1 Introduction

1.1 Background

The world relies heavily on combustion to provide energy in useful forms for human consumption; combustion currently represents over 80% of the world energy production [1] and is predicted to decrease in importance only slightly by 2040 [2]. In particular, the transportation sector accounts for nearly 40% of the energy use in the United States and of that, more than 90% is supplied by combustion of fossil fuels [3]. Unfortunately, emissions from the combustion of traditional fossil fuels have been implicated in a host of deleterious effects on human health and the environment [4] and fluctuations in the price of traditional fuels can have a negative impact on the economy [5].

Despite its shortcomings, combustion is currently the only energy conversion mechanism that offers the immediate capability to generate the sheer amount of energy required to run the modern world. Since we cannot eliminate combustion as an important energy conversion method, we must instead ameliorate the shortcomings of a primarily combustion-based energy economy. A two-pronged approach has developed to achieve the necessary improvements. These prongs include: 1) development of new fuel sources and 2) development of new combustion technologies. First, using new sources of fuel for combustion-based energy conversion can reduce the economic impact of swings in the price of current fuels, in addition to potentially reducing emissions. Second, using new combustion technologies can reduce harmful emissions while simultaneously increasing the efficiency of combustion processes, thereby reducing fuel consumption.

Many new sources of fuels have been investigated recently. The most promising of these in the long term are renewable biological sources, which are used to produce fuels known as biofuels. The advantage of biofuels over traditional fuels lies in their feedstocks. Whereas traditional fuel feedstocks generally require millions of years to be produced, biofuel feedstocks are replenished on an annual basis. Furthermore, biofuels offer the potential to offset carbon emissions created from their combustion by reusing the emitted carbon to grow the plants from which the fuels are produced.

However, the combustion properties of biofuels may be substantially different from the traditional fuels they are intended to replace. This makes it difficult to quickly switch the energy economy to biofuels and necessitates medium-term investigation of alternative sources for traditional fuels. These sources include shale oil and liquefied coal, which have different chemical compositions than traditional fuel sources and therefore fuels made from these alternative sources have different combustion properties. Collectively, all of these fuels created from non-traditional sources are known as alternative fuels.

In addition to new fuel sources, new engine technologies are rapidly being developed. These include engines capable of operating in favorable combustion regimes, such as so-called Low Temperature Combustion (LTC) engines and Homogeneous Charge Compression Ignition (HCCI) engines. These devices avoid regions in the temperature-equivalence ratio space where combustion generates a large amount of emissions and operate in regions where efficiency is maximized and emissions are reduced. Other devices, such as the well-known catalytic converter, operate on the exhaust after it leaves the cylinder to improve emissions characteristics.

Neither of these approaches is able to mitigate all of the negative impacts of combustion by itself. By switching to biofuels but retaining the same engines, the efficiency and emissions targets may not be met; by only developing new engines, our sources of fuel will continue to cause economic distress, turmoil, and negative effects on the environment. It will take a concerted effort to bring these two pathways of innovation together.

Unfortunately, there are many roadblocks on the way to combining new fuels in new engines. For instance, one can imagine the design and testing process of new engines and fuels becoming circular: the "best" alternative fuel should be tested in the "best" engine, but the "best" engine depends on which is selected as the "best" alternative fuel. One way to cut this circle short is by employing computer-aided design and modeling of new engines with new fuels to design engines to be fuel-flexible. Accurate and predictive models of combustion processes can be used to computationally test the efficacy of new technologies and fuels before they undergo expensive real-world testing. The key to this process is the development of accurate and predictive combustion models.

Substantial work has been put forth recently to develop and validate predictive combustion models for several alternative fuels. These studies include calculation and measurement of reaction rate coefficients, measurement of global and local combustion properties, and development of model construction methodologies. Nevertheless, much of the work is still ongoing, and there is substantial room for extending the state-of-the-art knowledge, especially at high-pressure conditions relevant to combustion in engines.

A combustion model for the combustion of a given fuel in a given device must necessarily accurately model the complete interaction of the operating elements of the device. This includes sub-models for the chemical reactions that the fuel and oxidizer undergo as well as the interaction of the fuel/oxidizer mixture with the operation of the device. The first of these is known as a chemical kinetic model or reaction mechanism; the second typically includes such effects as turbulence interaction, heat transfer, liquid spray dynamics, fluid mechanics, etc., each of which are typically modeled independently.

Chemical kinetic models for the combustion of large molecules are typically built in a hierarchical fashion, as described by Westbrook and Dryer [6]. That is, the model for the combustion of heptane contains the model for the combustion of hexane added to the model of combustion for pentane, and so on down to the models for hydrogen and carbon monoxide combustion. Therefore, it is important to thoroughly validate the models for smaller species while building models of higher hydrocarbons and other molecular types. Work has been ongoing to explore the chemistry of small molecules for decades. Notable recent kinetic mechanisms to emerge from this work include the GRI-Mech series of mechanisms (most recently, version 3.0 [7]), USC-Mech v2 [8], and the AramcoMech series of mechanisms, most recently version 1.3 [9].

