



# Chapter 1

## Introduction

“Though the river’s current never fails, even the water flowing at every instance is never the same. Where the current pools, bubbles forming on the surface burst and disappear as others rise to replace them and none of them last long.” (Kamono-Chomei, Hojoki, 1212)

The combustion phenomena, i.e., “chemical-reaction flow,” at low temperatures can be explained in a similar manner to the “river’s current” in the above sentence. During the oxidation process of fuels at low temperatures, intermediates are formed and are consumed (i.e., further oxidization). In other words, reaction flow is preserved if unburned fuel remains and the consumption of the intermediates is greater than their formation. Although intermediates are accumulated due to interrupted flow, other products may come into existence because of recombination reactions. This phenomenon can be explained by the dynamic behavior of the bubble in the sentence above.

Combustion technology based on chemical reactions has a rich history, and can be found in a wide range of applications such as power generation and heating, and the evolution of this technology has contributed to advancements in various fields worldwide [1]. However, the negative impact of emissions on the environment is inevitable and is being investigated with the highest priority. The development of methods for the minimization of pollution [2, 3, 4, 5] and greenhouse gases, which absorb infrared radiation from the Earth’s surface and atmosphere [6, 7, 8], are the key topics in combustion research. Since the 1970s, when carbon dioxide ( $CO_2$ ) was first identified as a greenhouse gas, three major technologies have been developed to reduce  $CO_2$  emissions. The first technology, which is still under discussion, is the capture of  $CO_2$  from exhausts and its storage underground [9, 10, 11]; and the second technology still being investigated is the use of high-efficiency combustion systems for industrial applications, such as high

temperature air combustion technology (HiCOT) or moderate and intensive low oxygen dilution (MILD) combustion [12, 13], and the third method is the use of low-carbon, plant-based fuels or surrogate fuels with lighter hydrocarbon species [14, 15, 16]. Recently, methane ( $CH_4$ ) has also been recognized as a greenhouse gas. As  $CH_4$  is a major component of natural gas, which is widely used in industry, methods to improve its combustion efficiency have been intensively studied [17, 18]. Amongst atmospheric pollutants, nitrogen oxides ( $NO_x$ ) including nitric oxide ( $NO$ ) and nitrogen dioxide ( $NO_2$ ) have been found to have a strong impact on human health, and their forming mechanisms from fuel nitrogen ( $N$ ) [19] and atmospheric nitrogen ( $N_2$ ) [20] have been investigated. These evaluations were applied to industrial applications such as the prediction of  $NO_x$  formation [21, 22, 23, 24, 25]. Since the 1980s, investigations regarding the strong influence of nitrous oxide ( $N_2O$ ) on the atmosphere as a greenhouse gas have been conducted [26, 27]. In spite of the critical consequences, our lives strongly depend on the energy generated using combustion technology. It is necessary to reduce these negative impacts on the environment by improving technology and exploring alternative energy sources. For example, since Japan became highly dependent on nuclear power for its industrial activities and transportation, its civil life faces critical problems at times of disaster, as experienced following the Fukushima earthquake on 11<sup>th</sup> March 2011. Therefore, we need to accelerate the use of alternative sources such as solar, wind, and geothermal energies. Although these energies are considered a wise substitute, their technologies still need to be improved. Hence, the efficiency of conventional energy sources, with the exception of nuclear, has to be enhanced until they can be referred to as “practical energy sources.” To satisfy such requirements, lean combustion at low temperatures is found to be a possible solution. In general, this method decreases flame temperatures and combustion emissions. However, combustion phenomena become unstable at low temperatures, and such instabilities retard the application of these technologies in many areas such as homogeneous charge compression ignition (HCCI) engines [28]. In order to predict these phenomena in such applications, combustion chemistry has been intensively studied.

