Reduced Reaction Mechanisms for Ethanol under Ultra-lean Conditions in Internal Combustion Engines

Carla S. T. Marques* and José R. M. da Silva

ABSTRACT: Chemical kinetics models for ethanol under ultra-lean engine conditions were evaluated to couple with CFD multidimensional simulations of a spark-assisted homogeneous charge compression ignition (HCCI) rotary engine. Five reduced reaction sets proper for CFD simulations and two detailed reaction mechanisms for comparison were tested by simulating ignition delay times, laminar flame speeds, and a single-cycle HCCI engine with virtual piston dimensions. The simulated results of the new mechanism with 188 reactions were well-fitted to both experimental ignition delay times for ultra-lean ethanol/air conditions and laminar flame speeds at high pressures. This reaction set resulted in better-simulated ignition delay times at 30 and 40 bar for ultra-lean ethanol/air conditions than other chemical kinetics models. Maximum temperatures and pressures of 2500–2580 K and 280–289 bar, respectively, were observed for hydrous ethanol/air under ultra-lean conditions in HCCI engine. In addition, the simulation results of the HCCI ethanol engine presented high pressure rise rates of 8–26 bar/CAD at 3600 rpm. These results indicated that the engine test should be carried out at 2500 rpm with 2 bar of boost pressure for CFD model calibration with the new optimized reaction mechanism.

1. INTRODUCTION

The increasing concerns of global warming and the growing energy demands are causing many regions of the world to expand their energy matrix using alternative and renewable sources of energy. Among these renewable fuels, ethanol is a primary alternative to fossil fuel and has been widely applied as an additive in gasoline engines in the USA and Europe and as a pure fuel in spark-ignition (SI) engines in Brazil, where engines are more resistant to misfires and knock owing to the higher compression ratio as compared to similar reciprocating engines. During each full rotation of the rotor in a Wankel engine, three combustion events take place that result in improved performance at high speeds with smooth engine operation. Moreover, Wankel engines are a type of rotary engine that is simpler, more compact, has less moving parts, and a higher power-weight ratio as compared to similar reciprocating engines. Generally, these types of rotary engines produce a lower amount of noise and vibrations and have lower power losses than conventional reciprocating engines. During each full rotation of the rotor in a Wankel engine, three combustion events take place that result in improved performance at high speeds with smooth engine operation. Moreover, Wankel engines are more resistant to misfire and knock owing to the physical separation of the combustion chamber from the exhaust port and the nonexistence of the exhaust valve; these geometric characteristics help prevent pre-ignition and backfire in the engine. However, there are some specific drawbacks, for example, they consume a large amount of fuel, they have low thermal efficiency, and they emit high levels of CO and unburned hydrocarbons.

Recent studies employing different methods such as direct-injection stratified charge and turbocharged systems and changes in the geometric design parameters have been carried out with goals of improving Wankel engine efficiency and reducing pollutant emissions. Another strategy that has been proposed to this end is the HCCI (homogeneous charge compression ignition) mode that decreases the heat losses to the combustion chamber and results in cleaner combustion. Furthermore, numerous studies have considered alternative fuels such as hydrogen, natural gas, ethanol, butanol, whose specific chemical properties improve the combustion process in these rotary engines. Ethanol-fueled Wankel engines enhance the thermal efficiency and lower the unburned hydrocarbon emissions owing to the higher flame propagation velocity and reduction of flame quenching by...
is still required for more complete ethanol combustion. Engine optimization is still required for more complete ethanol combustion.

The advantages of using ethanol as a fuel have motivated the development of reaction mechanisms for better understanding of its combustion chemistry and to be incorporated into CFD multidimensional simulations, which can help to establish new engine designs and optimize engine performance. The chemical kinetics and growth of the radical pool are fundamental for ignition, propagation, and knock predictions in the combustion processes.

In this work, certain reduced chemical kinetics for ethanol combustion were evaluated to find those suitable to the CFD multidimensional simulations of a spark-assisted HCCI rotary engine fueled with ethanol under ultra-lean conditions. The 0-D and 1-D simulations with reduced and detailed reaction sets were carried out to simulate ignition delay times, laminar flame speeds, and a single-cycle HCCI engine by applying CONVERGE CFD software.

2. COMPUTATIONAL METHOD

2.1. Reaction Mechanism

Over the past decades, several reaction mechanisms have been proposed for ethanol combustion. However, under ultra-lean and high-pressure conditions, few reaction mechanisms are available.