In addition, validation of kinetic models for the combustion of larger fuels has proceeded in parallel with the small molecule chemistry. Given their projected importance to combustion, one focus of the larger molecule work has naturally been on biofuels. These biofuels typically include chemical species such as alcohols and esters – neat alcohols can be used as fuels, while esters are typically found as components of biodiesel fuels. A review by Kohse-Höinghaus et al. [10] covers

much of the experimental data available until 2010. Since then an enormous amount of data has been produced for both alcohols and esters. Since the focus of this study is on alcohols, I will highlight alcohols in the following sections.

Model construction and validation has also been focused on alternative "traditional" fuels, that is, fuels that are chemically similar to traditional fuels but produced from alternative sources such as shale oil or coal liquefaction. Traditional fuels and alternative "traditional" fuels typically contain hundreds or thousands of chemical components. This makes building and using models containing every species present in the fuel intractable on current computer hardware. Therefore, a more useful approach to building models for these fuels is to define a surrogate fuel. Surrogate fuels are made of a limited number of chemical components to ensure that model building and use are tractable, but the components are chosen so that the surrogate fuel faithfully reproduces the physical and chemical properties of the real fuel.

Much progress has been made recently to construct surrogates for typical transportation fuels. For instance, work on diesel surrogate formulation has recently been reviewed by Pitz and Mueller [11], work on gas turbine fuel surrogates has been briefly summarized by Dooley et al. [12], and work on gasoline surrogates has been summarized in the work of Anand et al. [13] and Pitz et al. [14]. One typical component class in the surrogate formulations is a cycloalkane, due to this class' presence in nearly all transportation fuels [14–17]. One particular cycloalkane, methylcyclohexane (MCH), has been suggested in several surrogate formulations, including those by Bieleveld et al. [18] and Naik et al. [19]. Recent work on MCH combustion will also be highlighted in the following sections.

Due to its relevance in predicting the performance of a fuel in existing and advanced engines, ignition delay is a very common measure of the global performance of a kinetic mechanism. Ignition delays for homogeneous systems are typically measured in shock tubes or RCMs, where the effects of fluid motion and turbulence are generally minimized.

1.2 Combustion Chemistry of Alcohols

Among the alcohols being considered as biofuels, two criteria are typically used to judge the suitability of a species: 1) its ease of production and 2) its potential as a "drop-in" replacement for current fuels. Because of these criteria (among others), much research recently has focused on the isomers of butanol, the C_4 alcohols, and *i*-pentanol, a C_5 alcohol. This is because these fuels are easy to produce by a number of biological pathways [20] and offer similar properties as gasoline for use in typical automotive transportation applications.

One of the most common biofuels currently in use is ethanol (C_2H_6O). Although ethanol is ubiquitous at gasoline pumps, it suffers from several disadvantages that suggest it needs to be replaced [21]. In particular, ethanol has a much lower energy density than gasoline, reducing volumetric fuel economy, and ethanol is typically produced from crops that would otherwise be used as food sources [22].

n-Butanol has recently been identified as one of a suite of so called "second generation" biofuels intended to supplement or replace the "first generation" biofuels currently in use, such as ethanol [23, 24]. The second generation biofuels will help alleviate some of the problems identified with the first generation biofuels, including concerns about feedstocks. In addition to the normal (*n*) isomer, there are three other isomers of butanol— *s*-, *i*-, and *t*-butanol. Biological production pathways have been identified for *n*-, *s*-, and *i*-butanol [24, 25], but *t*-butanol is a petroleum derived product. Nevertheless, *t*-butanol is currently used as an octane enhancer in gasoline.

In the last five years, research into the combustion characteristics of the isomers of butanol has exploded, so exemplary references are provided here except for the articles of particular interest to this work. In addition to applied engine research [26–28] fundamental combustion measurements have been made using many different systems. These include laminar flame speeds [29], jet-stirred reactor chemistry [30], low-pressure flame structure [31, 32], atmospheric pressure flame structure [33], pyrolysis [34], flow reactors [35], and ignition delays, which will be discussed in more detail.

Several studies of ignition delay of the butanol isomers have been conducted in both shock tubes and RCMs, including work in shock tubes by Black et al. [36], Heufer et al. [37], Moss et al.

[38], Noorani et al. [39], Vasu et al. [40], Vranckx et al. [41], Vasu and Sarathy [42], Zhu et al. [43], Zhang et al. [44], Yasunaga et al. [45], and Stranic et al. [46] and work in RCMs by Karwat et al. [47], Weber et al. [48], and Weber and Sung [49].These studies have covered a wide range of temperature-pressure regimes, from 1–90 bar and 675–1800 K.