Developing a validated chemical kinetics model for sCO$_2$ combustion and implementation in CFD

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Owen Pryor is a Graduate Student at UCF. He has worked with Dr. Subith Vasu on experiments to determine ignition delay times and species time histories using the shock tube located at UCF. He has coauthored many publications on combustion kinetics experiments and modeling. He is currently working on experiments for CO_2 diluted methane and syngas mixtures behind reflected shockwaves. He received his Bachelor's in Aerospace Engineering in 2014 and is currently working towards completing his Master's in Aerospace Engineering.

Dr. Jay Kapat is the Lockheed Martin Professor at University of Central Florida. He has received his Sc.D. from MIT, M.S. from Arizona State and B.Tech (Hons) from IIT Kharagpur – all in Mechanical Engineering. He joined UCF in 1997 as an Assistant Professor, and then got promoted to Associate Professor in 2001 and Professor in 2005. Dr. Kapat serves as the Associate Director for Florida Center for Advanced Aero-Propulsion, and the founding Director for Center for Advanced Turbomachinery and Energy Research (CATER). Prof. Kapat has over 25 years of research experience in various areas of energy and thermal-fluids sciences with key research interests in Advanced Turbines and Energy Systems: aerodynamics and heat transfer for gas turbines and turbo machineries, cooling techniques, system calculations, alternative fuels. His research has been funded by DOE, AFRL, NSF, NASA, Siemens, GE, Alstom, Aerojet, FTT, AFOSR, Lockheed Martin, Rini Technologies, and the US Army. He has authored 1 book chapter and over 200 peer-reviewed papers in journals and conference proceedings. 10 patents have been issued to him with another 12 pending.

Dr. Artem Masunov received his B.S./M.S. in Chemistry from Moscow State University in Russia and Ph.D. in Theoretical Chemistry from City University of New York. After spending three years in Los Alamos National Lab, he joined UCF as an Assistant Professor in 2005 and was promoted to Associate Professor in 2010. His main research interests are Density Functional Theory studies and Molecular Dynamics simulations on molecular aggregation, reactivity and optical properties. Dr. Masunov also served as both single PI and co-PI on NSF and DOD sponsored projects. He has authored 1 book chapter and over 100 papers in peer-reviewed journals.

Dr. Scott Martin spent eight years with Siemens Energy in Orlando, FL as a combustion engineer focused on fuels and advanced combustor design. During this time he was assigned to work on the DOE funded H_2 Gas Turbine project tasked to develop premixed combustors for synthetic and hydrogen fuels at up to 30 bar pressures. Scaled combustors were designed and tested at university laboratories and full scale combustors were tested at national labs in Canada, Germany, and Italy. This work led to 3 US patents with 4 more pending. An integral part of this work was developing numerical models, 1-D and 3-D, plus chemical kinetic mechanisms. Here the premixed CMC turbulent combustion model that he developed in graduate school was adapted to the open source CFD code OpenFOAM. During this time, Dr. Martin worked with researchers at Georgia Tech, UCF, University of Texas, University of Iowa and Purdue, and published a number of papers related to this field. Dr. Martin received his initial leadership and management training in the US Marine Corps, followed by progressively more responsible positions in industry and now in academia where he is the leader of the propulsion group at the Eagle Flight Research Center at ERAU. During periods at The Boeing Company and Ford Motor Company he led teams that were tasked to solve specific problems. At Siemens he was the head of the combustion kinetics groups and the liaison between the combustion group and universities.

Abstract

In this paper, we discuss the development and validation of a combustion chemical kinetic mechanism for supercritical CO_2 (sCO_2) oxy-methane/syngas combustion that can be used for computational fluid dynamic code (CFD) simulations in oxy-combustion development. This model will be validated using unique experiments conducted in CO_2 diluted methane/syngas mixtures and for pressures up to 300 bar. The created model will then be implemented in an open source CFD code for industry dissemination. This work will enable industry to tackle challenges associated with oxy-combustion systems in directly heated sCO_2 power cycles. Acquiring experimental data is critical in the development of a sCO_2 detailed kinetic mechanism as there is currently none available for methane at very high pressures approaching 300 bar and for CO_2 diluted methane mixtures even at normal pressures. The experienced experimental and combustion modeling team will couple the mechanism to the combustion CFD model and develop/modify CFD sub-models for real gas effects in the super critical regime. The final model will have the ability to study a variety of topics regarding direct-fired sCO_2 oxy-methane combustors and will be the first step in developing an accurate tool for computer design optimization of the next generation super critical engine cycles.

