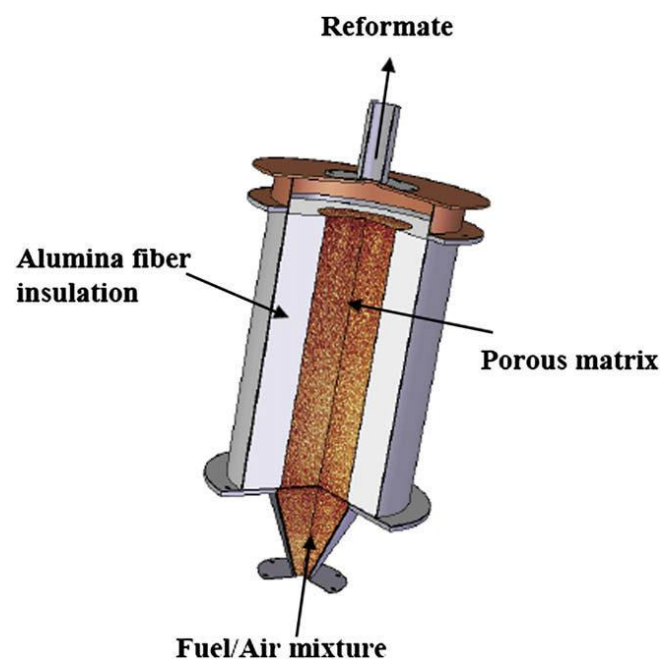

Figure 6. Reformer based on the partial oxidation of methane to hydrogen in a thermal porous matrix [79] (copyright with permission from [79], Elsevier, 2008).

To obtain syngas and hydrogen by the conversion of lower gaseous hydrocarbons under conditions of superadiabatic filtration combustion in a porous medium, temperatures are characteristically higher than during adiabatic conversion. This makes it possible to convert mixtures with a large excess of methane over oxygen and increases the thermal efficiency of the process. The transfer of heat from the outgoing gases by a solid coolant towards the flow back into the reaction zone and cold gas in such reactors also reduces energy losses with the products leaving the reactor (energy recuperation reactor).

The ability to convert methane with higher energy efficiency and at a higher temperature eliminates the need for expensive catalysts, thereby eliminating the problems of coking and catalyst poisoning. This is an important advantage of filtration combustion compared to catalytic partial oxidation. The concept of thermochemical conversion of methane to syngas in a self-sustaining mode has been clearly demonstrated in practice. The optimum equivalence ratio for maximum syngas yield in a POX process is $\varphi = [CH_4]/[O_2] = 3$–3.5. According to literature data, in the case of air filtration combustion of hydrocarbon gases, the maximum hydrogen content in gaseous products can reach 34% by volume, but practice has shown that in most cases the content does not exceed 25%.

In [80], when implementing the partial oxidation process, it was proposed to use a divergent packed bed two-layer burner. To study the temperature and distribution of POX products, we used data on the divergent angles, the interface location and the diameter of granules of the porous medium. Increasing the divergent angle within a certain range increases the conversion of methane (of the five considered angles, the angle of 15° turned out to be optimal). It has been established that the divergent region of the burner with the packed bed weakens the effect of the inlet velocity and contributes to the stability of the oxidation process as a whole.

An example of natural gas conversion based on superadiabatic combustion is the matrix conversion method [81]. This is a process of flameless near-surface combustion of hydrocarbons, which provides partial heat recuperation from the conversion products back into the mixture of fresh reagents supplied to the reactor. The difference from filtration combustion lies in the fact that partial oxidation in such a converter occurs in the gas phase near the inner surface of a closed volumetric matrix permeable to the gas mixture, made of a heat-resistant material. A mixture of fuel and oxidant (atmospheric air, oxygen-enriched air or technical oxygen) enters a matrix made of a gas-permeable material. As such a matrix material, for example, perforated ceramics, refractory foam metal or extruded wire made of refractory metals can be used. Near the inner surface of the matrix, flameless combustion occurs with the matrix itself when heated to 800–1000 °C. The fresh gas mixture, passing through the walls of the matrix, heats up and enters the combustion zone already heated to 600–800 °C, which significantly expands the limit of stable conversion of rich mixtures. The scheme of operation of a matrix converter with a permeable matrix is shown in Figure 7 [81].

