13th U.S. National Combustion Meeting
Organized by the Central States Section of the Combustion Institute
March 19–22, 2023
College Station, Texas

Effect of Products of Catalytic Oxidative Coupling on the Laminar Burning Velocity of Methane

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Abstract: Methane (CH_4) can be converted to higher molecular weight hydrocarbons, including ethylene and ethane, by a process known as the oxidative coupling of methane (OCM). From a combustion perspective, the inclusion of C_2 species dramatically affects several fundamental characteristics including flame thickness, ignition properties, instability formation, and front propagation. From a practical perspective, the inclusion of ethane (C_2H_6) and ethylene (C_2H_4) could enable the use of methane, the primary component of natural gas, in previously inaccessible engine-operation regimes. This study expands on previous experimental and computational work investigating the laminar burning velocity of binary blends of C_2 species with methane by observing spherically expanding flames of tertiary mixtures in a constant volume combustion chamber (CVCC). Furthermore, a computational approach is employed to extend the analysis of ethane-ethylene-methane blends into a wider compositional space and as a means of comparing existing reaction mechanisms to the obtained experimental results. Implications with respect to reported OCM products are discussed in relation to engine operating modes.

Keywords: oxidative coupling, methane, natural gas, compression ignition, laminar burning velocity

1. Introduction

Natural gas (NG) has seen a significant increase in global usage over the last decade, largely owing to its lower carbon intensity compared to other fossil fuels and an evolution in efficient extraction methods [1]. When it comes to reducing harmful emissions (particulate matter, carbon dioxide) from internal combustion engines, methane, the most prevalent species found in NG, has an edge over other conventional fuels [2]. Furthermore, it enables SI engines to achieve a higher compression ratio because of its intrinsic knock-resisting properties. But NG alone is not a viable option as a fuel for CI engines due to its low ignition reactivity from the lack of carbon-carbon bonds [3]. To counter this effect, dual fuel injection systems have been incorporated in CI engines where a pilot fuel (e.g. diesel fuel) is injected along with NG [4].

Previous studies indicate that higher-carbon number hydrocarbons such as ethane (C_2H_6), ethylene (C_2H_4), and propane (C_3H_8) can work as effective ignition enhancers for NG by increasing the mixture reactivity. Data from Shock tube [5–7] and jet stirred reactor experiments [8] along with simulation studies [9] all point towards the fact that the addition of such gaseous fuels (C_2 hydrocarbons) increases the ignition proclivity of methane-air mixtures. As such, methods that

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convert a small portion of methane in NG flow into more reactive species have recently gained interest amongst researchers. These include approaches like Partial Oxidation of methane (POx) [10] and Oxidative Coupling of Methane (OCM).

OCM is a fuel pre-treatment that converts methane into higher molecular weight hydrocarbons, unlike POx which converts methane into lighter syngas species. OCM first gained traction as an alternative process for the industrial synthesis of ethylene from NG [11]. This heterogeneous catalytic reaction was first discovered by Keller and Bhasin [12] in 1982. In this method, methane goes through H-abstraction on a charged oxygen surface followed by a gas phase reaction of methyl radicals producing ethane (C_2H_6). Ethane then goes through gas-phase dehydrogenation to produce ethylene (C_2H_4) [13].

Langille et al. [14, 15] proposed using OCM to convert methane into molecules of increased reactivity for various applications. They showed, both experimentally and through numerical simulations, that the ignition properties of methane-air mixtures were enhanced by the addition of C_2 species. Results also showed that the ignition temperature of the fuel blends decreased significantly with the increase of ethylene and ethane content in the mixture.

The addition of C_2 species to methane not only increases the mixture's reactivity, it also increases the laminar burning velocity (LBV). LBV is not only a fundamental property of a fuel mixture's composition, temperature, and pressure, but also a convenient tool for validating reaction mechanisms. It also has significant implications for combustion control strategies of practical applications. All of these reasons provide the necessary motivation for analyzing the burning velocities of methane and C_2 fuel blends. Early studies analyzed the laminar burning velocities of binary methane/C_2H_X blends [16–19], while a paper by Cho et al. [11] only recently simulated the laminar burning velocity of a ternary $CH_4 - C_2H_4 - C_2H_6$ blend.