Introduction

Here we report on our proposed approach towards development of a chemical kinetics model, its validation, and implementation in a CFD applicable to direct-fired Supercritical CO_2 (sCO_2) systems. The project is funded by the U.S. Department of Energy's (DOE) Fossil Energy division. This effort is led by the University of Central Florida (UCF) which is assisted by Embry-Riddle Aeronautical University (ERAU) and Stanford University. Supercritical CO_2 power cycles are one possible solution to the growing energy demand in the United States. It is believed that sCO_2 could achieve cycle efficiencies of up to 64% while capturing 99% of the CO_2 created, but there are concerns with thermal management and temperatures inside the turbine[1]. The issue is that such simulations are based on methane combustion that has only been validated for low pressures and without heavy dilution of CO_2. Here we consider two main kinetic models that are used for natural gas combustion, the GRI-3.0 and the recent Aramco-1.3 [2, 3]. Fig. 1 shows the differences in ignition delay times predictions between the GRI-3.0 mechanism and the Aramco-1.3 at two different pressures. At low pressures, these models show good agreement with each other and experimental data with minor differences between the predictions of two models[4, 5]. The problem is that the models are only valid at pressures much lower than the design conditions for sCO_2. Above the validation pressures, the models start behaving differently. Even at 20 bar (see Fig. 1), the Aramco-1.3 mechanism starts to taper off at the end while the GRI-3.0 Mechanism continues the same trends regardless of pressure [2, 3]. The difference in magnitudes is also evident. At the desired test condition of 300 bar, the GRI-3.0 Mechanism predicts an ignition delay time that is three times greater than the Aramco-1.3 mechanism at low temperatures. These are two of the most widely used mechanisms for natural gas combustion available, validated by many researchers and experiments. However, a need for a new mechanism has become apparent with technological needs require higher pressures than these were conceived for.
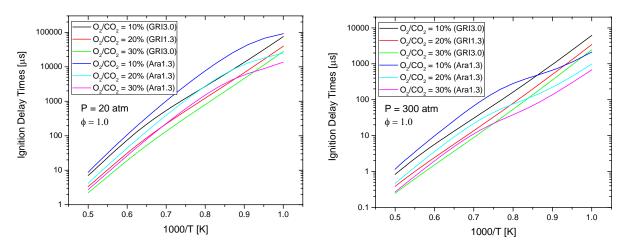
Fig. 1. LEFT: Ignition Delay Times of CH_4 Oxidation in a CO_2 bath gas at 20 bar. **Right:** Ignition Delay Times of CH_4 Oxidation in a CO_2 bath gas at 300 bar. The two models shown above clearly show different results for the two conditions showing that there is a lack of understanding at the conditions for supercritical CO_2. (ϕ=1). Simulations conducted using the CHEMKIN PRO software[6].

There are variations in the predictions of chemical mechanisms used for simulating the ignition delay times of natural gas such (e.g. GRI 3.0 and Aramco 1.3 Mechanisms) in CO_2 diluted gas mixtures even at 1 atm [4, 5]. Figure 2 (a) gives the comparison of methane time-history predictions of two different reaction mechanisms; namely the GRI 3.0 and the AramcoMech 1.3 [2, 3], for stoichiometric combustion of 3.5% CH_4 in argon bath gas diluted with 30% CO_2 at 1600K and 1 atm. The results were obtained using the constant-volume, internal energy (constant-U,V) assumption with the CHEMKIN PRO tool [6]. The discrepancy in the ignition delay time between the two mechanisms turned out to be $\Delta\tau_{ign}$ = 462.5 µs. Figure 2 (b) shows CH_4 time-histories during its ignition when the gas mixture contains different mole fractions of CO_2 ranging from 0 up to 60% according to the simulations done with the AramcoMech 1.3 mechanism. The differences in the ignition delay times were $\Delta\tau_{ign}$ = 293 and 236 µec when X_{CO2} was increased from 0 to 0.3 and 0.3 to 0.6, respectively.