A 3D calculation of the performance of burners of various designs (Figure 8) was carried out to optimize the process of high-pressure non-catalytic reforming of natural gas based on data from a semi-industrial test facility in Freiberg (Germany) [82]. The converters operated at a pressure of 61 atm and an outlet temperature of about 1688 K. The model was verified on the basis of optical measurements of the flame structure. It has been established that the optimization of the burner design can lead to an increase in the conversion of natural gas. This makes it possible to develop a more compact design of the reactor or to increase the productivity of existing industrial facilities. Optical measurements have shown that the CFD model is able to successfully reproduce complex 3D flame structures in the burner and reliably predict overall reactor performance.
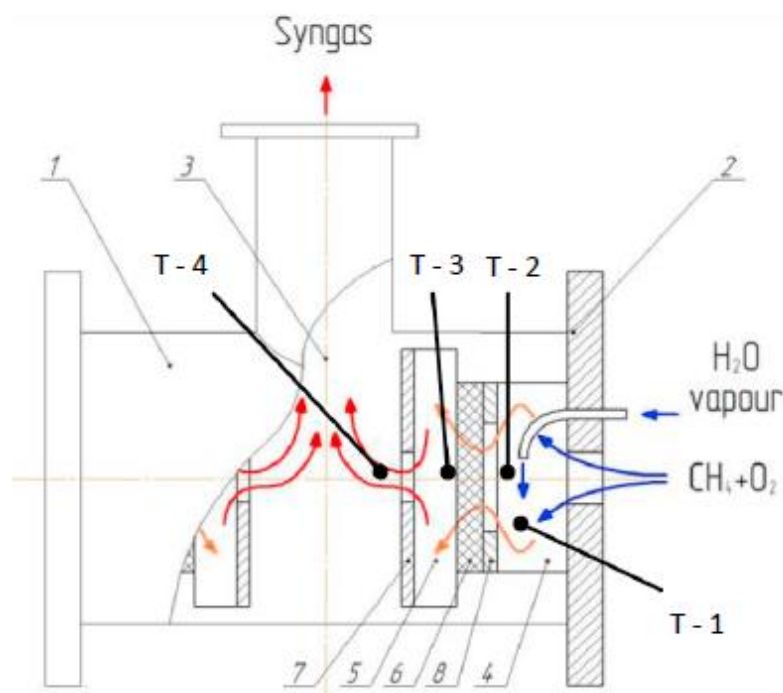
Figure 7. The principle of operation of the converter with a permeable matrix: 1—core vessel; 2—flange; 3—discharge nozzle; 4—mixing chamber; 5—combustion chamber; 6—matrix; 7—radiation screen; 8—inlet aperture [81] (reproduced with permission from [81], Elsevier, 2019).
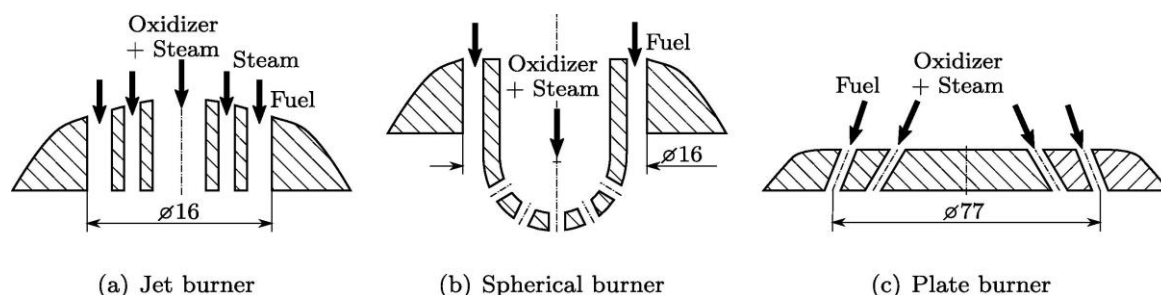

Figure 8. Burner designs used to optimize the HP POX process [82] (copyright with permission from [82], Elsevier, 2017).

The conversion of biogas to syngas makes it possible to obtain fuels with a higher energy density. Studies on the production of syngas from biogas were carried out in a reactor with an inert porous medium in the mode of filtration combustion with the addition of steam [83]. The reactor was operated on biogas, consisting of 60 vol.% natural gas and 40 vol.% CO_2 at a constant filtration rate of 34.4 cm/s with a stoichiometric excess of oxidizer equal to 2.0. The ratio of steam to carbon varied from 0.0 to 2.0, while the total volumetric steam flow remained constant at 7 L/min. The temperature and propagation velocity of the combustion wave, the gas composition of the resulting product, the composition of the reagents and the selectivity of the process with respect to H_2 and CO were measured depending on the vapor/carbon ratio. The optimal parameters for biogas conversion have been determined. It has been determined that the steam/carbon ratio of 2.0 leads to maximum concentrations of 9.98 vol.% CO and 10.34 vol.% H_2, and the highest efficiency of 64.2%. It is shown that an increase in the amount of steam supplied together with the reagents contributes to an increase in the conversion of biogas into syngas.