This study focuses on the numerical simulation of laminar flame speeds of various ternary blends of $CH_4 - C_2H_4 - C_2H_6$ over a range of equivalence ratios using GRI Mech 3.0 [20] and Aramco 1.3 [21] mechanisms. In order to validate which of the two mechanisms predicts the velocity more accurately, two particular blends with the highest velocity difference and the blend tested by Cho et al. [11] were experimentally examined in a constant volume combustion chamber (CVCC) equipped with Z-type Schlieren visualization.

2. Methodology

2.1 Numerical Simulation

Laminar burning velocity (LBV) is an important parameter that affects combustion duration [22] in applications, such as the flame propagation in an internal combustion engine. This study utilizes two mechanisms, GRI Mech 3.0 and Aramco 1.3, to calculate the LBV over a range of equivalence ratios and fuel blends of $CH_4 - C_2H_4 - C_2H_6$. GRI Mech 3.0 is one of the widely used mechanisms for natural as; it contains 53 species and 325 reactions. The Aramco 1.3 mechanism is a more detailed mechanism with 346 species. Both mechanisms include C_2 hydrocarbons. It has been shown in the literature [23] that for pure methane fuel, GRI 3.0 yields the best performance at lean and stoichiometric conditions when predicting LBV whereas Aramco 1.3 delivers more accurate results at fuel-rich conditions. Additionally, the Aramco 1.3 mechanism is more suitable for fuel blends where higher number carbon fuels (C_2H_4, C_2H_6) are present [21].

The LBV calculations were carried out for 66 different ternary blends of $CH_4 - C_2H_4 - C_2H_6$ at

each equivalence ratio (ranging from $\Phi = 0.5$ to $\Phi = 1.5$ with an interval of 0.1) using GRI Mech 3.0 in Cantera 2.6. All these blends were again tested using Aramco 1.3 for three equivalence ratios- $\Phi = 0.8$, 1 and 1.2. These values were compared with performed experimental cases and literature values to decide which mechanism is more suited to predicting LBV at different equivalence ratios and fuel blend configurations.

2.2 Experimental Setup

An optically-accessible constant volume combustion chamber (CVCC) with Z-type Schlieren visualization and central ignition is used to record spherically expanding flames with a high-speed camera (Edgertronic SC2+). The complete setup and experimental procedure have been described in detail in a previous publication [24]. The chamber and supply lines are vacuumed down to 400 millitorrs before introducing any gas to the system. The gases ($CH_4, C_2H_4, C_2H_6, O_2,$ and N_2) are supplied to the chamber in increasing order of partial pressure in the mixture. The three blends that have been experimentally tested in this study have the following initial configuration which is shown in Table 1.

Table 1: Initial conditions and fuel blend configuration of the cases tested.

Case	Gas Blends			Equivalence Ratio	Initial Pressure	Initial Temperature
	CH_4 (%)	C_2H_4 (%)	C_2H_6 (%)			
1	90	1	9	1	1 bar	298K
2	90	9	1	1	1 bar	298K
3	93.8	2.7	3.5	1	1 bar	298K

The images recorded using the Schlieren setup are digitally processed to calculate the unstretched flame speed and laminar burning velocity. This method has been discussed in detail in previous publications [25–28].

3. Results and Discussion

3.1 GRI Mech 3.0

The ternary heat map of the laminar burning velocity of $CH_4 - C_2H_4 - C_2H_6$ blends at an equivalence ratio of $\Phi = 1$ is shown in Figure 1. This is based on the simulation data for a total of 66 blends denoted by the intersects of three iso-axis (Methane, CH_4 ; Ethane, C_2H_6 ; Ethylene, C_2H_4). This plot shows the shifts in LBV for any composition of the three fuels, unlike the earlier studies which only focused on the binary blends of methane/ethane and methane/ethylene. According to the ternary plot, the LBV of these blends shows an upward trend with increasing C_2 fuels in the blend. As expected, the fastest blend out of all the cases is the one with the highest amount of C_2H_4 present and the slowest is the pure methane sample.

