On methane pyrolysis special applications

D C Toncu¹, G Tonecu² and S Soleimani³
¹Kazakh-British Technical University, School of Chemical Engineering, 51 Tole-bi Street, 050000 Almaty, Kazakhstan
²Ovidius University Constanta, Faculty of Mechanical, Industrial, and Maritime Engineering, 124 Mamaia Blvd., 900527 Constanta, Romania
³Politecnico di Milano University, Department of Chemistry, Materials, and Chemical Engineering Giulio Natta, LaBS, 32 Piazza Leonardo da Vinci, Milano, Italia

E-mail: dctoncu@gmail.com

Abstract. Methane pyrolysis represents one of the most important processes in industrial use, with applications rising from the chemical and petrochemical industry, combustion, materials and protective coatings. Despite the intense research, experimental data lack kinetic aspects, and the thermodynamics involved often leads to inaccurate results when applied to various systems. Carrying out a comparative analysis of several available data on methane pyrolysis, the paper aims to study the phenomenon of methane pyrolysis under different environments (combustion and plasma), concluding on the most possible reaction pathways involved in many of its applications. Computer simulation using different database underlines the conclusion, helping to the understanding of methane pyrolysis importance in future technologies.

1. Introduction
The thermal decomposition of methane has formed the study object for decades, but the reaction mechanism is not completely known. Between the two suggested initial reactions in the homogeneous decomposition process, the methyl CH₃ is more probable than methylene CH₂ radical [1]:

CH₄→CH₃+H (1)

CH₄→CH₂+H₂ (2)

The methyl formation also represents the rate determining step of the methane dissociation. Though small amounts of C₂ hydrocarbons can be found in the equilibrium composition, practically only hydrogen, carbon, and methane are the relevant species up to 1700°C. Experiments also confirmed that hydrogen plays the key role as energy carrier, the C₂ hydrocarbon intermediates and byproducts may lose importance in alternate reaction mechanisms. The activation energy for thermal dissociation of methane was assigned values from 312 to 450 kJ/mol, but under catalyst presence, decreases at 89 … 236 kJ/mol [2].

The initial formation of the methyl radical leads to the uniform deposition on the walls of the reaction vessel, later aimed in special coating processes. The feeding methane is much more stable than methyl radical, and therefore it cannot efficiently decompose into the carbon deposit on the walls, which leads to the conclusion that the chemical specie methyl is predominantly responsible for the carbon deposits. The epitaxial growth process on metal surface results in a highly crystalline carbon form.
Further experiments carried out with various diluent gases, such as hydrogen and argon, revealed that methane reactivity is lower at 1100°C than at 1000°C, while there is deposition rate even at zero residence time, which underlined the ability to form pyrocarbon of C\textsubscript{1} species. Furthermore, the deposition rates increased exponentially with residence time, stronger than C\textsubscript{2}-hydrocarbons \[3\].

Even later studies showed that the overall reaction of methane decomposition involves high temperature dehydrogenation \[4\]:

\[
2\text{CH}_4 \rightarrow 2\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow 2\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow 2\text{C} + \text{H}_2
\] \hspace{1cm} (3)

The difference in experimentally determined activation energies for tubular flow reactors, shock tube reactors, and plasma reactors rises from the heat transfer inside them and the resulting difference in temperature between reaction bulk and reactor walls. The above-mentioned study also revealed that pyrolysis rate of methane on molybdenum carbides in much higher than on tungsten carbides, which leaded many scientists to use molybdenum substrates for carbon coatings. Methane was found more efficient than acetylene for diamond-like-carbon film growth \[4\].

In most cases, the overall methane decomposition is believed to be a first order reaction, with an order decrease in case of dilution hydrogen environment. The amount of energy required is 216 kJ/mol for CH\textsubscript{4} at 298 K and products at 2000 K \[5\]:

\[
\text{CH}_4 \rightarrow \text{C} + \text{H}_2 \text{ with } \Delta H^\circ \approx 75 \text{ kJ/mol} \] \hspace{1cm} (4)

The effect of dilution gas on methane pyrolysis has been intensively studied also, conclusions being made for different employed gas.