Since methane, which is contained in biomass gasification products, is difficult to use in further syntheses to obtain chemicals and fuels, it can be converted into gases suitable for further transformations, such as H_2 and CO. In [84], at atmospheric pressure, the non-

catalytic partial oxidation of CH_4 in gasification products, consisting mainly of steam and hydrogen, was studied. The experiments were carried out in reactors with a system of burners operating without preliminary mixing of gases. The results showed that the ratio of oxygen to fuel has a strong influence on the conversion of methane, while the influence of the pre-heating of gases and the presence of steam is negligible. The highest methane conversion (67%) was achieved with the highest O_2 to fuel ratio of 0.77. In the process of oxidation, with an increase in the ratio of oxygen to fuel, the amount of not only the formed hydrocarbons, but also hydrogen, decreased. However, in an environment with steam content of 60%, the level of CO content improved markedly. Thus, while the concentrations of methane and hydrogen decreased by 23% and 10%, respectively, the concentration of CO increased by 39% relative to the incoming syngas (at an O_2 to fuel ratio of 0.24). To achieve complete conversion of hydrocarbons, the authors proposed to combine partial oxidation and catalytic reforming. In this case, the oxidation will provide the heat needed to carry out the catalytic reforming.

In [85], the possibility of efficient matrix conversion of biogas with a high content of CO_2 into syngas is shown. In [86], the possibility of creating cost-effective low-tonnage plants for the production of GTL products based on the matrix conversion of biogas with atmospheric air and the subsequent catalytic synthesis of hydrocarbons and liquid fuel from syngas ballasted with carbon dioxide and nitrogen in a series of sequential reactors is considered.

4. Possibilities of Obtaining Other Chemical Products by Hydrocarbon POX

In the processes of non-catalytic partial oxidation, by controlling the selectivity of the process, in addition to syngas, other valuable products can be obtained. In [87], the gas-phase kinetics of oxidative transformations of methane into ethylene in a jet-stirred flow reactor was studied based on the construction of a 0D model of the reactor using nine gas-phase kinetic models. Various operating parameters of the oxidation process were investigated, including temperature, process time and CH_4/O_2 ratio. Simulation results using AramcoMech 3.0, CRECK, NUIGMech 1.1, GRI-Mech 3.0, Schwarz and USC Mech II gas phase models successfully described the experimental trends of the overall oxidation process. However, the results of calculations using the Sun, Karakaya and Quiceno models developed to describe catalytic processes did not agree with the experimental data obtained. This indicates that, under the conditions of heterogeneous processes, the gas-phase kinetics has a slightly different behavior. It is concluded that the NUIGMech 1.1 model is the best model for describing the gas-phase kinetics of oxidative methane conversion, including the formation of C_3 hydrocarbons.

Oxidative pyrolysis of methane-containing hydrocarbons is widely used in the chemical industry for the production of acetylene by partial oxidation of methane under conditions of oxygen deficiency [88]. The process temperature is 1200–1400 °C, the residence time of the components in the reaction zone is several milliseconds. An obligatory stage of the process is product fixation, which consists in rapid cooling to a temperature below 300 °C by introducing a cooling medium, water or oil, into the flow. This is necessary to prevent the decomposition of acetylene into carbon and hydrogen. A common disadvantage of technologies based on this process is the low yield of acetylene, as well as soot formation. The temperature of the gas mixture as a result of quenching in water during the partial oxidation of natural gas to acetylene drops sharply to 90 °C, which excludes the possibility of heat recovery. An analysis of the process of partial oxidation of methane to produce acetylene and syngas showed that the reactions of exothermic oxidation and endothermic pyrolysis are closely related, which limits the yield of acetylene [89].

The processes of partial oxidation and oxidative cracking of light alkanes and the prospects for the development of new methods for the production of light olefins on their basis have been considered in [90–92]. The possibility of a good qualitative and even quantitative description of the kinetics of partial oxidation of light alkanes in laboratory-scale reactors based on modern detailed kinetic mechanisms, taking into account heterogeneous

processes on the reactor surface, is shown. The possibility of obtaining a significant yield of ethylene and propylene in these processes is shown.

5. Conclusions

The main industrial process for obtaining syngas and hydrogen, which are widely demanded on the market, despite its technological complexity and high energy and capital intensity, is the conversion of carbon-containing gases. To overcome the shortcomings of traditional methods and increase their efficiency, it is necessary to create fundamentally new, more cost-effective technologies for the conversion of hydrocarbon gas feedstock into syngas and hydrogen. Great prospects are associated with the use of non-catalytic partial oxidation of hydrocarbon gases. POX has a number of significant advantages, such as technological flexibility, the absence of catalysts, the possibility of using hydrocarbon gases of almost any composition and origin and low capital and operating costs. These advantages make it possible to create simple low-tonnage processes for the processing of hydrocarbon gases directly at the places of their production, including in field conditions. POX-based technologies can reduce losses and environmental damage from burning of hydrocarbon gases and their release into the atmosphere.

The development and optimization of processes based on POX require a large amount of experimental and theoretical research with a wide range of temperatures and feedstock compositions. The experimental results presented in the review, reflecting the kinetics of the processes, in combination with the results of kinetic and gas-dynamic modeling of the processes, reveal the possibility of developing more efficient processes based on POX and optimizing their conditions.