Furthermore, the increase in LBV is more sensitive to the presence of ethylene compared to ethane, which supports the findings by Ravi et al. [19]. The enhancement of LBV of methane with the addition of C_2H_X is primarily an Arrhenius effect, which is more dominant with the presence

of ethylene compared to ethane. Also, ethane goes through a radical chain mechanism at certain temperatures which slows it down compared to ethylene [29].
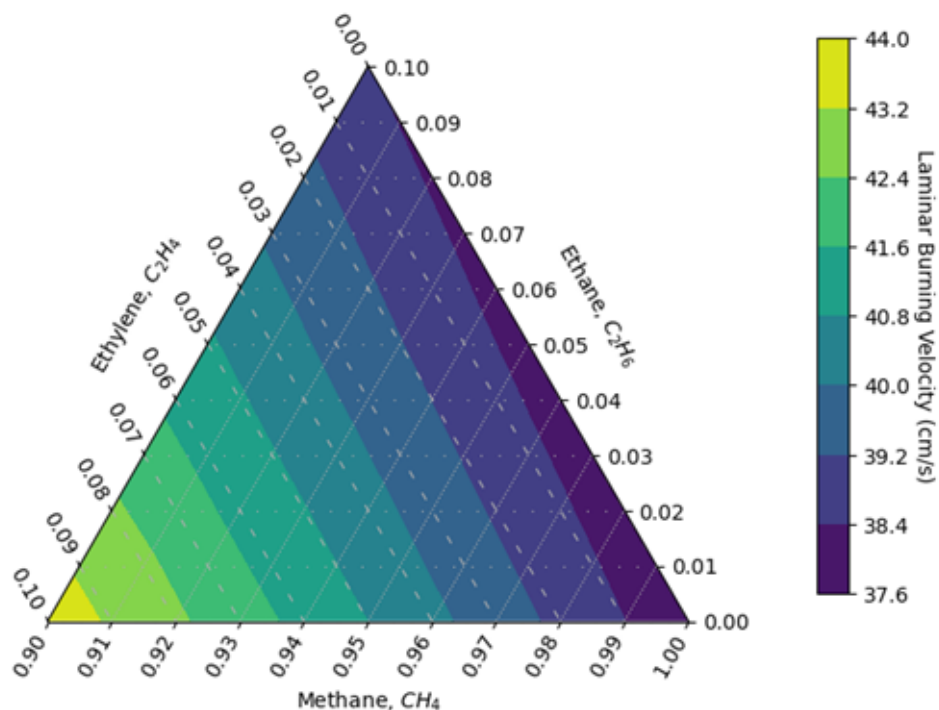

Figure 1: LBV of methane, ethylene and ethane blends at $\Phi = 1$

This same simulation was performed for 11 different equivalence ratios (ranging from $\Phi = 0.5$ to $\Phi = 1.5$) to observe its effect on LBV. Figure 2 displays 5 different equivalence ratios to highlight the overall trend. It is interesting to note the at $\Phi = 1$, the change in LBV is almost parallel to the iso-ethylene line at a higher concentration of C_2H_4. However, the shift in LBV is more noticeable in lower iso-ethylene zones. As the mixture moves away from the stoichiometric ratio, this effect is also predicted at the higher iso-ethylene blends. The subtle color changes at the lower and upper ranges of the equivalence ratio also suggest that the shift in LBVs is mild in the flame lean and flame rich mixtures compared to the stoichiometric blends.

3.2 Comparison with Aramco 1.3

While GRI Mech 3.0 is primarily used for natural gas and CH_4, the Aramco 1.3 was also chosen for this study because it starts with a C_1 sub-mechanism and grows by the inclusion of larger carbon species such as ethane, ethylene, acetylene, and higher $C_3 - C_4$ and oxygenated species. Furthermore, this mechanism has been validated against a large array of experimental measurements including data from shock tubes, rapid compression machines, flames, jet-stirred reactors, and plug-flow reactors.

