



Category: Chemistry

Type of Paper: Original Research Article

Received: November 22, 2025, **Accepted:** April 15, 2026, **Published:** April 23, 2026

DOI: [10.54503/0321-1339-2026.126.1-10](https://doi.org/10.54503/0321-1339-2026.126.1-10)

Features of non-catalytic conversion of light alkanes

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Running title: Features of non-catalytic conversion

Abstract

The kinetics of non-catalytic gas-phase pyrolysis and oxidative conversion of light hydrocarbons in the temperature range of 1400-1800 K. has been analyzed. Their fundamental difference from the kinetics of the corresponding catalytic processes has been established. Unlike catalytic processes, at these temperatures the oxidative conversion of C₂+ hydrocarbons does not begin with the oxidative stages, but with their pyrolysis, which proceeds much faster than oxidation; and in the specified temperature range C₂+ hydrocarbons transform faster than oxygen. The thermal stage of conversion of C₂+ alkanes leads to the formation of ethylene, and then the oxidation process proceeds almost identically for all these hydrocarbons. Therefore, the additives of all C₂+ alkanes have the same effect on the oxidation and ignition of methane and, consequently, their impurities have the same effect on the knock characteristics of methane. Unlike its homologues, the oxidation of methane proceeds much more slowly and directly when interacting with oxygen, so the conversion of methane and oxygen proceeds similarly. When there is a lack of oxygen, after oxygen conversion is completed, thermal methane pyrolysis occurs at the reached temperature, mainly into acetylene. The subsequent conversion of latter into hydrogen and CO occurs as a result of its interaction with H₂O and CO₂ formed in the mixture.

Keywords: light hydrocarbons, alkanes, non-catalytic processes, thermal conversion, oxidative conversion, kinetic modeling

Introduction

The scale of modern energy and the low energy efficiency EROI (Energy Return On Invested) values of renewable energy sources (RES), usually not exceeding 3,¹ exclude the possibility of its transition to alternative energy sources. Therefore, fossil hydrocarbons remain the main source of energy for the foreseeable future. Contrary to the concerns that arose at the end of the last century, which initiated a series of studies commissioned by the Club of Rome,² it is now obvious that the lack of hydrocarbon resources does not threaten the global economy, but the majority of them are represented by unconventional natural gas resources, primarily shale gas and gas hydrates.¹ This makes

it inevitable that gaseous hydrocarbons and, above all, methane will be used more widely, not only for the production of energy, but also as a raw material for producing a wide range of petrochemicals.

Main components of natural and associated gases, which are the resource base of gas chemistry, are light alkanes, which, as a rule, have lower free energy than the target products of their chemical conversion. This is especially true for methane, the principal component of natural gases, which is the most thermodynamically stable hydrocarbon under normal conditions. Therefore, gas-chemical processes require high temperatures and consumes a lot of energy for their implementation, and even in the presence of catalysts, the role of gas-phase reactions in their course can be significant, and in some cases, predominant.

The most difficult and energy-consuming stage of most large-scale methane conversion processes is the initial stage, its activation, which requires breaking the very strong (104 kcal/mol) first C-H bond in this molecule. If we exclude the relatively low-tonnage processes of producing halides-containing, sulfur-containing and nitrogen-containing compounds, then the list of products that can be obtained directly from methane is small (Fig. 1). It is represented by two main groups. The first is products formed as intermediates in the nonequilibrium kinetic processes of methane oxidation and pyrolysis, such as oxygenates (methanol, formaldehyde, peroxides), ethane, ethylene, and aromatic compounds. Their maximum achievable yield is usually low, so it is difficult to count on the possibility of creating economically attractive technological processes based on them.

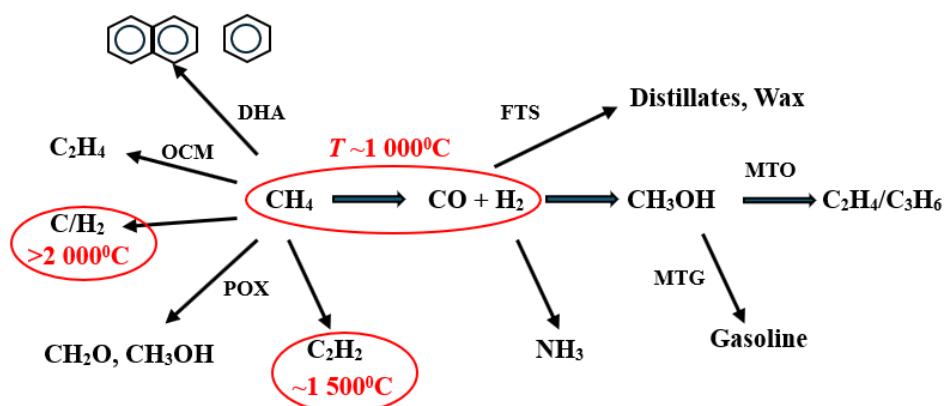


Figure 1. Possible products of methane conversion.