Author Contributions: Conceptualization, I.A.M. and V.S.A.; methodology, I.V.S.; formal analysis, I.A.M.; resources, E.A.S.; data curation, I.A.M.; writing—original draft preparation, I.V.S.; writing—review and editing, E.A.S. and V.S.A. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Global Syngas Market (2022 to 2028). Size, Forecast, Insights and Competitive Landscape Dehaze. Research and Markets. 2022. Available online: https://www.globenewswire.com/en/news-release/2022/02/25/2392165/28124/en/Global-Syngas-Market-2022-to-2028-Size-Forecast-Insights-and-Competitive-Landscape.html (accessed on 17 November 2022).
2. Rouwenhorst, K.H.R.; Travis, A.S.; Lefferts, L. 1921–2021: A Century of renewable ammonia synthesis. *Sustain. Chem.* **2022**, *3*, 149–171. [CrossRef]
3. Power Technology Research. Global Hydrogen Review 2022. International Energy Agency (IEA). 2022. Available online: https://powertechresearch.com/global-hydrogen-review-2022/ (accessed on 19 January 2023).
4. Hydrogen Demand is Growing, with Positive Signals in Key Applications. Executive Summary. Available online: https://www.iea.org/reports/global-hydrogen-review-2022/executive-summary (accessed on 19 January 2023).
5. Hydrogen Council. Available online: https://hydrogencouncil.com/en/ (accessed on 12 October 2022).
6. Makaryan, I.A.; Sedov, I.V. The state and development prospects of the global Hydrogen energy sector. *Russ. J. Gen. Chem.* **2021**, *91*, 1912–1928. [CrossRef]
7. Hydrogen Scaling, Up. A Sustainable Pathway for the Global Energy Transition. Hydrogen Council. 2017. Available online: https://hydrogencouncil.com/wp-content/uploads/2017/11/Hydrogen-Scaling-up_Hydrogen-Council_2017.compressed.pdf (accessed on 11 March 2023).
8. Arutyunov, V.S. On the sources of hydrogen for the global replacement of hydrocarbons. *Acad. Lett.* **2021**, 3692. [CrossRef]
9. Arutyunov, V.S. Hydrogen energy: Significance, sources, problems, and prospects (A review). *Pet. Chem.* **2022**, *62*, 583–593. [CrossRef]

10. Arutyunov, V.; Belyaev, A.; Arutyunov, A.; Troshin, K.; Nikitin, A. Autoignition of methane–hydrogen mixtures below 1000 K. *Processes* **2022**, *10*, 2177. [CrossRef]

11. Makaryan, I.A.; Sedov, I.V.; Salgansky, E.A.; Arutyunov, A.V.; Arutyunov, V.S. A Comprehensive review on the prospects of using hydrogen–methane blends: Challenges and opportunities. *Energies* **2022**, *15*, 2265. [CrossRef]

12. Preuster, P.; Papp, C.; Wasserscheid, P. Liquid organic hydrogen carriers (LOHCs): Toward a hydrogen-free hydrogen economy. *Acc. Chem. Res.* **2017**, *50*, 74–85. [CrossRef]

13. Makaryan, I.A.; Sedov, I.V.; Maksimov, A.L. Hydrogen storage using liquid organic carriers. *Russ. J. Appl. Chem.* **2020**, *93*, 1815. [CrossRef]

14. Ghoneim, S.A.; El-Salamony, R.A.; El-Temtamy, S.A. Review on innovative catalytic reforming of natural gas to syngas. *World J. Eng. Technol.* **2016**, *4*, 116–139. [CrossRef]

15. Arutyunov, V.S.; Savchenko, V.I.; Sedov, I.V.; Fokin, I.G.; Nikitin, A.V.; Strekova, L.N. New concept for small-scale GTL. *Chem. Eng. J.* **2015**, *282*, 206–212. [CrossRef]

16. Albrecht, B. Reactor Modeling and Process Analysis for Partial Oxidation of Natural Gas. Ph.D. Thesis, Bogdan Albrecht, Enschede, The Netherlands. 2004. Available online: https://ris.utwente.nl/ws/portalfiles/portal/6119955/thesis_Albrecht.pdf (accessed on 20 December 2022).

17. SynCOR™—Autothermal Reformer (ATR). Available online: https://www.topsoe.com/our-resources/knowledge/our-products/equipment/syncortm-autothermal-reformer-atr (accessed on 27 November 2022).

18. Sharma, S.; Ghoshal, S.K. Hydrogen the future transportation fuel: From production to applications. *Renew. Sust. Energ. Rev.* **2015**, *43*, 1151–1158. [CrossRef]

19. Rui, Y.; Zhu, B.; Tang, Q.; Yang, C.; Wang, D.; Pu, W.; Tang., X. Experimental study of the feasibility of in-situ hydrogen generation from gas reservoir. *Energies* **2022**, *15*, 8185. [CrossRef]

20. Al-Mufachi, N.A.; Rees, N.V.; Steinberger-Wilkens, R. Hydrogen selective membranes: A review of palladium-based dense metal membranes. *Renew. Sust. Energ. Rev.* **2015**, *47*, 540–551. [CrossRef]

21. Ma, R.; Xu, B.; Zhang, X. Catalytic partial oxidation (CPOX) of natural gas and renewable hydrocarbons/oxygenated hydrocarbons—A review. *Catal. Today* **2019**, *338*, 18–30. [CrossRef]

22. Wright, H.A.; Allison, J.D.; Jack, D.S.; Lewis, G.H.; Landis, S.R. ConocoPhillips GTL technology: The COPox™ process as the syngas generator. In Proceedings Published 2003 by the American Chemical Society. *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* **2003**, *48*, 791–792.