The Aramco 1.3 mechanism was used to simulate the LBV of similar blends at three equivalence ratios $\Phi = 0.8$, 1 and 1.2 and the differences were calculated. Figure 3 contains the difference between the two LBV values generated by the two different mechanisms. It is evident that the
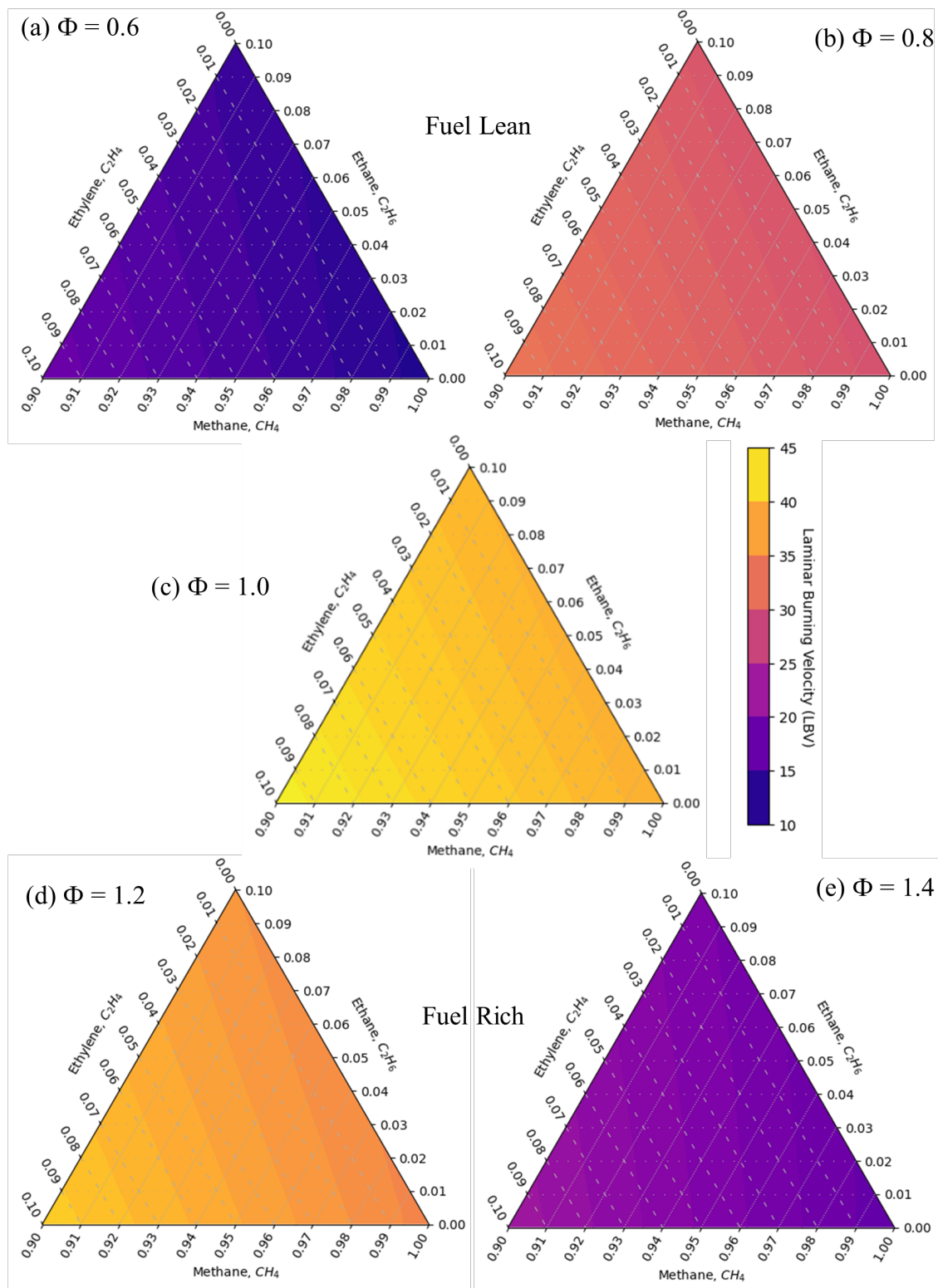
Figure 2: LBV of methane, ethylene and ethane blends at equivalence ratios of (a) Φ = 0.6, (b) Φ = 0.8, (c) Φ = 1.0, (d) Φ = 1.2, (e) Φ = 1.4