Although not shown in Figs. 2 (a) and (b), the discrepancies in the predicted ignition delay times between the two mechanisms were noticed in N_2 and Ar bath gas even without any CO_2 dilution. These ignition delay time simulations at different bath gasses and CO_2 dilutions at 1600 K and 1 atm are summarized in Table 1. It can be seen from the table that as the CO_2 dilution was increased from 0 to 60%, the differences ($\Delta\tau_{dif}$) between the two mechanisms raised from 405.5 µs to 477.5 µs in argon bath.
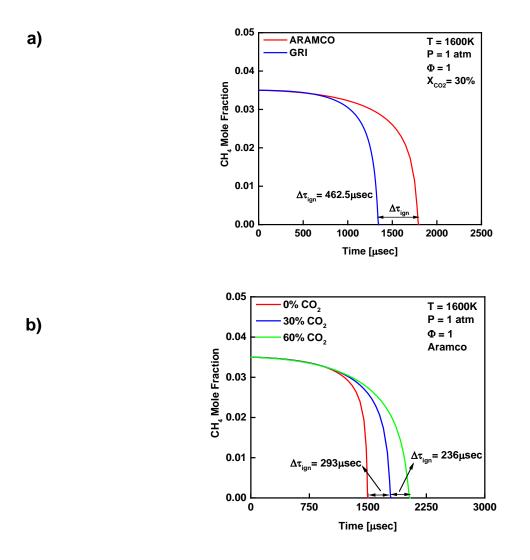
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a)

b)

Fig. 2 (a) Comparison of methane time-history predictions obtained from GRI 3.0 and AramcoMech 1.3 mechanisms for the stoichiometric combustion of 3.5% CH_4 in 30% CO_2 in argon bath gas at 1600K and 1 atm; **(b)** methane time-histories during its ignition when the bath gas contains different percentages of CO_2 ranging from 0 up to 60% according to the AramcoMech 1.3 mechanism.

However, the difference between the two mechanisms remained the same (499.4 µs < $\Delta\tau_{dif}$ < 503.3 µs) when nitrogen was used as the bath gas. Also, differences in the ignition delay times within the mechanisms themselves were seen as the CO_2 dilution was raised. This was already exemplified in Fig. 2 (b), but further detailed in Table 6-1. As the CO_2 amount was increased, it was observed that the changes in the ignition delay time were more significant when the bath gas included argon (e.g. an increase from 1495.5 to 2024.9 µs for AramcoMech 1.3 mechanism) than nitrogen (e.g. an increase from 1665.8 to 2059.4 µs for AramcoMech 1.3 mechanism).

The new mechanism developed by this team will seek to understand the nature of high pressure methane combustion as well as the fundamental effect that CO_2 addition could play in the combustion chemistry. Once the mechanism has been developed, it will be validated using shock tube experiments, and applied to high pressure, multi-step combustion CFD model that is being developed in conjunction with the mechanism. This new CFD model will then been applied to different combustor designs to test their performance in high fidelity CFD. It is not clear at this point how direct-fired sCO_2 combustor systems will

operate and various designs have been under consideration with the DOE's sCO₂ program. Note that ignition can either be carried out at a lower pressure (and gradually the flame is brought to operating pressures) or autoignition can be utilized at design pressure conditions. Hence it is important to have a validated kinetic mechanism and CFD code that is applicable over a range of pressures spanning 1-300 bar.