23. Reimert, R.; Marschner, F.; Renner, H.-J.; Boll, W.; Supp, E.; Brejc, M.; Liebner, W.; Schaub, G. Gas Production, 2. Processes. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley Online Library: Hoboken, NJ, USA, 2011. [CrossRef]

24. SGP (Shell Gasification Process). Available online: https://decarbonisationtechnology.com/videos/9/shell-gasification-process#.Y5DTME1UCM8 (accessed on 23 June 2022).

25. Speight, J.G. Hydrocarbons from syngas. Texaco gasification process. In *Handbook of Industrial Hydrocarbon Processes*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2020. Available online: https://www.sciencedirect.com/topics/engineering/partial-oxidation-gasification (accessed on 4 April 2022).

26. Equipment EVT—Pilot Plants—Bergakademie Freiberg. Available online: https://tu-freiberg.de/en/iec/evt/groups/equipment/pilot-plants (accessed on 12 October 2022).

27. Air Liquide. GAS POX. Available online: https://www.engineering-airliquide.com/ru/gas-pox-chastichnoe-okislenie-prirodnogo-gaza (accessed on 11 November 2022).

28. Speight, J.G. Syngas and the Fischer–Tropsch Process. In *The Refinery of the Future*, 2nd ed.; Chapter 12; Elsevier: Amsterdam, The Netherlands, 2020; pp. 427–468. [CrossRef]

29. Kalamaras, C.M.; Efstathiou, A.M. Hydrogen production technologies: Current state and future developments. *Conf. Pap. Sci.* **2013**, *2013*, 690627. [CrossRef]

30. Saeidi, S.; Fazollah, F.; Najari, S.; Iranshahi, D.; Baxter, L.L. Hydrogen production: Perspectives, separation with special emphasis on kinetics of WGS reaction: A state-of-the-art review. *J. Ind. Eng. Chem.* **2017**, *59*, 11. [CrossRef]

31. Nikolaidis, P.; Poullikkas, A. A comparative overview of hydrogen production processes. *Renew. Sust. Energ. Rev.* **2017**, *67*, 597–611. [CrossRef]

32. Makaryan, I.A.; Sedov, I.V. Cost-Effectiveness Assessment of the scale of hydrogen production by various methods. *Russ. J. Gen. Chem.* **2021**, *91*, 2743–2757. [CrossRef]

33. Carbon Capture Projects See Meteoric Growth in 2022. 2022. Available online: https://e360.yale.edu/digest/carbon-capture-storage-ccs-growth (accessed on 19 November 2022).

34. IEAGHG. Techno-Economic Evaluation of SMR Based Standalone (Merchant) Plant with CCS. 2017. Available online: https://ieaghg.org/exco_docs/2017-02.pdf (accessed on 19 November 2022).

35. The Shell Blue Hydrogen Process. Available online: https://www.shell.com/business-customers/catalysts-technologies/licensed-technologies/refinery-technology/shell-blue-hydrogen-process.html (accessed on 12 December 2022).

36. Benson, J.; Celin, A. Recovering Hydrogen—And Profits—From Hydrogen-Rich Offgas. CEP. 2018, p. 55. Available online: http:www.aiche.org/cep (accessed on 12 February 2021).

37. Zhu, J.N.; Zhang, D.K.; Bromly, J.H.; Barnes, F.; King, K.D. Characteristics of methane partial oxidation at intermediate temperatures between 800 and 1100 K. In Proceedings of the Third Asia-Pacific Conference on Combustion, Seoul, Republic of Korea, 24–27 June 2001; pp. 481–484.

38. Zhu, J.N.; Zhang, D.K.; King, K.D. Reforming of CH4 by partial oxidation: Thermodynamic and kinetic analyses. *Fuel* **2001**, *80*, 899–905. [CrossRef]

39. Beretta, A.; Groppi, G.; Lualdi, M.; Tavazzi, I.; Forzatti, P. Experimental and modeling analysis of methane partial oxidation: Transient and steady-state behavior of Rh-coated honeycomb monoliths. *Ind. Eng. Chem. Res.* **2009**, *48*, 3825–3836. [CrossRef]

40. Arutyunov, V.; Savchenko, V.; Sedov, I.; Nikitin, A. Non-catalytic gas phase oxidation of hydrocarbons. *Eurasian Chem. Technol. J.* **2022**, *24*, 13–20. [CrossRef]