mechanisms show different values for the same blend at different equivalence ratios. The difference stays within 7.5% in all the cases tested. Furthermore, both stoichiometric and lean conditions follow similar trends in that the difference is the highest in the blends with more ethylene and the least when the blend is high in ethane content. Furthermore, the Aramco 1.3 mechanism always predicted a lower value of LBV for a particular blend when compared to the value generated by GRI Mech 3.0 at lean and stoichiometric conditions.
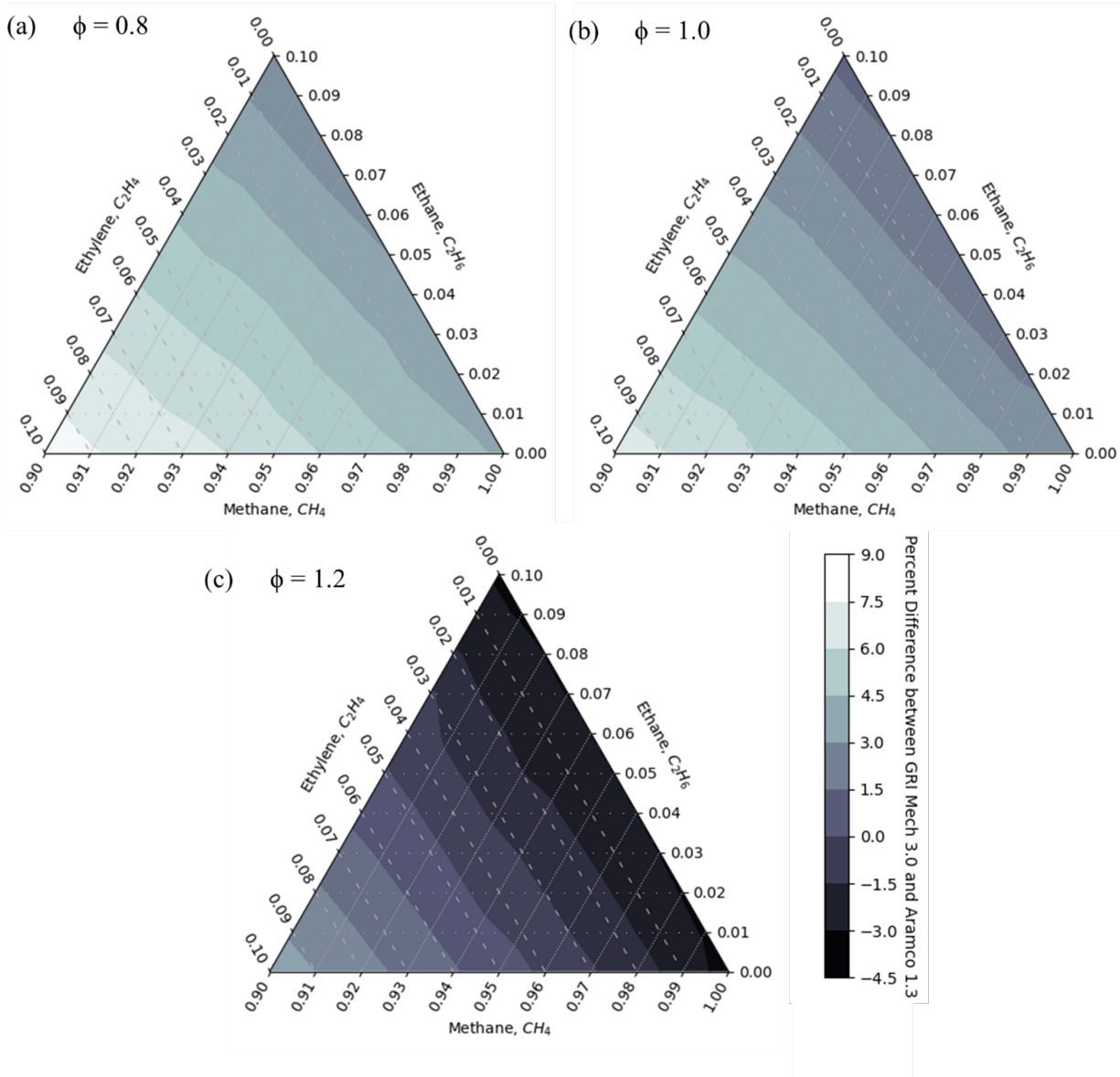