Table 1- Ignition Delay Time Simulation Predictions at 1600 K and 1 atm

	X_{AR}	X_{N2}	X_{CH4}	X_{O2}	X_{CO2}	$T_{AramcoMech\ 1.3}$ [μs]	$T_{GRI\ 3.0}$ [μs]	ΔT_{dif}
	0.895	0			0	1495.5	1090.1	405.5
Ar bath	0.595	0	0.035	0.07	0.3	1788.3	1325.8	462.5
	0.295	0			0.6	2024.9	1547.4	477.5
	0	0.895			0	1665.8	1164.8	501.0
N₂ bath	0	0.595	0.035	0.07	0.3	1865.8	1362.5	503.3
	0	0.295			0.6	2059.4	1560.0	499.4

Experimental Data

The experimental data taken for validation will be performed in shock tubes located at University of Central Florida and Stanford University. A shock tube is an excellent lab facility to generate conditions (high pressure- up to 300 bar, high temperature-up to 2000 K) that are present during the sCO₂ oxy-methane/syngas combustion. The shock tube works by separating a tube into two sections of different pressure. When the barrier is removed between the two sections the gases strive for equilibrium resulting in a normal shock wave. The shock wave eventually hits the end wall of the tube and causes a stagnation point as the wave reflects. This stagnation point is the test location. Figure 3 shows an image of the shock tube process. The shock wave raises the temperature, pressure and density of gases as it travels and in the reflected region producing gases which have been heated twice. The entire process happens within micro second time-scales (therefore there is negligible heat loss from the system) and until the arrival of expansion waves from the driver side at the test location (typically located 1-2 cm from the end wall) the system holds very high pressures and temperatures. The process can be repeated for different test conditions. At the test location the gas is considered to be at a static condition until the expansion waves arrive. During this time the gases are capable of auto-igniting.

Preliminary results have shown that the test times available in UCF and Stanford shock tubes are enough for the planned experiments. Lexan polymer and aluminum diaphragms (depending on the final test conditions) will be used. A good vacuum system is important for minimizing impurities in the system especially for kinetic experiments. The shock tube leak-plus-outgassing rate will be kept less than 5 μTorr/min. Incident shock velocities will be measured using piezoelectric transducers (PCB 113A) spaced axially along the last meter of the tube and linearly extrapolated to the endwall. Average incident shock wave attenuation rates are expected between 0.6% and 2% per meter. Fill pressure (P_1) will be monitored using two static pressure transducers (MKS Baratron).

Ignition delay times will be measured in methane and syngas mixtures with CO_2 mixtures covering pressure ranges up to 300bar. For the proposed experiments, the ignition delay time will be considered as the time between the arrival of the reflected shockwave and the start of the emissions. The emissions for the low pressure experiments are from OH* and CH* formation that are centered at 308nm and 430 nm wavelengths, respectively. The high pressure experiments will be based on similar methods for the ignition delay times. Ignition delay times will be based on IR emissions centered at 3.3 μm wavelength that is seen when the methane ignites in the experiments.
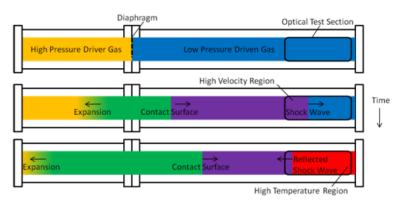

Fig. 3. Example of a shock tube experiment. The top image shows the shock tube before the diaphragm ruptures. The middle image shows the normal shock traveling down the tube. The third shock shows the reflected wave and the high temperature test region. Figure adapted from C.T. Johansen [7].

For further validation data, key species will be measured using direct laser absorption spectroscopy. Using the Beer-Lambert Law, the mole fraction of a particular species can be measured by measuring the ratio of the intensity with the species present over the vacuum intensity. This method is applied in the shock tube by measuring the intensity of light at different wavelengths over the duration of an experiment.