41. Arutyunov, V.S.; Strekova, L.N. The interplay of catalytic and gas-phase stages at oxidative conversion of methane: A review. *J. Molec. Catal. A Chem.* **2017**, *426*, 326–342. [CrossRef]

42. Savchenko, V.I.; Zimin, Y.S.; Busillo, E.; Nikitin, A.V.; Sedov, I.V.; Arutyunov, V.S. Equilibrium composition of products formed by non-catalytic conversion of hydrocarbons. *Pet. Chem.* **2022**, *62*, 515. [CrossRef]

43. Salgansky, E.A.; Tsvetkov, M.V.; Zaichenko, A.Y.; Podlesniy, D.N.; Sedov, I.V. Thermodynamic evaluation of noncatalytic conversion of natural gas with the production of syngas. *Russ. J. Phys. Chem. B* **2021**, *15*, 969. [CrossRef]

44. Zhu, J.; Zhang, D.; Bromly, J. A study of CH4 partial oxidation reforming with detailed mechanisms. *J. Therm. Sci.* **2000**, *9*, 176. [CrossRef]

45. Han, S.; Park, J.; Song, S.; Chun, K.M. Experimental and numerical study of detailed reaction mechanism optimization for syngas (H-2 + CO) production by non-catalytic partial oxidation of methane in a flow reactor. *Int. J. Hydrogen Energy* **2010**, *35*, 8762–8771. [CrossRef]

46. Konnov, A.A.; Zhu, J.N.; Bromly, J.H.; Zhang, D. Non-catalytic partial oxidation of methane into syngas over a wide temperature range. *Combust. Sci. Technol.* **2004**, *176*, 1093–1116. [CrossRef]

47. Zhou, X.; Chen, C.; Wang, F. Modeling of non-catalytic partial oxidation of natural gas under conditions found in industrial reformers. *Chem. Eng. Process. Process Intensif.* **2010**, *49*, 59–64. [CrossRef]

48. Savchenko, V.I.; Nikitin, A.V.; Sedov, I.V.; Ozerskii, A.A.; Arutyunov, V.S. The role of homogeneous steam reforming of acetylene in the partial oxidation of methane to syngas in matrix type converters. *Chem. Eng. Sci.* **2019**, *207*, 744–751. [CrossRef]

49. Savchenko, V.I.; Nikitin, A.V.; Zimin, Y.S.; Ozerskii, A.V.; Sedov, I.V.; Arutyunov, V.S. Impact of post-flame processes on the hydrogen yield in matrix partial oxidation reformer. *Chem. Eng. Res. Des.* **2021**, *175*, 250–258. [CrossRef]

50. Buzillo, E.; Savchenko, V.I.; Arutyunov, V.S. On the Mechanism of Methane Conversion in the Noncatalytic Processes of Its Thermal Pyrolysis and Steam and Carbon Dioxide Reforming. *Pet. Chem.* **2021**, *61*, 1228–1233. [CrossRef]

51. Wang, F.; Zhou, X.; Guo, W.; Dai, Z.; Gong, X.; Liu, H.; Yu, G.; Yu, Z. Process analysis of syngas production by non-catalytic POX of oven gas. *Front. Energy Power Eng. China* **2009**, *3*, 117–122. [CrossRef]

52. Bilera, I.V.; Buravtsev, N.N.; Rossikhin, I.V. Effect of hydrogen addition on noncatalytic partial oxidation of natural gas with oxygen in a flow reactor with increased calorific intensity. *Russ. J. Appl. Chem.* **2020**, *93*, 456–465. [CrossRef]

53. Dagde, K.; Akpa, J.G. Computer-aided design of a non-isothermal plug flow reactor for non-catalytic partial oxidation of methane to syngas. *Chem. Process Eng. Res.* **2014**, *28*, 9.

54. Shi, J.; Mao, M.; Li, H.; Liu, Y. Influence of chemical kinetics on predictions of performance of syngas production from fuel-rich combustion of CO_2/CH_4 mixture in a two-layer burner. *Front. Chem.* **2020**, *7*, 902. [CrossRef]

55. Xu, Y.; Dai, Z.; Li, C.; Li, X.; Zhou, Z.; Yu, G.; Wang, F. Numerical simulation of natural gas non-catalytic partial oxidation reformer. *Int. J. Hydrogen Energy* **2014**, *39*, 9149–9157. [CrossRef]

56. Rehm, M.; Seifert, P.; Meyer, B. Theoretical and numerical investigation on the EDC-model for turbulence-chemistry interaction at gasification conditions. *Comp. Chem. Eng.* **2009**, *33*, 402–407. [CrossRef]

57. Guo, W.; Wu, Y.; Dong, L.; Chen, C.; Wang, F. Simulation of non-catalytic partial oxidation and scale-up of natural gas reformer. *Fuel Proc. Technol.* **2012**, *98*, 45–50. [CrossRef]

58. Walter, S. *The HP POX Pilot Plant—A Door Opener to a New Era of Natural Gas Valorization*; IEC Gasification Conference Publication: Frankfurt am Main, Germany; Lurgi Company: Frankfurt am Main, Germany, 2005; Available online: http://tu-freiberg.de/sites/default/files/media/professur-fuer-energieverfahrenstechnik-und-thermische-rueckstandsbehandlung-16460/publikationen/2005_walter.pdf (accessed on 18 October 2022).

