

Methane Combustion's Chemical Kinetic Mechanisms

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Methane is an important fuel for gas turbine and gas engine combustion, and the most common fuel in fundamental combustion studies. As Computational Fluid Dynamics (CFD) modeling of combustion becomes increasingly important, so do chemical kinetic mechanisms for methane combustion.

chemical kinetics

comprehensive mechanism

methane

reduced mechanism

hydrogen

detailed mechanism

CFD

1. Introduction

Combustion of methane, CH_4 , is of significant importance in practical applications and for research purposes. Methane is a main component in biogas, as well as in fossil natural gas, and can be part of the important transition from fossil fuel to biofuel use. As the main component of natural gas methane can be considered as a relatively environmentally friendly fossil fuel, due to its advantageous combustion properties resulting in fewer harmful pollutants compared to other gaseous or liquid fossil fuels [1]. In combustion research methane is the fuel of choice in phenomenological studies due to its ease of use and wide availability. Due to its wide use and the fact that it is a relatively small fuel molecule the chemical kinetics of methane combustion is fairly well understood [2], at least compared to the significantly larger and more complex fuel molecules that are components of diesel or gasoline. Detailed chemical kinetics mechanisms for methane/air combustion are capable of predicting combustion characteristics over a wide range of conditions with respect to temperature, pressure and equivalence ratio, even though there still are quite large uncertainties at extreme conditions of low temperature and/or high pressure of many real combustion applications. Methane is also the fuel for which the largest number of simplified kinetic mechanisms, for use in Computational Fluid Dynamic (CFD) simulations, have been developed.

To further improve the understanding of methane combustion and to develop the industrial combustion systems, CFD simulations with explicit chemistry are needed [3]. Due to limitations in computational capacity, modeling has mainly been performed with highly simplified chemical descriptions, so-called global chemistry, or the flamelet approach [4]. These methods do not, however, resolve the interactions between chemistry and turbulence on the smallest scales [5]. They are also not useful for characterization of pollutant formation, an aspect that becomes increasingly important as a result of environmental concerns [6]. Large Eddy Simulations (LES) are suitable for the modeling of turbulent combustion coupled with chemical kinetics, but due to the computational cost implementation of highly detailed kinetic schemes is not feasible. With the current computational capacity and LES modeling

approaches, kinetic mechanisms of about 20–30 species and 80–100 reactions represent an upper limit in terms of mechanism size. It has been shown that this number of species is adequate to model important combustion characteristics of common hydrocarbon fuels [5].

The choice of mechanism for a CFD simulation is limited by the need for short computational time and varying demands with respect to output parameters, depending on the task at hand. The community of researchers with expertise in CFD simulations are, commonly, not experts in chemical kinetics modeling. Unfortunately, lack of knowledge among CFD experts or lack of communication between kineticists and CFD scientists, sometimes results in poor choice of mechanism for CFD simulations. Expert assessment of kinetic mechanisms needs to be made available for CFD scientists, to ensure that the most suitable mechanisms are incorporated in CFD simulations.

As CFD simulations are becoming increasingly important in the development of industrial burners and engines the requirements on the models may change compared to pure research cases. An example of this is that in idealized laboratory research systems or simulations the combustible mixture commonly consists of only one fuel component and the oxidizer. Most kinetic mechanisms are developed for pure fuels burning in dry air. However, in a real system there might be elevated levels of water vapor and exhaust gas recirculation increasing the levels of CO₂ [7]. Methane is the dominating component of natural gas, biogas, and bio-syngas [7][8][9][10], fuels that also contain one or several of CO₂, CO, H₂, higher hydrocarbons and possibly also the inert N₂. In addition, a real system is never completely dry, but H₂O will be present to different extent depending on temperature and other conditions. In [Table 1](#), common compositions that can be encountered in a real system are listed [7][8][9][10]. Natural gas is exemplified by two quite extreme cases considering methane content [10], but also a typical range of compositions as specified by Uniongas.

Table 1. Composition of relevant fuel mixtures incorporating methane, in volume-%. “High HC” stands for Higher Hydrocarbons, i.e., with two carbon atoms or more.