Figure 3: Percentage difference in the predicted LBV values by GRI Mech 3.0 and Aramco 1.3 at equivalence ratios of (a) $\Phi = 0.8$, (b) $\Phi = 1.0$ (c) $\Phi = 1.2$

However, this trend flips when the rich cases are considered, and Aramco 1.3 starts predicting higher LBV values compared to GRI Mech 3.0 for low ethylene blends. The difference becomes smaller as ethylene content is increased gradually and both mechanisms start predicting almost

the same value at around the iso-ethylene lines of 0.04 and 0.05. When the ethylene content is increased further, the delta starts to creep up again as GRI Mech 3.0 again predicts a higher value of LBV.

3.3 Validation with experimental and literature data

Three specific blends, shown in Table 1, were chosen to perform optically accessible CVCC experiments. The first two blends represent two extreme points in the ternary plot where the methane is constant at 90% but ethylene concentrations are 1% and 9% respectively. The third blend is identical to that from Cho et al. [11] which was generated from a methane stream over a benchtop catalyst reactor.

Figure 4 shows the different stages of flame front propagation of a spherically expanding flame inside the optically accessible CVCC. Since all the cases had a very similar LBV, the difference is almost negligible to the naked eye and almost impossible to have a qualitative assessment. Hence only the blend of 0.9 CH_4 - 0.09 C_2H_4 - 0.01 C_2H_6 is shown in Figure 4.
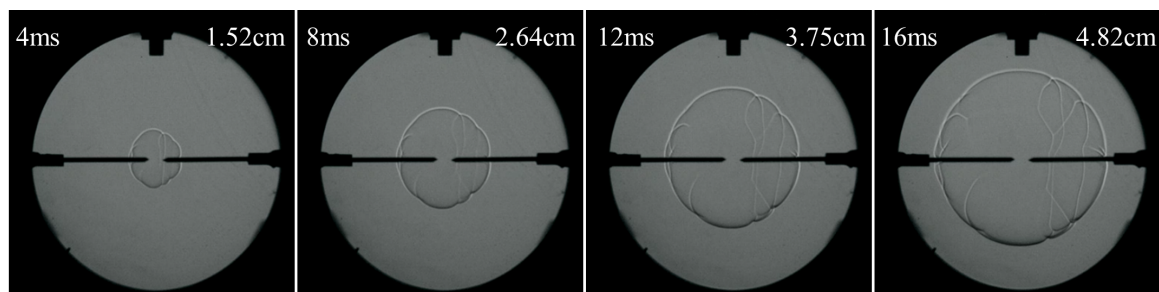

Figure 4: Schlieren images of propagating flame inside CVCC from 0.9 CH_4 - 0.09 C_2H_4 - 0.01 C_2H_6 blend at $\Phi = 1$ and an initial pressure of 1 bar.

Table 2 presents the different values of LBV calculated from the Schlieren experiments, GRI Mech 3.0, and Aramco 1.3. It is evident from the experimental data that both the blend with lowest and highest C_2H_4 content fall closer to the Aramco 1.3 dataset as it incorporates the thermal properties of the higher C_2 species.