Despite the detrimental effect of hydrogen dilution on methane conversion and the competition between C\textsubscript{2} formation and carbon deposition, the coke formation decreased and even diamond synthesis was reached. Furthermore, the carbon deposit and the metal wall or substrate may act as catalyst \[6\]:

\[
\begin{align*}
2\text{CH}_4 &\leftrightarrow 2\text{CH}_3 + \text{H}_2 \\
2\text{CH}_3 + 2\text{s} &\leftrightarrow 2\text{CH}_3 \cdot \text{s} \\
\text{H}_2 + 2\text{s} &\leftrightarrow 2\text{H} \cdot \text{s} \\
2\text{CH}_3 \cdot \text{s} + 2\text{H} \cdot \text{s} &\rightarrow 2\text{C} + \text{H}_2 + 2\text{s}
\end{align*}
\] \hspace{1cm} (5-8)

During methane combustion, kinetics plays the same vital role. When comparing different mechanisms, it was found that it is feasible to use reduced schemes in engine simulation, though when elementary chemical reactions are based on Arrhenius law, there are discrepancies of temperature profiles between detailed and reduced mechanisms \[7\]. Kinetic mechanism for two methane combustion mechanisms are given in Table 1, while Arrhenius rate parameters are offered in table 2.

The rate coefficient is expressed as:

\[
k = A \cdot T^m \cdot e^{-E_a / RT} \] \hspace{1cm} (9)

The temperature is:

\[
T_a = E_a / R \] \hspace{1cm} (10)

Another important aspect concern the missing pollutant or byproduct gases that a first step mechanism cannot predict, since there are no pathways for such compounds.

Another source mentions, for the overall combustion reaction of methane, an Arrhenius coefficient of 8.3*10\textsuperscript{11} cm\textsuperscript{3}/mol s and an activation energy of 30000 cal/mol \[8\].

Detailed kinetics can be found also in \[9\], when laminar diffusion flames in vitiated environments are analysed.
Table 1. Kinetic parameters for various methane combustion mechanisms [7].

| Reaction Mechanism          | A            | m  | Ta   |
|-----------------------------|--------------|----|------|
| Global one-step mechanism   | 1.5·10^{13}  | 0  | 20000|
| Four-step mechanism         | 4.4·10^{14}  | 0  | 30000|
| CH₄+0.5O₂→CO+2H₂O           | 3·10^{11}    | 0  | 30000|
| H₂+0.5O₂→H₂O                | 2.5·10^{19}  | -1 | 40000|
| CO+H₂O→CO₂+H₂               | 2.75·10^{12} | 0  | 20000|

Table 2. Some Arrhenius rate parameters of some reactions involved in methane oxidation [9].

| Reaction          | Arrhenius pre-exponential factor, cal/cm³ | Temperature exponent | Activation energy, cal |
|-------------------|------------------------------------------|----------------------|------------------------|
| H₂→2H             | 7.15·10⁴                                 | -0.82                | 103328.3               |
| H₂O→H+OH          | 2.2·10¹³                                | 0                    | 105217.9               |
| CO+OH→CO₂+H       | 1.5·10⁸                                 | 0                    | 100.5                  |
| CO+O→CO₂          | 6.7·10⁷                                 | 0                    | 0                      |
| 2CH₄+O₂→2CO+4H₂   | 1.75·10⁷                                | 1                    | 24265                  |

Soot formation involves methane pyrolysis rather than oxidation reactions, especially for temperature interval of 1500 – 1800 K [10].

Some chemical kinetic databases contain information regarding the uncertainty of rate parameters, which form the main input of uncertainty analysis [11].

The present work aims to test various parameters of Arrhenius reaction rates corresponding to several possible pathways involved in methane pyrolysis, either in plasma deposition or soot formation during methane combustion, and their thermodynamic range interval in which such parameters show better match between experimental data and computer simulations. Whenever such parameters allow good correspondence between experiments and simulation, one can conclude that the involved pathways are the right ones involved in reaction mechanisms.