The second group consists of products into which methane can be converted under certain conditions with almost complete or sufficiently high selectivity. At temperatures above 2000 °C, the equilibrium products of methane pyrolysis are solid carbon and hydrogen. The process is considered as one of the possible industrial sources of hydrogen. However, high energy costs and the formation of a large volume of fine carbon, the real need for which is insignificant, raise doubts about its prospects.

At temperatures in the region of ~1500 °C, acetylene becomes one of the equilibrium products of methane pyrolysis. This is the basis of a number of industrial processes for producing this valuable product, but along with significant consumption of energy, the carbon yield of acetylene is relatively low, about 30%.

The most attractive product for gas chemistry, which can be obtained directly from methane, is syngas, into which methane can be converted almost entirely at a relatively moderate temperature of ~1000 °C. In addition to the high selectivity of formation and not very high production temperature, syngas is attractive as an intermediate product, on the basis of which there are already well-developed large-scale synthesis processes for the most large-scale chemical products: ammonia, hydrogen,

methanol, synthetic liquid hydrocarbons (synthetic oil). The last two processes open up a practical way to obtain all other petrochemicals from natural gas.

However, despite the formally existing possibility of using significantly cheaper and more affordable compared to oil natural gas resources for the production of petrochemicals, the contribution of gas chemistry to their production remains small. The reason is the high energy consumption and the great complexity of the existing technologies of the basic process of gas chemistry – the conversion of methane into syngas, associated with overcoming its thermodynamic stability. Currently, in the production from natural gas of such basic gas chemistry products as methanol and synthetic liquid hydrocarbons, this stage accounts for up to 60-70% of their cost.³

Thus, the prospects for expanding the contribution of gas chemistry to the production of petrochemicals depend on increasing energy efficiency and reducing the technological complexity of industrial processes for converting natural gas into syngas. The purpose of this paper is to analyze the features and prospects of alternative processes based on non-catalytic conversion of light hydrocarbons.

Matrix reforming as an example of non-catalytic conversion of light hydrocarbons

Gas-phase matrix reforming has been developed as one of the promising opportunities to increase energy efficiency and reduce the technological complexity of converting natural gas into syngas.^{4,5} In matrix reforming, the possibility of converting very rich mixtures of hydrocarbon gases with an oxidizer, necessary to obtain a high yield of syngas, is realized through internal heat recuperation from hot conversion products into a fresh gas mixture entering the conversion. Such preheating of the reagents makes it possible to significantly expand the limits of stable oxidation (combustion) of hydrocarbons and, consequently, to ensure a high yield of syngas.

In matrix reformers, such recuperation is realized by organizing flameless near-surface combustion of natural gas. The flame front is stabilized at a short distance from the surface of the matrix made of a heat-resistant material permeable to a gas mixture of hydrocarbons and oxidizer (Fig. 2). Such materials can be perforated ceramics, foam metals, metal felt or pressed metal wire. Heat recuperation occurs due to intensive convective and (in the presence of a screen or in a geometrically closed matrix) radiative heat exchange between the flame front and the solid matrix. As a result, the temperature of the outgoing conversion products is reduced by 400-500 °C, and the working surface of the matrix is heated to 900-1000 °C. Due to this, the fresh reaction mixture, passing through the matrix, heats up and enters the flame front already preheated.