59. Richter, A.; Seifert, P.; Compart, F.; Tischer, P.; Meyer, B. A large-scale benchmark for the CFD modeling of non-catalytic reforming of natural gas based on the Freiberg test plant HP POX. *Fuel* **2015**, *152*, 110–121. [CrossRef]

60. Voloshchuk, Y.; Vascellari, M.; Hasse, C.; Meyer, B.; Richter, A. Numerical study of natural gas reforming by non-catalytic partial oxidation based on the VIRTUHCON Benchmark. *Chem. Eng. J.* **2017**, *327*, 307–319. [CrossRef]

61. Voloshchuk, Y.; Richter, A. Reduced order modeling and large-scale validation for non-catalytic partial oxidation of natural gas. *Chem. Eng. Sci.* **2022**, *255*, 117620. [CrossRef]

62. Jeon, S.; Kwon, M.; Kim, Y. Multi-environment PDF modeling for non-catalytic partial oxidation process under MILD oxy-combustion condition. *Int. J. Hydrogen Energy* **2018**, *43*, 5486–5500. [CrossRef]

63. Haworth, D.C. Progress in probability density function methods for turbulent reacting flows. *Prog. Energy Combust. Sci.* **2010**, *36*, 168–259. [CrossRef]

64. Jaehyeon, K.; Namsu, K.; Yongmo, K. Multi-environment PDF modeling for turbulent piloted premixed jet flames. *Proc. Combust. Inst.* **2019**, *37*, 2573–2581. [CrossRef]

65. Caballero, J.J.B.; Zaini, I.N.; Yang, W. Reforming processes for syngas production: A mini-review on the current status, challenges, and prospects for biomass conversion to fuels. *Appl. Energy Combust. Sci.* **2022**, *10*, 100064. [CrossRef]

66. Salgansky, E.A.; Tsvetkov, M.V.; Tsvetkova, Y.Y.; Zaichenko, A.Y.; Podlesniy, D.N.; Sedov, I.V. Thermodynamic evaluation of biogas conversion with the production of hydrogen and syngas. *Russ. J. Phys. Chem. B* **2022**, *16*, 1085–1091. [CrossRef]

67. Lugvishchuk, D.S.; Kulchakovsky, P.I.; Mitberg, E.B.; Mordkovich, V.Z. Soot formation in the methane partial oxidation process under conditions of partial saturation with water vapor. *Pet. Chem.* **2018**, *58*, 427–433. [CrossRef]

68. Tindall, B.M.; Crews, M.A. Alternative technologies to steam-methane reforming. *Hydrocarb. Process.* **1995**, *74*, 75–82.

69. Liu, K.; Deluga, G.D.; Bitsch-Larsen, A.; Schmidt, L.D.; Zhang, L. Catalytic partial oxidation and autothermal reforming. In *Hydrogen and Syngas Production and Purification Technologies*; Liu, K., Song, C., Subramani, V., Eds.; Wiley: New York, NY, USA, 2010; pp. 127–155.

70. Oortwijn, P.; Wentinck, H.M.; Martens, F.J.A. A Process for Preparing. Syngas. Patent WO 97/22547, 26 June 1997.

71. Li, C.; Burke, N.; Gerdes, K.; Patel, J. The undiluted, non-catalytic partial oxidation of methane in a flow tube reactor—An experimental study using indirect induction heating. *Fuel* **2013**, *109*, 409–416. [CrossRef]

72. Li, C.; Kuan, B.; Lee, W.J.; Burke, N.; Patel, J. The non-catalytic partial oxidation of methane in a flow tube reactor using indirect induction heating—An experimental and kinetic modelling study. *Chem. Eng. Sci.* **2018**, *187*, 189–199. [CrossRef]

73. Rasmussen, C.L.; Jakobsen, J.G.; Glarborg, P. Experimental measurements and kinetic modeling of CH_4/O_2 and $CH_4/C2H_6/O_2$ conversion at high pressure. *Int. J. Chem. Kinet.* **2008**, *40*, 778–807. [CrossRef]

74. Buravtsev, N.N.; Kolbanovskii, Y.A.; Rossikhina, I.V.; Bilera, I.V. Effect of the calorific intensity of combustion chamber on production of syngas in partial oxidation of methane–oxygen mixtures in the combustion mode. *Russ. J. Appl. Chem.* **2018**, *91*, 1588–1596. [CrossRef]

75. Dorofeenko, S.O.; Polianczyk, E.V. Conversion of hydrocarbon gases to syngas in a reversed-flow filtration combustion reactor. *Chem. Eng. J.* **2016**, *292*, 183–189. [CrossRef]