The CH_4 time histories will be measured using a distributed feedback interband cascade (IC) laser centered at 3403 nm from Nanoplus and two thermoelectrically cooled HgCdTe detectors (Boston Electric PVI-2TE-3.4). The species will be measured using a differential (peak minus valley) absorption scheme with a time resolution of 20 μs that has been applied in UCF's shock tube[4]. Sample absorption scheme and time-histories[4] are shown below in Fig. 4. It is seen that GRI 3.0 and Aramco differ in their predictions during methane ignition diluted with CO_2 even at low pressures. Similarly, the CO time-histories will be measured using a distributed feedback quantum cascade laser from Thorlabs centered at 4.6 μm. This method has been used before in Spearrin et al. [8]. Both of these wavelengths were determined using the HITRAN2012 molecular spectroscopic database [9]. The spectral plots that have been shown in Fig. 4 were made using the HITRAN data base. This database and others (PNNL[10]) will be queried for determining initial efforts. Not only can pressure broadening occur, also pressure shift of wavelengths is known to occur[11] as has been pointed out, and can be seen in Fig. 4, at these conditions individual lines will overlap to form new, broader bands as well as peak center wavelength shifts. Parameters of interest will include line strength, line position, self-broadening coefficient, etc. We have significant experience in conducting shock tube ignition and laser diagnostics (for chemical kinetics experiments) for a variety of combustion systems including methane and syngas[4, 12-16].
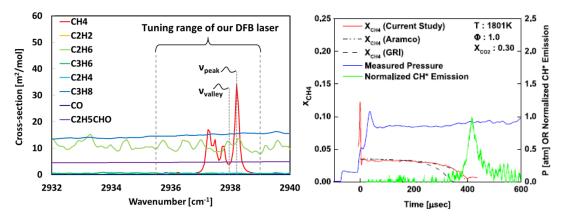
Figure 4: LEFT: The major hydrocarbon species formed located at a wavelength of 3403 nm. Our distributed feedback laser system (from Nanoplus) enables the interference free measurements of methane by means of the peak-minus-valley wavelength scheme at v_{peak} = 2938.24 and v_{valley} = 2938.01 cm^{-1}. It is clear that interfering species can be accounted for in this task. **RIGHT:** Methane time-histories measurements from UCF shock tube [4] and comparisons with GRI 3.0 and Aramco mechanism predictions.

Detailed Chemical Kinetic Mechanism

In order to build a kinetic model for the supercritical fluid, it is necessary to establish the kinetic behavior of reactions over wide pressure and temperature ranges. Simulations of this behavior are capable of (1) showing what physics or chemistry may be missing, (2) testing experimental uncertainties, and (3) providing a view outside the window for experimental observation. Variation of the physical and chemical properties of supercritical fluid upon heating makes kinetic analysis of reacting systems rather complex. Following the transition state theory (TST) the bimolecular reaction A+B→C can be considered as a two-step process: A+B↔TS≠→C. Here the transition state (TS) complex AB is formed in a reversible step and coexists in thermal equilibrium (as governed by Boltzmann statistics) with the reactants, and is converted to the product C irreversibly. The solvent (either supercritical or liquid) can modify predictions of this model in three ways: (1) changing the ability to reach the equilibrium by the reactants and/or TS, (2) shifting this equilibrium, and (3) changing probability of TS to convert to the products [17].

A large body of research is available for methane oxidation, including high-pressure studies with the shock tubes [18-20] and in supercritical water (35-380 bar) [21, 22]. The dominating mechanism for methane oxidation depends strongly on the temperature and pressure regime. Therefore, pressure dependence of the rate coefficient is of critical importance. Although the NUI Galway kinetic mechanism (the latest version of this is the Aramco 1.3), introduced by Curran et al.[18] is widely popular; the kinetic model that includes Troe parameters for many important reactions was developed by Rasmussen et al. [23] and included as a subset into comprehensive model RD2010 [24]. These models demonstrated satisfactory agreement with both the high- and low-pressure experimental data, but ignored the effects of supercritical solvent. We will base our new kinetic model development on C1-C2 subset of RD2010 model.