Table 2: Comparison amongst experimental and numerical LBV values

Blend	Laminar Burning Velocity (cm/s)		
	Schlieren	Gri Mech 3.0	Aramco
0.9 CH_4- 0.01 C_2H_4- 0.09 C_2H_6	34.82	38.88	38.15
0.9 CH_4- 0.09 C_2H_4- 0.01 C_2H_6	37.42	43.08	40.69
0.938 CH_4- 0.027 C_2H_4- 0.035 C_2H_6	35.56	36.5	37.5

The third blend generates a flame with an LBV of 35.56 cm/s, which falls closer to the value from GRI Mech 3.0. This may be attributed to the fact that during the extrapolation of flame speed vs stretch rate curve, a linear model was selected instead of a non-linear one. This could be reduced by opting for a non-linear model for the stretch-rate calculation, but further considerations are needed before adopting this methodology.

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4. Conclusions

Ethane and ethylene are two of the major components generated by OCM, which increases the re-activity of methane, thereby improving thermal efficiency of IC engines. In this study, a numerical approach was taken to understand how different blends of these three species affect the laminar burning velocity of a fuel mixture. Three selected ternary blends were tested in a CVCC to compare the LBV data from the two different mechanisms tested in this study and past literature. The conclusions can be summarized as follows:

- Both GRI Mech 3.0 and Aramco 1.3 predicted that the fastest blend was 90% CH_4 – 9% C_2H_4- 1% C_2H_6 for all the equivalence ratios tested whereas 90% CH_4 – 1% C_2H_4- 9% C_2H_6 was the slowest.

- At stoichiometric conditions, the shift in LBV values were parallel to the iso-ethylene lines at its higher percentages. This means that one would not see a big difference in LBV with changing fuel blends while keeping ethylene percentage constant. But as the presence of ethylene in the blends reduces, the LBV sees a significant shift along the iso-ethylene lines, which indicates that the percentage of methane and ethane in the blends from that region (top and right side of the pyramid) has a significant impact in the calculated LBV.

- Upon moving away from the stoichiometric mixtures, this trend is noticeable even in the higher ethylene ranges and a shift is observed in the LBV values along the iso-ethylene lines.

- Aramco 1.3 predicts the LBV of all the blends to be lower than that predicted by GRI Mech 3.0 at fuel lean and stoichiometric conditions. At the fuel rich conditions, the values calculated by Aramco 1.3 are higher than that by GRI Mech 3.0 at low ethylene regions (0% - 4%) then again starts predicting lower LBVs at higher ethylene (greater than 5%) regions.

- The difference in the LBV values predicted by the two mechanisms is the highest at lean conditions with a mean of 4.71% at $\Phi = 0.8$ (across the whole pyramid) and lowest at rich conditions with a mean of 1.74% at $\Phi = 1.2$.

- At $\Phi = 1.2$, the two mechanisms predict almost similar values around the iso-ethylene line 0f 0.05. It implies that the blends with about 5% constant ethylene have similar LBV values predicted by both the mechanisms even when methane and ethane percentages are changed.

- Data from the Schlieren experiments support the theory of high ethylene percentage blends having higher laminar burning velocity as the blend with 1% ethylene propagated inside the CVCC with a LBV of 34.76 cm/s. The 9% ethylene blend had LBV of 37.42 cm/s with an increase of 7.65% which comes closest to the predicted values from Aramco 1.3 with a 6.65% increase between the similar two blends. GRI Mech 3.0 had a higher delta between LBV values of these two blends presenting an increase of 10.81%.

- The third blend had a LBV of 35.56 cm/s, which is higher than that of the 1% ethylene blend but less than the 9% ethylene blend. The value being closer to the LBV of the blend with lower ethylene content also supports the findings from the other simulations performed

in this study. It is interesting to note that this value falls closer to the LBV from literature generated by GRI Mech 3.0 (a difference of 2.64%) compared to the Aramco 1.3 generated value with a delta of 5.45%. Choosing a more accurate non-linear extrapolation method for flame speed vs stretch rate curve could shift it closer to the Aramco 1.3 data.

5. Acknowledgements

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