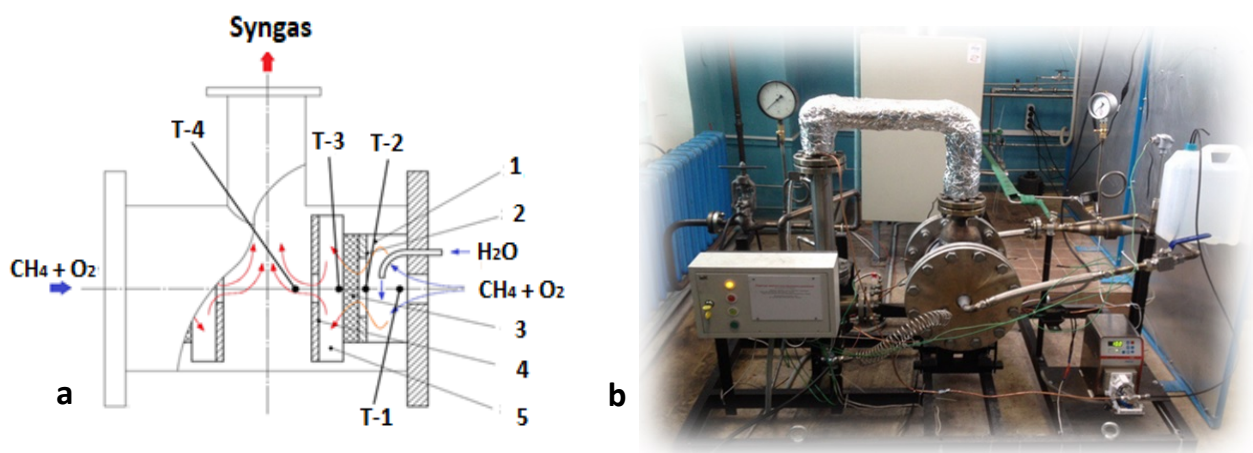
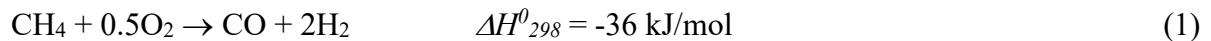


Figure 2. a) The scheme of matrix reformer: 1 – mixing chamber; 2 – inlet diaphragm; 3 – matrix; 4 – radiation screen; 5 – reaction volume; T-1 – T-4 – thermocouples. b) General view of the matrix reformer with an operating pressure of up to 10 atm and a gas flow up to 10 m³/h.

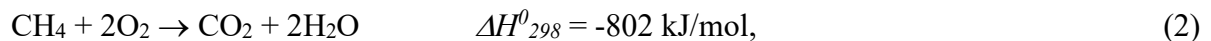


The most complete conversion of methane and the maximum yield of syngas components H_2 and CO are achieved at the values of the oxidant excess coefficient $\alpha = [O_2]/2[CH_4] = 0.34-0.36$, which are optimal for this process. At lower α values, the syngas yield decreases due to a decrease in methane conversion, and at higher values, due to an increase in the yield of products of complete oxidation. The H_2/CO ratio, which is very important for the subsequent use of syngas, does not strongly depend on the value of α and is in the range of 1.7-1.8. The reforming process, with the exception of the thermal regime of the matrix, is practically independent of the presence of nitrogen, the concentration of which in the oxidizer affects only the concentration of the components of the syngas produced, therefore atmospheric air, oxygen-enriched air and oxygen can be used as an oxidizer.^{4,5}

We briefly note the main advantages of matrix reforming of natural gas, which make it attractive for many technological applications. First of all, it is an autothermal process that does not require external heat or energy sources. The transformation of rich mixtures of hydrocarbon gas (methane) with an oxidizer occurs due to the fact that, in parallel with weakly exothermic reaction (1) of its partial oxidation into syngas



a small part of it undergoes complete oxidation by reaction (2):



thereby providing the necessary energy to maintain the autothermal process, ensuring maximum energy efficiency of hydrocarbon raw materials in this technological process.

The conversion takes place completely in the gas phase behind the surface of the matrix, which makes the process easily controllable and removes the problem of carbon formation, which is critical for catalytic processes of natural gas conversion.

The absence of a catalyst not only simplifies the process, but also significantly reduces the requirements for gas preparation and purification, making it insensitive to many impurities, which are catalytic poisons, and allowing the direct use of hydrocarbon gases of almost any composition, including associated and refinery gases.

Matrix conversion has a very high specific volumetric capacity, at least an order of magnitude higher than the specific capacity of catalytic steam reforming of methane, which makes it possible to reduce specific capital costs accordingly and create cost-effective low-tonnage installations based on it.

The use of atmospheric air, enriched air, or oxygen does not change the nature of the process, its kinetics, or the H_2/CO ratio, affecting only the content of ballast nitrogen in the resulting syngas. The possibility of using atmospheric air not only significantly reduces the cost of the technological process, but also makes it safe to use directly in places of production and processing of combustible hydrocarbons.