2. Computational simulation with different kinetic parameters

2.1. Methane pyrolysis with hydrogen carrier

The methane pyrolysis in hydrogen plasma was simulated for the geometry of a real chemical vapor deposition existent at IFP CNR Milano: a cylindrical stainless steel reactor with 0.3 m diameter and 0.3 m length. For simplification, only the volume regarding the deposition was simulated, meaning the symmetrical deposition substrate and the gas nozzle with 0.178 mm situated 2 mm above the substrate.

The chemical kinetics used in the simulation methodology was simplified as much as possible, in order to allow errors elimination and computational complications in the reaction mechanism. The four gas phase reactions and one surface reaction chosen as model, due to their importance in the process and high occurrence during various deposition techniques, were the ones identified during optical emission spectroscopy diagnosis of plasma gas used in experimental depositions of carbon materials, ranging from crystalline diamond to fullerene and graphite. Acetylene was excluded from the model, since if it resulted, the volume would increase with at least 50%. The kinetic parameters for this case are given in table 3.

Input data comprises methane concentration in hydrogen-methane mixture, velocity of the gas mixture, and, very important, the rate parameters.
Table 3. Kinetic parameters for methane pyrolysis with hydrogen carrier used for simulation.

| Reaction                  | Pre-exponential factor A | Temperature exponent m | Activation energy Ea J/mol |
|---------------------------|--------------------------|-------------------------|----------------------------|
| \( \text{H}_2 + \text{e} \rightarrow 2\text{H} + \text{e} \) | 1.2E16                   | 0                       | 943685.5                   |
| \( \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 \) | 2.2E4                    | 3                       | 36610                      |
| \( \text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + \text{H}_2 \) | 7.2E14                   | 0                       | 63178                      |
| \( \text{CH}_4 + \text{H} \rightarrow \text{CH} + \text{H}_2 \) | 4E13                     | 0                       | 0                          |
| \( \text{CH} + \text{H} \rightarrow \text{C(s)} + \text{H}_2 \) | 2.14 mole/cm\(^3\) s    | 0                       | 30515                      |

2.2. Methane combustion

For simplifications, eddy-dissipation model for methane gas combustion with ambient air was simulated in a 0.2 m diameter and 1.8 m length tubular reactor (or cylindrical combustor) using finite-rate chemistry. In order to allow comparison, methane flow rate, equivalence ratio, and flow regime were kept constant. The simulation methodology implies standard k-ε turbulence model and chemical species transport and reaction. The eddy-dissipation turbulence - chemistry computes the rate of reaction under the assumption that chemical kinetics are fast compared to the rate at which reactants are mixed by turbulent fluctuations. Reactions were volumetric, with diffusion energy source, and mixture material methane-air. Calculation was performed assuming that all properties except density are constant, an acceptable assumption for the case of fully turbulent flow, where molecular transport properties play a minor role. Boundary conditions imply velocity air inlet, velocity fuel inlet, and pressure outlet.

Starting with the global one-step reaction mechanism, and assuming complete conversion of the methane to carbon dioxide and water vapor, simulation used several reaction rates, from those existent in the software’s database to those found in the literature. The rate-limiting process was assumed to be the turbulent mixing.

The eddy-dissipation reaction model only uses the mixing rate parameters, so the Arrhenius rate are those included in the database, as the turbulent transport plays the major role. However, the rate parameters were changed accordingly, and different output resulted.

3. Results and discussions

3.1. Methane pyrolysis with hydrogen carrier

The kinetic parameters in the presence of major hydrogen gas completely changed the species involved as well as deposited carbon. Hydrogen does not only represent the energy carrier, but also changes the first order elementary reaction into a second order reaction, which involves hydrogen as collision partner.

Methane conversion increases with residence time that much that, by doubling the residence time from 0.027 s to 0.054 s, conversion shifts from about 1.3 % to 99 %. Methane conversion also increases with increasing temperature, due to increased decomposition and transformation through collisions.

Hydrogen yield increases with reactor temperature and residence time, depending also on methane concentration in the feed mixture and conversion. Obviously, hydrogen-consuming reactions are balanced by those generating it.

Surface chemistry is the most dependent on rate parameters, as the presence of carbonaceous material decreasing the activation energy up to about one fifth.