Combustion chemistry, comprising many elementary reactions (the reaction mechanism), has a long history, and has been investigated both experimentally and numerically. Experimentally, it has been investigated using various experimental apparatus such as shock tubes (STs), rapid compression machines (RCMs), jet-stirred reactors (JSRs), and flow reactors (FRs). The ST is mainly employed for investigations at high temperatures and high pressures. Due to the pressure-driven shock wave, boundary conditions can be precisely measured and can be compared with numerical simulations. Studies of combustion chemistry using STs until the 1960s were summarized by Bauer [29] and Nettleton [30], and clearly



pointed to the potential of this experimental apparatus. A number of research groups (e.g., those of Hanson (Stanford, USA) [31], Petersen (Texas, USA) [32], Roth (Duisburg-Essen, Germany) [33], Adomeit (Aachen, Germany) [34, 35], and Simmie (Galway, Ireland) [36]) have developed STs, and have contributed to the understanding of the fuel oxidation process under a wide range of temperatures and pressures. Recently, experimental data has been obtained not only for single component fuel, but also for binary component fuels that represent natural gas [17, 37, 38, 39, 40]. RCMs were originally developed to study engine-related phenomenon such as engine knock. During the 1960s, the main focus of RCMs was towards their usage in the automotive industries, as summarized by Levedahl (NIST, USA) [41]. However, the focus has since shifted from industrial to academic purposes because of their reusable experimental capability<sup>1</sup>, and also because experiments can be conducted at relatively lower temperatures than those in STs. Recently, several types of RCMs (e.g., single piston, dual piston, air driven piston) have been developed by the research groups of Sung (CWRU, USA) [42], Simmie (Galway, Ireland) [43], Keck (MIT, USA) [44], Boulouchos (ETH, Switzerland) [45], Wooldridge (Michigan, USA) [46], and Sochet (CNRS, France) [47, 48], producing valuable data for detailed reaction mechanism validations. Although STs and RCMs have been used for about half a century to provide an insight into experimental investigations of combustion chemistry, auto-ignition phenomena in these apparatus were spontaneous. In principle, the auto-ignition delay time (i.e., overall ignition delay time) can be measured using these apparatus, but species concentration as a function of time cannot be measured. To overcome this issue, Hanson's group reported hydroxide (*OH*)-time history measurements using a ST, thus demonstrating its potential [49, 50]. However, the available species in these time-history measurements are limited by the restrictions of current laser-diagnostics techniques. Therefore, in order to cover the requirements of reaction mechanism development, experimental investigations at not only high temperatures but also intermediate time histories have to be conducted.

A JSR is widely used to measure intermediate species at low temperatures during auto-ignition processes (i.e., low-temperature chemistry (LTC)). JSRs were first built by Longwell [51] to study intermediate concentrations during the fuel oxidation process. By controlling the residence time of the mixture in the reactor, intermediates species can be measured using a JSR. Due to the longer ignition delay time at low temperatures, they have been used for investigations in LTC. Two types of JSR have been developed by Dagaut's [52, 53, 54, 55, 56, 57, 58] and Ciajolo's [59, 60] groups. Experimental data from both of these JSRs have been used for detailed reaction mechanism development. Dagaut's JSR has been used for the study of various fuels (or specific stable intermediates) in their ox-

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<sup>1</sup>ST needs to replace the diaphragm for each experiment.

idation process, and quantitative species concentrations have been measured by Battin-Leclerc's group [61, 62, 63]. Ciajolo's JSR has been used to study oscillatory phenomena in the JSR itself, and results were reported by Cavaliere's group [64, 65]. Although JSRs allow the observation of intermediate concentrations during the fuel oxidation process, the ignition delay time and intermediate concentration measurements cannot be directly related because of the change in spontaneous residence time of the mixture. Recently, sequential ignition and extinction phenomena in the JSR were reported [66], but the interdependence between ignition delay time and measured species concentration has not been well investigated.