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Fuel Components	Typical Range ^a	Natural Gas		Biogas [7][8]	Bio-Syngas [9]
		Frigg (North Sea) [10]	Lacq (France) [10]		
CH ₄	87–97	95.7	69.2	50–75	8–11
H ₂	Trace	-	-	0–1	22–32
CO ₂	0.05–1	0.3	9.3	25–50	21–30
CO	-	-	-	-	28–36

Fuel Components	Typical Range ^a	Natural Gas		Biogas ^{[7][8]}	Bio-Syngas ^[9]	d on 1
		Frigg (North Sea) [10]	Lacq (France) [10]			
High HC	1.5–10	3.6	5.2	- [11]	-	been an

increasing interest in co-firing natural gas with hydrogen, H₂, in gas turbines. This is motivated by the fact that hydrogen is a carbon-free energy carrier but also because it affects the flame properties and allow combustion at leaner conditions [12]. Extensive research on combustion of methane/hydrogen blends has been performed on all scales, from idealized laboratory flames [12] to real gas turbine burners [13][14][15]. As reviewed by Tang et al. [16], hydrogen addition to a hydrocarbon fuel result in increased chemical reactivity giving a shortened ignition delay time and an increased flammability range. The same group published an analysis of the effects of hydrogen addition on the laminar flame speed of a hydrocarbon [16] investigating the kinetic, thermal, and diffusion effects, concluding that the kinetic effects dominated. There is also an increasing interest to use natural gas in Compression Ignition (CI) engines, commonly in a dual fuel system together with Diesel. Recently there have been significant improvement in predictive capability in modeling of dual fuel engines with natural gas (methane as main component), and in this context we like to highlight the works of research groups at Graz University [17] and Istituto Motori [18][19] who validated modeling approaches that advance the development of these engines.

Experimental studies on laminar burning velocities of hydrocarbons have been reviewed by, among others, Konnov et al. [20] and Ranzi et al. [21], while mixtures of hydrocarbons with hydrogen were considered in the review by Tang et al. [12]. These publications include detailed discussions on flame chemistry, of relevance to development and performance of comprehensive kinetic mechanisms. The curious reader who wants a more thorough understanding of flame chemistry and laminar flame speed is encouraged to read these works.

As already mentioned, chemical kinetic mechanisms are most often aimed at modeling of pure fuel/oxidizer mixtures in ideal laboratory systems. However, mechanisms that are validated also for mixtures of fuel with water or carbon dioxide are few. While in the ideal case the pure systems should be understood in large detail before more complicated gas mixtures are addressed, this is not a realistic approach, considering the need for simulation of complex systems. Fisher and Jiang [7] conclude in their analysis of ignition delay simulation results that the chemical kinetics of methane combustion combined with H₂, CO, or CO₂ is not yet fully understood, and that also highly detailed mechanisms are unable to accurately represent the chemistry. However, despite the fact that the understanding of combustion chemistry is far from complete there is a need for simplified kinetic schemes for implementation in CFD simulations.

The aim of the present study is to give an overview of common mechanisms for methane combustion, evaluate their performance, and discuss their potential use in CFD modeling. As part of the evaluation of the mechanisms, CPU time for 1D flame simulations is used as a metric for the computational cost. Mechanisms on all levels of complexity, from highly detailed to global, are compared with respect to performance for prediction of combustion properties related to ignition, propagation, and extinction phenomena. It is not an exhaustive review, but the aim is to include mechanisms that have been extensively referenced in the CFD literature, and the evaluation of these acts as a foundation for a general discussion. Particular focus is on reduced mechanisms that are small enough to

be used in finite rate combustion LES, but with high enough detail in the chemistry to predict combustion characteristics sensitive to chemistry. This includes an ability to predict formation of major products (CO, CO₂, H₂, H₂O) and a range of intermediate species (for example CH₂O, CH, OH). To investigate the comprehensiveness of the mechanisms they are not only investigated for their performance in CH₄/air combustion but also for the fuels mixtures containing the smaller fuels CO and H₂ that are inevitably part of any hydrocarbon mechanism. The applicability of the mechanisms is further tested for relevant real-world conditions by simulating flames with elevated levels of CO₂ and H₂O.

With the present work we provide the modeling community with a roadmap in the selection of existing mechanisms, by pointing out strengths and weaknesses of the common mechanisms in the literature. We also highlight the important aspects to consider in further development and use of simplified chemical kinetics schemes, based on the understanding gained from existing mechanisms.

2.Discussion and Recommendations

2.1. Detailed Mechanisms

The detailed mechanisms have, as referenced in the early sections of this work, been evaluated elsewhere but there are some important comments to make about the mechanisms in relation to CFD and reduced mechanism development. Aramco Mech, San Diego, and USC II have in common that they are regularly updated as a response to new experimental evidence. This is not true for the GRI 3.0 Mech, and the use of this mechanism outside conditions for which it was initially validated for is not recommended.