We will determine the effect of CO_2 on elementary reactions. Other modifications of zero hypothesis were further delineated by Akiya and Savage [25]. Regarding reactions in supercritical water, they identified three main types of effects: (1) chemical effects from the participation of solvent in elementary reaction steps, (2) solvation effects arising from intermolecular interactions between solvent and reacting species, and (3) physical effects such as collisional energy transfer, diffusion limitations, and solvent cage effects. For instance, at larger solvent density ionic mechanisms may play more important role as solvation stabilizes the charged species. Along these lines, each of the key elementary reactions will be simulated to determine the degree of these solvent effects.

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Here we will use well established methods of quantum chemistry (such as CCSD(T) and Density Functional Theory) in order to explore potential energy surface (PES) for the system, including reactants and several CO_2 molecules. New transition states and intermediates will be identified and characterized. If found, zero hypothesis mechanism will be updated with this new information. Also, we will use the activation energies from CCSD(T) theory level to fit the empirical reactive force field parameters, which will be deployed in Molecular Dynamics simulations. We previously conducted computational PES exploration in the systems $NO+O_2$ and $C_2H_4+O_3$ using various theory levels.[26-28]

Computational methods for prediction of solvation thermodynamics are also well established. They include free energy perturbation (FEP), where Molecular Dynamics with empirical force field is being used. The solute is placed in periodical box, filled with solvent (state A), and the equilibrium trajectory is obtained. Next, all the force field parameters, associated with solute, are scaled down by a small fraction, and equilibration is repeated (state B). In a sequence of several steps, the solute gradually disappears into the void. The associated total energies E_A and E_B are substituted into the formula for free energy change:

$$\Delta G(A \rightarrow B) = G_B - G_A = -k_B T \ln \left\langle \exp \left(-\frac{E_B - E_A}{k_B T} \right) \right\rangle_A$$

where T is temperature, k_B is Boltzmann constant, and angular brackets stand for averaging along the trajectory.

Historically, two approaches to atomistic simulation of the reaction rate coefficient were prevalent: classical Transition State Theory (TST), and quantum Rice-Ramsperger-Kassel (QRRK) method, also known as Master Equation approach. TST implies equilibrium (Boltzmann statistical) distribution of the reactants, activated complexes, and intermediates. QRRK implies non-equilibrium situation, when intermediates are "hot" (highly excited in selected vibrational modes) and may be more reactive, than they would be in equilibrium state. While gas phase reactions often proceed coherently, and are better described by non-equilibrium case, reactive systems in solutions experience frequent collisions with the solvent molecules (ultrafast interactions with the bath, also known as solvent friction), and are often assumed to exist in equilibrium and described well by classical (sometimes variational) TST. Clearly, reactions in supercritical solvent fall in between these two limits. In order to describe them accurately, we will use Molecular Dynamics.

Reactions with high activation barriers present challenge for classical Molecular Dynamics (MD). Barrier crossing is an infrequent event and requires very long simulation time to be observed. A variety of accelerated MD protocols have been proposed. One of the techniques, known as Umbrella Sampling/Weighted Histogram Analysis method is capable to estimate the free energy profile along the reaction coordinate called potential of mean force (PMF). In 2003, we used Umbrella Sampling in order to obtain PMF between organic ions in ambient water[29]. The thermodynamic stability for contact and solvent separated ion pairs, and activation barriers between them were obtained (Fig. 5).

Direct MD simulations will also be used to allow detailed analysis of non-equilibrium dynamical properties in the post-transition state region, including caging effect and recrossing rate. Diffusion rates for reactants will be also estimated, in cases where the experimental measurements are missing.

sCO$_2$ CFD Development

A CFD code will be developed in the open source C++ code OpenFOAM with the intention of incorporating a thermo-physical library and chemical kinetics mechanism that are applicable to the super critical regime. The resulting code will be able to simulate reacting and non-reacting CO$_2$ flow through a large range of thermodynamic conditions, as experienced in a theoretical super
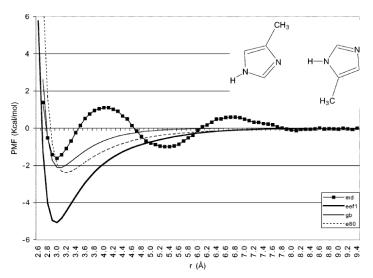

Fig. 5. PMF and effective energy curves for His^0...His^0 molecular pair; r is the distance between the two N atoms [29].

critical engine cycle. Developing a reacting CFD code to run at super-critical conditions requires the following three major modifications; implementation of a real gas equation of state, access to a super critical thermodynamic library and coupling to a sCO$_2$ chemical kinetics mechanism. These three modifications will be accomplished in this work.