The other investigations to measure intermediate species during the ignition process have used FRs. An FR is mainly designed to measure the intermediate species at similar conditions as a function of time, as in a JSR. By using a probe and gas-and/or mass-chromatography, detailed species concentrations over time can be measured during the auto-ignition process. FRs used in the field of chemical engineering since the 1960s [67, 68, 69] have been adapted to aid the understanding of combustion phenomena. For example, several FRs have been developed by the groups of Dryer (Princeton, USA) [70], Koert (Drexel, USA) [71, 72], Mantzaras (PSI, Switzerland) [73, 74], Bowman (Stanford, USA) [75], Maas (KIT, Germany) [76], Beerer (UCI, USA) [77], and Frenklach (PSU, USA) [78]. Under steady conditions, optical measurements examined by Ghermay et al. [74] realized a number of advantages in comparison to JSRs. In addition, by measuring chemiluminescence, ignition delay times at low temperatures (i.e., a temperature range not available for STs or RCMs) were measured using FRs [77, 79]. However, the measured species concentrations and ignition delay times (i.e., first-stage ignition delay time,  $\tau_{1st}$ ) were not obtained simultaneously. Note that experimental data demonstrate only the results of possible elementary reactions. Precisely, the balanced concentrations occurring due to the production and consumption of related reactions are measured by the species concentration<sup>2</sup>.

Although each experimental apparatus has its advantages and disadvantages, together they provide a wide range of temperatures and pressures for reaction mechanism development. Based on these experiments, numerical simulations of the fuel oxidation process have been established. The experimental database contributes to the detailed reaction mechanism development. In general, there are two philosophies relating to the detailed reaction mechanisms development. According to the first philosophy, detailed and generalized reaction mechanisms are developed. By involving oxidation reaction pathways from not only one but several fuels, the detailed reaction mechanism can be used for another fuel under

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<sup>2</sup>Few elementary reactions can be directly measured [80, 81].



various conditions. This philosophy is based on the principle that oxidation pathways of hydrocarbon species have a hierarchical structure. Based on this idea, for example, three of many reaction mechanisms have been established by the research groups of Ranzi (Milan, Italy) [82, 83, 84, 85, 86], Warnatz (Heidelberg, Germany) [87, 88], and Williams (UCS, USA) [89]. Remarkably, the detailed reaction mechanism from Ranzi's research group involves the largest variety of fuels within a reaction mechanism, and it is therefore used for this study. Recently, the concept of a hierarchical structure has also been applied to blended fuels such as gasoline, diesel, and jet fuels. Gasoline and diesel fuels have been investigated using surrogate fuels (e.g., primary reference fuel (PRF) [90, 91] or a mixture characterized by using research octane number (RON) and motor octane number (MON) [92]). Another research angle is the investigation of suitable components for the surrogate, as was done by Pitsch and collaborators [93]. Jet fuel was also studied by investigating appropriate surrogate fuels [94, 95]. Recently, a surrogate fuel with a biomass-driven component has been focused upon, and its detailed investigation is in progress [91]. By using a general mechanism for the surrogate fuel that denotes the oxidation process of selected species, the combustion process in applications such as the internal combustion engine can be closely predicted.

According to the second philosophy, a fuel-specific mechanism is developed. By collecting all of the existing experimental data, prediction using the specific mechanism in the experimental investigations is optimized. An example of this philosophy is summarized in the gas research institute (GRI) mechanism [96]. It is well known that this mechanism is specialized for  $CH_4$  oxidation processes, but there are cases in which propane ( $C_3H_8$ ) and formaldehyde ( $CH_2O$ ) were also chosen as a reference. Another example comes from a research group led by Westbrook at the Lawrence Livermore National Laboratory (LLNL). They have established reaction mechanisms for a variety of fuels (e.g., hydrocarbon, oxygenated, and organophosphorus compounds). These mechanisms have been used as a reference for specific fuels. Two mechanisms from the LLNL research group, for dimethyl ether (*DME*) and n-heptane ( $nC_7H_{16}$ ), are used in this study. Besides these philosophies, Côme's and Green's groups have developed computational programs (i.e., EXGAS [97] and RMG [98]) to generate the reaction mechanism. These programs allow the generation of mechanisms for specific conditions (i.e., fuel concentration, temperature, and/or pressure).