76. Toledo, M.; Ripoll, N.; Cespedes, J.; Zbogar-Rasic, A.; Fedorova, N.; Jovicic, V.; Delgado, A. Syngas production from waste tires using a hybrid filtration reactor under different gasifier agents. *Int. J. Hydrogen Energy* **2018**, *172*, 381–390. [CrossRef]

77. Polianczyk, E.V.; Dorofeenko, S.O. Conversion of hydrocarbons to syngas in a counterflow moving bed filtration combustion reactor. *Int. J. Hydrogen Energy* **2019**, *44*, 4079–4089. [CrossRef]

78. Dorofeenko, S.O.; Polianczyk, E.V. Enhancing efficiency of hydrocarbons to syngas conversion in a counter flow moving bed filtration combustion reactor. *Int. J. Hydrogen Energy* **2019**, *44*, 30039–30052. [CrossRef]

79. Al-Hamamre, Z.; Voß, S.; Trimis, D. Hydrogen production by thermal partial oxidation of hydrocarbon fuels in porous media based reforme. *Int. J. Hydrogen Energy* **2008**, *34*, 827–832. [CrossRef]

80. Dai, H.; Zhu, H.; Dai, H.; Song, Z.; Wang, Z.; He, S.; Wang, X. Syngas production by methane-rich combustion in a divergent burner of porous media. *Int. J. Hydrogen Energy* **2021**, *46*, 23279–23291. [CrossRef]

81. Nikitin, A.; Ozersky, A.; Savchenko, V.; Sedov, I.; Shmelev, V.; Arutyunov, V. Matrix conversion of natural gas to syngas: The main parameters of the process and possible applications. *Chem. Eng. J.* **2019**, *377*, 120883. [CrossRef]

82. Förster, T.; Voloshchuk, Y.; Richter, A.; Meyer, B. 3D numerical study of the performance of different burner concepts for the high-pressure non-catalytic natural gas reforming based on the Freiberg semi-industrial test facility HP POX. *Fuel* **2017**, *203*, 954–963. [CrossRef]

83. Espinoza, L.; Guerrero, F.; Ripoll, N.; Toledo, M.; Guerrero, L.; Carvajal, A.; Barahona, A. Syngas production by non-catalytic reforming of biogas with steam addition under filtration combustion mode. *Int. J. Hydrogen Energy* **2018**, *43*, 15693–15702. [CrossRef]

84. Kertthong, T.; Schmid, M.; Scheffknecht, G. Non-catalytic partial oxidation of methane in biomass-derived syngas with high steam and hydrogen content optimal for subsequent synthesis process. *J. Energy Inst.* **2022**, *105*, 251–261. [CrossRef]

85. Shapovalova, O.V.; Chun, Y.N.; Lim, S.M.; Arutyunov, V.S.; Shmelev, V.M. Syngas and hydrogen production from biogas in volumetric (3D) matrix reformers. *Int. J. Hydrogen Energy* **2012**, *37*, 14040–14046. [CrossRef]

86. Arutyunov, V.; Nikitin, A.; Strekova, L.; Savchenko, V.; Sedov, I. Utilization of renewable sources of biogas for small-scale production of liquid fuels. *Catal. Today* **2021**, *379*, 23–27. [CrossRef]

87. Wang, H.; Shao, C.; Gascon, J.; Takanabe, K.; Sarathy, S.M. Noncatalytic oxidative coupling of methane (OCM): Gas-phase reactions in a jet stirred reactor (JSR). *ACS Omega* **2021**, *6*, 33757. [CrossRef]

88. Pässler, P.; Hefner, W.; Buckl, K.; Meinass, H.; Meiswinkel, A.; Wernicke, H.; Ebersberg, G.; Müller, R.; Bässler, J.; Behringer, H.; et al. Acetylene. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2008; pp. 11–12.

89. Zhang, Q.; Wang, J.; Wang, T. Enhancing the acetylene yield from methane by decoupling oxidation and pyrolysis reactions: A comparison with the partial oxidation process. *Ind. Eng. Chem. Res.* **2016**, *55*, 8383. [CrossRef]

90. Bryukov, M.G.; Palankoeva, A.S.; Belyaev, A.A.; Arutyunov, V.S. Partial oxidation of ethane in the temperature range 773–1023 K. *Kinet. Catal.* **2021**, *62*, 703–711. [CrossRef]

91. Palankoeva, A.S.; Belyaev, A.A.; Arutyunov, V.S. Oxidative cracking of propane in a plug-flow laboratory reactor. *Russ. J. Phys. Chem. B* **2022**, *16*, 399–406. [CrossRef]
92. Bryukov, M.G.; Belyaev, A.A.; Zakharov, A.A.; Arutyunov, V.S. Oxidation of rich propane mixtures in a temperature range of 773–1023 K at pressures of 1–3 atm. *Kinet. Catal.* **2022**, *63*, 653–659. [CrossRef]