The mechanism with best overall performance is the Aramco Mech which accurately reproduces all validation data in this work, except the CH concentration in flames. We recommend the use of Aramco Mech as benchmark in 0D/1D simulations, in particular when there is a significant interest in ignition. Regarding time consumption Aramco Mech is by far the slowest mechanism, requiring tens of minutes and up to hours to calculate laminar burning velocity at one set of conditions. This can be compared to GRI 3.0 which uses about one minute for the same simulation. The San Diego and USC II mechanisms are in fairly good agreement with Aramco Mech over a wide range of conditions and are significantly smaller and faster than Aramco Mech, which motivates their use when a detailed mechanism is needed but computational capacity is limited. Regarding time consumption, the USC II mechanism simulates a laminar flame in about ten times the time as GRI 3.0, while the San Diego mechanism is in between the two.

All the mentioned detailed mechanisms are used as starting points for mechanism reduction using automated reduction methods. From a point of view of comprehensiveness and accuracy of chemistry the Aramco Mech should be most suitable for mechanism reduction. However, considering the size of the mechanism it may be too time consuming. The GRI 3.0 is not suitable for automated mechanism reduction since it in itself does not include the most accurate chemistry, if a smaller detailed mechanism is needed for mechanism reduction it is more advisable to use San Diego or the USC II mechanism.

2.2. Reduced Mechanisms

For the three reduced mechanisms of similar size, SR35, SG35, and Z42, the simulation takes about 5% of the time for the GRI 3.0 mechanism to perform the corresponding simulations. To present the numbers: when GRI 3.0 use 1 min the reduced mechanisms need only in the range 2–4 s. The fastest mechanism is SG35, while SR35 and Z42 take about the same time. All of them are faster simulating flames at lean conditions (2–4 s) compared to rich conditions (4–8 s), which is an indication of the more complex chemistry at the rich conditions.

If the simulation targets are flames at lean conditions, below about $\phi = 0.8$, all the reduced mechanisms will give about the same results for flame propagation, heat release, and major species concentrations. Even though the computational time is very short for all of them, SG35 is the winner in a case where small reduction in computational time is a significant advantage. For other cases we would like to recommend the Z42 mechanism since it is useful over a wide range of flame conditions, and also performs best for ignition delay time. Z42 is also the reduced mechanism that has reactions in best agreement with the detailed mechanisms, as shown using sensitivity analysis. The reduced mechanism that we cannot recommend for use is the SR35, it show overall least agreement with experiments and detailed mechanisms, and it appeared to miss some of the important high pressure chemistry.

All three highly reduced mechanisms have too low reactivity for ignition, resulting in too long ignition delay times. The DRM22 with its 104 reactions does a much better job for ignition, indicating the need to include more reactions, but that a quite small mechanism is still possible.

The addition of H_2 , CO_2 , and H_2O is handled almost as accurately as pure methane for SG35 and Z42, while SR35 also in these cases is inferior. Based on this we could recommend the use of Z42 for various mixtures of relevance for example in simulation of gas turbine combustion. Additionally, SG35 would perform fairly well at lean conditions.

2.3. Global Mechanisms

Regarding global mechanisms, it is necessary to use them only for conditions that they are parameterized for, and not where accurate ignition or extinction events need to be modelled. While the early mechanisms by Westbrook and Dryer and Jones and Lindstedt include reactions that are of relevance to any global mechanisms, we cannot advise using their original parameterization outside the very specific range of conditions that they are valid for. The more recent global mechanisms use better parameterization and should be preferred.

Global mechanisms have the advantage that there are few species and reactions, but sometimes they unfortunately have a considerable stiffness. The experience from running the simulations in CHEMKIN and Cantera is that there are often convergence problems with global mechanisms and the computational time is actually close to that for the reduced mechanisms of around forty reactions.

2.4. Summary and Outlook

Regarding all detailed mechanisms, it is advisable to use them for mechanism reduction only within the parameter space they have been validated in. However, we are very well aware that reduced mechanisms often are needed at conditions for which no detailed mechanism has been evaluated. The present work has investigated the common detailed mechanisms over a wider parameter range than they were originally constructed for and the results can be used as a guide in selection of detailed mechanism for automated reduction.

For CFD, where the DRM22 mechanism with its 22 species and 104 reactions can be afforded, we recommend its use since it is in good agreement with the benchmark over a wide range of conditions for both flames and ignition. When a smaller mechanism is needed, the Z42 with only 42 irreversible reactions is highly recommended. For flame propagation Z42 is as good as DRM22, while the larger mechanism is more accurate in predictions of ignition.

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