Although such a detailed reaction mechanism predicts combustion phenomenon accurately, it involves a large number of species and reactions, which may prove to be disadvantageous. As an example, in computational fluid dynamics (CFD), due to limited computational resources, the nonlinearity of a system has to be minimized. Thus, in CFD, it is difficult to consider all species in the detailed reaction mechanisms. Hence, mechanism reduction has been considered as one of



the main topics in combustion chemistry since the 1970s. In order to reduce the detailed reaction mechanism, i.e., reactions and species, Ranzi's group has developed a lumping method that considers their chemical structures (especially isomers) [84, 99, 100]. Even after the lumping process, the detailed reaction mechanism still involves significantly more species and reactions than the CFD calculations are capable of handling. To overcome this issue (to convey detailed information from the reaction mechanism to the CFD calculations), several mechanism reduction methods have been developed based on the time scale in the chemical reaction. Based on the findings of Dixon-Lewis [101], the influence of the reaction time scale has been the focus by removing unimportant reactions and species from the detailed reaction mechanism, thus establishing a reduced mechanism.

There are two major mechanism reduction strategies. The aim of the first strategy is to reduce the mechanism to a manageable level for the CFD calculations by partially neglecting the chemical kinetics. The computational singular perturbation (CSP) method was then initiated by Lam and Goussi [102]. By using this concept, the groups of Maas and Law proposed intrinsic low-dimensional manifolds (ILDM) [103] and directed relation graphs (DRG) [104, 105], respectively. These methods locally resolve the stiffness of a reaction mechanism based on the time scale of the chemical reaction. Fuel oxidation processes can be predicted from their initiation by time dissolution considerations. Further methods proposed from 2008 to 2011 include, the directed relation graphs with error propagation (DRGEP) method established by Pepiot-Desjardins and Pitsch [106], principle component analysis by Esposito and Chelliah [107], level of importance analysis by Løvås [108], and path flux analysis by Ju et al. [109]. These methods reproduce the results obtained using detailed reaction mechanisms, and successfully reduce the number of species and reactions. In addition, the reduced mechanisms can be applied to predict flame propagation and its structure (e.g., 1-D flame calculations). In other words, the fuel oxidation process and mass diffusion can be predicted. However, due to locally resolved reaction mechanisms by the above mentioned methods, the reduced mechanism still surpasses the capabilities of current simulation techniques. Therefore, for CFD calculations, further modeling such as representative interactive flamelets (RIFs) [110], multi-zone [111], or tabulated models [112] are required to convey the necessary information.

The aim of the second mechanism reduction strategy is to express the combustion (i.e., oxidation process) analytically from the systematic reduction of nonlinearity in combustion chemistry. In terms of time scale considerations, this strategy is similar to that mentioned above. However, by considering the order of magnitude of the reaction mechanisms, only time scales of leading order are considered. In particular, the slow time scale (i.e., that corresponding to the slow manifold in the ILDM method) is extracted as the leading order time scale. Since corresponding



time scales are neglected, this method does not allow the prediction of oxidation processes at the beginning of the reaction. However, instead of inaccurate predictions, the stiffness of the reaction mechanisms is further reduced as compared to the first strategy. The oxidation process can thus be analyzed analytically by this method. Especially, this reduction considers obvious difference in terms of the flame propagation. This strategy was initiated by Peters and Williams, and it explicitly demonstrates the oxidation process of  $CH_4$  by global reactions based on quasi-steady state and partial equilibrium assumptions with asymptotic theory [113, 114]. This procedure has been applied to laminar premixed flames [115], partially premixed flames [116], and diffusion flames [117] to demonstrate the oxidation and diffusion processes. In addition, this procedure has been successfully applied to turbulent flames [118]. As mentioned, due to the simplifications of the analytical expressions, slightly less accurate results may be achieved than from the detailed reaction mechanism [119]. However, as shown in a recent publication from Williams' group, this analytical expression can be applied with reasonable accuracy in the numerical studies of gas-turbines [120].