Efficient heat recuperation of products makes it possible to convert gases with a high content of inert components (N_2 , CO_2 , H_2O), including biogas, into syngas,⁶ which opens up the possibility of obtaining petrochemicals from renewable bioproducts or waste.

By subsequent catalytic steam reforming of part of the formed CO into hydrogen by the water gas shift reaction (WGSR) (3):



it is possible not only to regulate the ratio of H_2/CO in the resulting syngas in accordance with the requirements of subsequent processes of its use, but also to obtain hydrogen-containing gas with an H_2 concentration of up to 75%.⁷ Moreover, the process remains autothermal, even taking into account the heat consumption for steam generation in a volume sufficient to completely convert the resulting carbon monoxide into hydrogen. At the same time, in comparison with the production of hydrogen by

catalytic steam reforming of methane, the specific consumption of fuel gas is reduced by almost 4 times, the consumption of steam is almost 3 times, and the specific volumetric productivity is increased by an order of magnitude.

A combined process has been developed and patented that combines gas-phase matrix and subsequent catalytic steam reforming of methane and a portion of CO into syngas,⁸ which further allows the production of methanol and hydrogen with virtually zero CO₂ formation.^{7,9} The possibility of using enriched air with a given N₂/O₂ ratio in the matrix reformer makes it possible to obtain in one stage a hydrogen-nitrogen mixture for the synthesis of ammonia.

Features of kinetics of non-catalytic conversion of light hydrocarbons

The prospects of practical use of matrix reforming of natural gas and a number of other non-catalytic gas-phase processes based on pyrolysis and oxidative conversion of light hydrocarbons have stimulated interest in studying their kinetics in the region of relatively moderate temperatures of 1400-1800 K.¹⁰⁻¹² Kinetic analysis of non-catalytic processes of C₁-C₄ hydrocarbons conversion: their thermal pyrolysis, partial oxidation, steam and carbon dioxide reforming was carried out on the basis of the most detailed and reliable kinetic mechanism of light hydrocarbons oxidation NUI Galway (2010),¹³ and its results were qualitatively confirmed by experiments on matrix reforming of hydrocarbon gases.

As a result of kinetic modeling of these processes, it was found that at temperatures of 1400-1800 K under isothermal conditions, the processes of non-catalytic conversion of all C₂+ hydrocarbons begin with the stage of their thermal pyrolysis, which proceeds approximately the same way in the presence of various gases (Ar, N₂, O₂, H₂O, CO₂). This is a consequence of the fact that during the pyrolysis of C₂+ hydrocarbons, the breakaway of atom H[•] and the subsequent conversion of alkyl radical C_nH_{2n+1}[•] proceed at a higher rate than their reactions with other components of the reaction mixture, including with oxygen-containing compounds O₂, H₂O, CO₂. Figure 3 shows that the conversion of C₂-C₄ hydrocarbons proceeds much faster than the conversion of oxygen, and is completed long before its complete conversion.

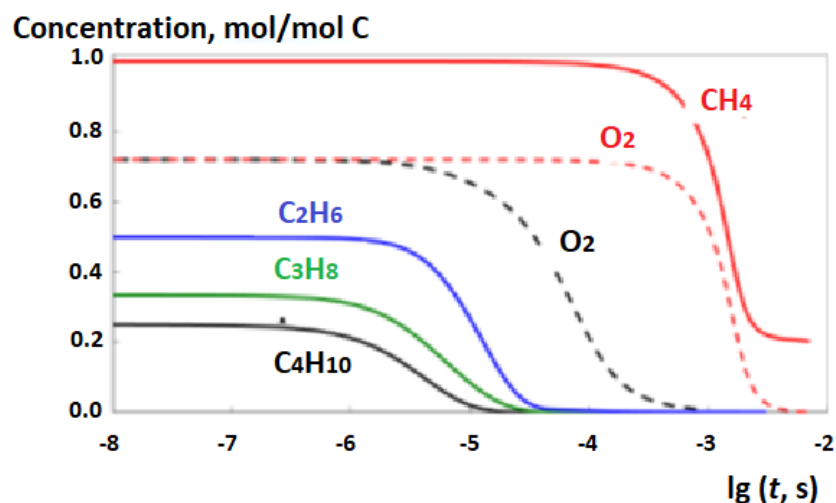


Figure 3. Kinetics of isothermal ($T = 1600$ K) non-catalytic partial (oxidant excess coefficient $\alpha = 0.36$) oxidation of C₁-C₄ hydrocarbons. The solid curves represent the conversion of the corresponding hydrocarbon, and the dotted curves represent the conversion of oxygen. For C₂-C₄ hydrocarbons, the oxygen conversion curves practically coincide.¹²