The OpenFOAM library suite offers the ability to interpolate thermodynamic data from an external database (generated by REFPROP), choose from a limited selection of real gas EOS' or the ability to develop and easily implement an original real EOS. It is proposed that the effects of the EOS on CFD at super critical conditions are to be analyzed by implementing the discussed real gas EOS' along with their respective closures and comparing simulation results to one another and to measured validation cases. This effort will develop the CFD tools necessary to model super critical CO$_2$ fluids, and then use this tool to evaluate burner concepts.

To allow detailed chemical kinetic mechanisms with reasonable runtimes the compressible Tabulated Conditional Moment Closure (T-CMC) turbulent combustion model, developed by applications, will be used [31, 32]. The premixed version of this model has recently been incorporated into the LES version of OpenFOAM by the present authors[33, 34] and validated against recent PIV and laser measurements from DLR [35]. The T-CMC model, valid under well-mixed conditions, is desired for its ability to solve the chemical kinetics offline and have the CFD access the tabulated solution from the kinetic mechanism, during runtime. Effectively, the T-CMC model run times do not change based on the number of species or

reactions considered in the kinetic mechanism and allows for strong, two-way coupling between turbulent and combustion interactions while preserving low model runtimes which are comparable to non-reacting CFD simulations [23]. If the turbulent and chemical conditions in the super critical regime are not well-stirred, the full CMC model [36-38] is to be employed which is required to solve the chemical kinetics mechanism, along with the flow field equations, during runtime. This typically requires a reduction in the kinetic mechanism to decrease model runtimes which can become excessive (order of weeks) when running the full CMC method in a LES framework with detailed chemical kinetics for sCO_2 which typically involve close to 100 species and 100's of intermediate reactions. However, the full CMC approach makes no assumption of the combustion regime under consideration and accordingly is valid for the entire range of combustion and turbulent time scales which may be essential in simulating the large pressure ranges expected in a theoretical sCO_2 combustor. Once an adequate sCO_2 chemical mechanism has been developed it will be coupled to the CMC code and then validated against available experimental reacting data. Since the CMC model is also based on the general energy equation, the governing equation must also be re-formulated for each EOS employed to model the thermodynamic behavior of the working fluid at super critical conditions.

Summary

In this 3 year project that started in 2015, we focus on the development and validation of a combustion chemical kinetic mechanism for sCO_2 oxy-methane/syngas combustion that can be used for computational fluid dynamic code (CFD) simulations in oxy-combustion development.. Our model will be validated using unique experiments conducted in CO_2 diluted methane/syngas mixtures and for pressures up to 300 bar. The created model will then be implemented in an open source CFD code for industry dissemination. This work will immensely benefit the DOE's goals and will enable industry to tackle challenges associated with oxy-combustion systems in directly heated sCO_2 power cycles. Acquiring experimental data is critical in the development of a sCO_2 detailed kinetic mechanism as there is currently none available for methane at very high pressures approaching 300 bar and for CO_2 diluted methane mixtures even at normal pressures. Through the use of shock tube experiments and laser diagnostics, detailed measurements will be taken for non-reacting and reacting sCO_2 covering a wide range of pressures up to 300 bar. With the data collected and computational chemical calculations, a new mechanism will be created for sCO_2 power cycles covering pressures up to 300 bar. The experienced experimental and combustion modeling team will couple the mechanism to the combustion CFD model and develop/modify CFD sub-models for real gas effects in the super critical regime. The final model will have the ability to study a variety of topics regarding direct-fired sCO_2 oxy-methane combustors and will be the first step in developing an accurate tool for computer design optimization of next generation super critical engine cycles.

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