As described above, better insight into combustion chemistry is obtained by reducing the detailed reaction mechanism. Although the detailed reaction mechanism is well-validated and accurately predicts the experiments, most of the elementary reactions involved in the mechanism are estimated (i.e., estimated reaction pathway and Arrhenius parameters). A lack of experimental data concerning minor intermediates leads to insufficient feedback from the reduced to detailed reaction mechanism level, and also from experiments to a specific intermediate. Fortunately, due to the development of measurement techniques, a wide range of intermediates are now measurable to a certain extent. For instance, Kohse-Höinghaus' group demonstrated measurements of a burner-stabilized flame on a low-temperature burner [121, 122]. The research groups of Qi, Battin-Leclerc, and Taatjes measured intermediates in LTC, and realized further possible improvements to the detailed reaction mechanism using state-of-the-art measurement techniques [61, 123, 124, 125]. It can be inferred from these experiments that, once the important species in the oxidation process are determined by the reduced model, one can exclusively measure the concentration of specific species and improve the accuracy of a specific elementary reaction. Also, the specific target allows the quantum mechanics calculations to conduct further detailed validations, such as the thermal properties of the intermediates involved and the pressure dependency of the reaction. Once the detailed reaction mechanism has been improved, it is subsequently reflected in the accuracy of the reduced model. Therefore, obtaining an appropriate reduced model and theoretical understanding of the oxidation process are important steps for advancing combustion chemistry.

In this dissertation, low-temperature ignition is studied experimentally, numerically, and theoretically using a laminar flow reactor (LFR). This LFR is developed to obtain appropriate boundary conditions for numerical and theoretical investigations. The remainder of this dissertation is arranged as follows: chapter 2 describes the theory used in the numerical simulations and the theoretical investigations. The governing equations (species and energy equations) and the assumptions applied are described in this chapter. Chapter 3 describes the LFR and the measurement procedure in detail. This apparatus is capable of using liquid and/or gaseous fuel at atmospheric pressure. The available temperature range is 300–1000 K. The LFR is significantly different from conventional flow reactors. In chapter 4, the LFR is evaluated to examine its ability. Due to the restrictions of the LFR, 3-D simulations are used for these investigations. The homogeneity of the mixture in the LFR (i.e., flow and the mixing fields) is thoroughly investigated, and appropriate assumptions for numerical and theoretical investigations are discussed. In chapter 5, the methodology is developed to analytically express the low-temperature ignition of  $nC_7H_{16}$  in detail.  $nC_7H_{16}$  has been extensively studied in the combustion community, and is a suitable reference fuel. Heat loss due to the reactor walls is estimated using experimental data as a reference. By using this heat loss, detailed investigations of reaction pathways are conducted. Based on the experimental and numerical findings, a theoretical model is established and analytical solutions representing low-temperature ignitions are obtained. In chapter 6, the developed methodology is applied to *DME*. *DME* is used as an alternative fuel from biomass. The validity of the estimated heat loss is examined for different fuels. Three mechanisms (the LLNL and Ranzi mechanisms, as well as one generated by RMG) are compared, and their reaction pathways at low temperatures are discussed in detail. The theoretical model leads to an analytical expression for low-temperature ignition with *DME*. This analytical solution explicitly describes the importance of specific elementary reactions in LTC and provides criteria for the validation of the detailed reaction mechanism. In chapter 7, as a further development of the methodology, blended fuels consisting of *DME* and  $nC_7H_{16}$  are tested. These blended fuels represent the blending of conventional and biomass-driven fuels. In addition, the fuels demonstrate the interaction between hydrocarbon and oxygenated species in their oxidation processes. Based on inferences from the experiments, a blended mechanism (a combination of the LLNL and Ranzi mechanisms) is established to predict low-temperature ignition with blended fuels. These experiments and simulations aid the derivation of an analytical expression for low-temperature ignition of blended fuels. This low-temperature ignition explicitly demonstrates the rate-determining step in the oxidation process, and analytically expresses the nonlinear interaction between fuels. The obtained results are summarized in chapter 8, where an overview of future works is also presented.