3.2. Methane combustion

Simulations showed that temperature profiles differences between mechanisms decrease with increasing temperature, and especially above 1500 K, and increase with increasing equivalence ratio.

For the same equivalence ratio, detailed mechanisms including more than 4 reaction steps, predict a much lower carbon monoxide emission than reduced to 4-step mechanisms, while the single step mechanism cannot estimate carbon monoxide due to the lack of such a pathway.

For major species carbon dioxide and water, there is a good agreement between mechanisms prediction.
Taking into account the above-mentioned observations, results are displayed for the single-step reaction mechanism in figures 1-3. The temperature, for the case of constant heat capacity, raised till 3078 K, when applied an initial temperature of 2000 K corresponding to the engine spark (figure 1). In figure 2, methane mass fraction is higher at the nozzle exit, then decreases as the gas dissipates and mixes with combustion air. Carbon dioxide mass fraction is presented in figure 3, the profile corresponding to the reaction consumption with the oxygen present in the combustion air.

![Figure 1. Temperature profile for the CH$_4$ one-step combustion.](image1)

![Figure 2. CH$_4$ mass fraction during one-step mechanism combustion.](image2)

![Figure 3. CO$_2$ mass fraction during one-step mechanism combustion.](image3)
4. Conclusions
Despite the high scientific and industrial interest in methane pyrolysis, the appropriate kinetic data for many processes still miss. Different rate parameters, experimentally determined in various conditions, such as pressure, gas carrier, and catalyst presence, lead to different estimation results and often mislead conclusions regarding complex phenomena.

In the case of methane pyrolysis for protective coatings, the whole process depends on the accuracy of rate parameters. Plasma environment, metals and their compounds from the reactor material or substrate, carbonaceous material, nature of carrier, all change the rate parameters, giving a completely different reaction mechanism according to real conditions.

In the case of methane combustion and soot formation, differences in kinetic database may reduce significantly, especially when estimating combustion temperature, resulting water and carbon dioxide. For pollutants, from carbon monoxide, nitrogen oxides, to unburnt hydrocarbons, intermediate species and their reaction parameters dramatically change the results. Adjusting the reaction mechanism to the real process becomes more important, and reduced models to one-step reactions often fail to accurately represent the process.

References
[1] Evans E L et al. 1973 Growth of filamentary carbon on metallic surfaces during the pyrolysis of methane and acetone Carbon 11 pp 441-445
[2] Wullenkord M 2011 Determination of Kinetic Parameters of the Thermal Dissociation of Methane PhD Thesis (German Aerospace Center in Cologne, Germany)
[3] Becker A and Hüttinger K J 1998 Chemistry and kinetics of chemical vapor deposition of pyrocarbon – IV Pyrocarbon deposition from methane in the low temperature regime Carbon 36 pp 213-224
[4] Choudhary T V, Aksoylu E and Goodman D W 2003 Nonoxidative Activation of Methane Cat. Rev. 45 pp 151-203
[5] Rodat S et al. 2009 Kinetic modelling of methane decomposition in a tubular solar reactor Chem. Eng. J. 146 pp 120-127
[6] Rhee B S, Rhee M Y and Hüttinger K J 2001 CVD-kinetik of pyrolytic carbon from methane on the stainless steel 316L at 600°C CARBON Conf. (Lexington KY USA)
[7] Ennetta R, Hamdi M and Said R 2008 Comparison of different kinetic mechanisms of methane combustion in an internal combustion engine configuration Therm. Sci. 12 pp 43-51
[8] Rouband A et al. 2003 In-cylinder combustion modeling with simplified chemistry 14th Int. Multidimensional Engine Modeling User’s Group Meeting (USA)
[9] Tuovinen H 1994 Modelling of Laminar Diffusion Flames Vitiated Environments, Fire Safety Science 4 pp 113-124
[10] Li Q et al. 2012 Experimental study and kinetics modeling of partial oxidation in heavily sooting flames Chem. Eng. J. 207-208 pp 235-244
[11] Nagy T and Turányi T 2012 Determination of the uncertainty domain of the Arrhenius parameters needed for the investigation of combustion kinetic models Reliability Engineering and System Safety 107 pp 29-34