

# 1 Introduction

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 attempt to 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.

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].