The Figure 4 is clearly demonstrating that the kinetics of butane conversion during its partial oxidation and thermal pyrolysis practically coincide, while the rate of oxygen conversion is significantly lower compared to the rate of butane conversion. Thus, under these conditions, oxygen

has practically no effect on the conversion of light alkanes, and the conversion of oxygen itself occurs as a result of its interaction with products of pyrolysis of C_2+ alkanes, mainly ethylene, which is a more stable hydrocarbon in this temperature range, along with acetylene.

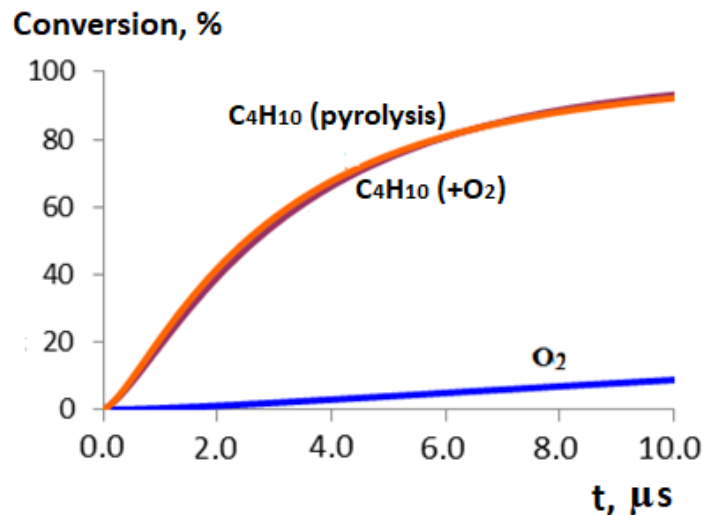
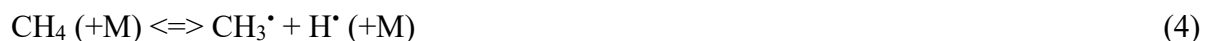


Figure 4. The conversion of reagents in a mixture of $0.25 C_4H_{10} + 0.72 O_2 + 1.0 Ar$ and at thermal pyrolysis of C_4H_{10} . $T = 1600 K$, $P = 1 atm$.

Ethylene formed at the initial stage of C_2+ alkane conversion (pyrolysis stage) in the chain of rapid reactions $C_nH_{2n+1} \cdot \rightarrow C_nH_{2n} \rightarrow C_2H_4$ is the main compound interacting with O_2 at the next oxidation stage. When there is a lack of oxygen, this leads mainly to the formation of CO and H_2O . Therefore, the rate of O_2 consumption during the partial non-catalytic oxidation of all light C_2+ hydrocarbons, including ethylene, is approximately the same. Partially, C_2H_4 is also consumed by the sequence of reactions $C_2H_4 \rightarrow C_2H_3 \cdot \rightarrow C_2H_2$, turning into the most stable hydrocarbon under these conditions, acetylene.

Unlike C_2+ alkanes, the conversion of methane in the presence of O_2 proceeds significantly faster than in its absence, since the reaction



is slower than the reactions of CH_4 with $O \cdot$ and $OH \cdot$ radicals. The presence of H_2O and CO_2 at $T < 1800 K$ has little effect on the rate of CH_4 conversion, since under these conditions its oxidative conversion is much faster. During the partial oxidation of methane, ethylene is also one of the compounds that interact with O_2 , but it is formed as a result of slower stages of pyrolysis of CH_4 : $CH_4 \rightarrow CH_3 \cdot \rightarrow C_2H_6 \rightarrow C_2H_5 \cdot \rightarrow C_2H_4 \rightarrow C_2H_3 \cdot \rightarrow C_2H_2$. Therefore, methane oxidation proceeds much slower than that of C_2+ alkanes, and similarly with oxygen conversion (Fig. 3).

After complete oxygen conversion, the gas mixture with $T = 1400-1800 K$ contains H_2 , CO , H_2O , CO_2 , minor amounts of C_2H_2 and unreacted CH_4 in a ratio far from equilibrium. Subsequent much slower conversion of C_2H_2 and CH_4 , in which the main oxidizing agents are H_2O and CO_2 , lead to the establishment of thermodynamic equilibrium between the components of the water gas shift reaction (WGSR): H_2 , CO , H_2O , CO_2 . Next, the system slowly approaches thermodynamic equilibrium. Under adiabatic conditions or at a given temperature profile, this sequence of stages is maintained.

In the case of an adiabatic process, at the initial stage of establishing thermodynamic equilibrium between the components of WGSR for mixtures of C_2+ hydrocarbons with a high concentration of H_2O , due to the exothermic reaction (3), proceeding at a higher rate than the endothermic conversion



of C_2H_2 and CH_4 , there is a region of temperature increase in the gas mixture outside the flame zone. Such an increase in temperature is not observed during partial oxidation of methane.

During non-catalytic steam or carbon dioxide reforming of methane in the temperature range of 1400-1800 K, unlike similar catalytic processes, its pyrolysis initially proceeds with the predominant formation of acetylene, which is practically not affected by the concentration of H_2O or CO_2 in the reaction mixture. And only then does the formed acetylene interact with these oxygen-containing components to form hydrogen and CO, i.e. syngas. In this case, the conversion of H_2O and CO_2 occurs mainly in reactions with radicals



The indicated sequence of processes occurring during the oxidative conversion of C_1-C_4 hydrocarbons made it possible to explain the reasons for the previously established identical effect of impurities of various C_2-C_6 alkanes on the ignition delay of methane in the temperature range $T < 900$ K,¹⁴ in which fuel mixtures ignite in gas piston engines.¹⁵ At these temperatures, the process of degenerate branched chain oxidation of methane begins, in which the leading role is played by CH_3OO^{\bullet} radicals formed in the equilibrium reaction



The subsequent formation of methyl hydroperoxide CH_3OOH in this process and its thermal decomposition provide a degenerate branching



This process develops relatively slowly, with a long induction period, but leads to a gradual increase in temperature, with an increase in which rapid pyrolysis of heavier methane homologues begins, leading to the formation of mainly ethylene. The subsequent rapid interaction of ethylene with oxygen leads to a sharp increase in the oxidation rate, a shortening of the induction period, and subsequent ignition of the entire mixture. Pyrolysis of C_2-C_6 alkanes into ethylene C_2H_4 before their interaction with oxygen explains their almost identical effect on the ignition of methane and, accordingly, the same effect of the admixtures of these alkanes on the knock resistance of gas-engine fuels.

For the C_2+ alkanes themselves, a similar mechanism of low-temperature branching through the corresponding RO_2^{\bullet} peroxide radicals is not realized due to the rapid isomerization of such alkyl peroxide radicals, followed by their decomposition into olefin Q^{\bullet} and the weakly reactive HO_2^{\bullet} radical



the formation of which at these relatively low temperatures is equivalent to chain termination.

Conclusions

The study of the kinetics of non-catalytic gas-phase processes of pyrolysis and oxidative conversion of light hydrocarbons has shown their fundamental difference from the kinetics of the corresponding catalytic processes. In addition, in the considered temperature range, until a sufficiently high concentration of radicals is formed as a result of reactions involving more reactive compounds (ethylene, acetylene) H_2O and CO_2 are not actually active reagents.

Unlike catalytic processes, the oxidative conversion of C_2+ hydrocarbons begins with their pyrolysis, rather than with oxidative stages. Pyrolysis at these temperatures proceeds much faster than oxidation, so they transform faster than oxygen. The thermal stage of the C_2+ alkane conversion leads



to the formation of ethylene, and therefore their further oxidation proceeds in almost the same way. As a result, the additives of all C_2+ alkanes have the same effect on the oxidation and ignition of methane and, consequently, its knock characteristics.

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Author's Contributions: V.S. Arutyunov: conceptualization, original draft preparation, revision and finalization for publication; V.I. Savchenko: conceptualization, methodology; A.V. Nikitin: experimental



studies; analysis and description of reaction routes; A.V. Ozerskii: kinetic simulation of gas-phase processes, interpretation and visualization of results; I.V. Sedov: analysis and interpretation of kinetic data, conclusions on common and distinct behavioral trends in non-catalytic conversion processes for hydrocarbons; L.N. Strekova: review of literature, graphical presentation.

Funding: This study was funded by the Russian Science Foundation (project no. 22-13-00324).

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

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