Table 1. Reaction Mechanisms for Ethanol Combustion

| mechanism | number of species | number of reactions | P (bar) | T (K) | Φ |
|-----------|------------------|---------------------|---------|-------|---|
| AramcoMech 3.0 | 581 | 3037 | 10/25/50 | 825–985 | 0.3/0.5/1.0 |
| Mittal et al. | 113 | 710 | 1/2/3.4/4.6 | 1120–1700 | 0.5/1.0/2.0 |
| San Diego | 58 | 270 | 1.8 | 750–2400 | 0.3–2.0 |
| Saxena | 59 | 288 | 20/30/40/50 | 770–1430 | 0.3/0.5 |
| Olm et al. | 47 | 251 | up to 91.2 | 358 | 0.5–1.0 |
| this work | 43 | 188 | 10/12 | 358 | 0.5–1.0 |
| this work | 44 | 205 | 20/30/40/50 | 770–1430 | 1.0 |

Table 2. Reactions Added to the Base Mechanism without NOx Chemistry

| reaction | A | n | E_a | refs |
|----------|---|---|-----|-----|
| r19. C_2H_5OH + HO_2 = C_2H_4OH + H_2O_2 | 7.864 × 10^9 | 1.119 | 32,534.24 | 28 |
| r20. C_2H_5OH = C_2H_5 + OH | 8.10 × 10^16 | –11.30 | 111,053.40 | 28 |
| r31. CH_3OH + O_2 = CH_2OH + HO_2 | 3.99 × 10^{-2} | 4.30 | 15,333.40 | 27 |
| r32. CH_3OH + HO_2 = CH_2HCHO + HO_2 | 6.47 × 10^{-7} | 5.30 | 10,533.10 | 27 |
| r9. 2HO_2 = H_2O_2 + O_2 | 1.6048 × 10^{-3} | 0.00 | 7825.6 | 28 |
| r14. H_2O_2 (+M) = OH + OH (+M) | 2.00 × 10^{12} | 0.90 | 48,749.0 | 30 |
| r40. CH_3CH_2O + M = CH_4 (+M) | 5.60 × 10^{14} | –5.90 | 12,732.76 | 28 |
| r52. CH_3 + H (+M) = CH_4 (+M) | 1.270 × 10^{16} | –0.630 | 192.75 | 28 |
| r138. CH_3OH + O_2 = CH_3OH + HO_2 | 3.580 × 10^{9} | 2.30 | 42,764.50 | 43 |

In this work, certain reduced chemical kinetics for ethanol combustion were evaluated to find those suitable to the CFD multidimensional simulations of a spark-assisted HCCI rotary engine fueled with ethanol under ultra-lean conditions. The 0-D and 1-D simulations with reduced and detailed reaction sets were carried out to simulate ignition delay times, laminar flame speeds, and a single-cycle HCCI engine by applying CONVERGE CFD software.
Furthermore, the combustion characteristics under ultra-lean conditions (Φ = 0.3–0.6) are very different from the other combustion conditions, owing to the low-temperature combustion and the burning velocity. Therefore, for evaluation and comparison, we selected the reaction sets (validated at ultra-lean and high-pressure conditions) suitable for integration into multidimensional CFD simulations with a low computational cost and yielded predictions well-fitted to experimental data of the engine conditions of interest. Also, two recent detailed reaction mechanisms,27,43 which exhibited excellent agreement with experimental data of ethanol combustion,25,30 were applied for comparative analysis. Furthermore, two new updated and optimized reaction sets from previous studies25,44 were also applied. The reaction mechanisms applied to the 0-D and 1-D simulations with the range that they should be preferably used. Owing to the problems in establishing the right convergence parameters, the reaction set from Olm et al. (2016) could only be used in the ignition delay simulations. The new reaction mechanisms proposed here were developed by adding elementary reactions to a base reaction mechanism without considering NOx chemistry.25,44 The base reaction mechanism is composed of 43 species and 179 reactions. Nine reactions were added to the base reaction set to build the 188-reactions mechanism and twenty-four reactions were added to the base mechanism to obtain the 205-reactions mechanism, including those nine initially added, as shown in Table 2. Moreover, the Arrhenius rate constant (k) parameters predominantly from Olm et al. (2016)28 and other reaction sets27,30,42,43 were used to update the reaction mechanisms. Two reactions each for ethanol decomposition (r19 and r20) and ethanol/HO2 reaction (r31 and r32) were included, accounting for their importance in high-temperature ignition and high-pressure combustion of ethanol.39

Mittal et al.7 reported a noticeable improvement in the ignition delay time predictions when the Arrhenius rate constant parameters of the C2H5OH + HO2 reactions were changed (r31 and r32), which motivated us to use the same parameters. Furthermore, the reactivity of ethanol combustion at high pressures is controlled by termination reactions.25 Therefore, the reaction that decreases the reactivity was duplicated (r9), whereas one that increases the reactivity was included (r14).

In addition, some important reactions to the main path of ethanol combustion and ignition27,28 were employed (r40, r52, and r138).

As acetaldehyde chemistry27,30 is very important in high-pressure ethanol combustion, another reaction set was developed from the first 188-reactions mechanism by adding the CH3HCO species and its corresponding reactions, which were adopted by Olm et al.28 (Table 2). The simulation results presented in the following sections demonstrate that acetaldehyde chemistry is very important in high-pressure ethanol only near the stoichiometric condition.

The important reactions of ethanol combustion (CH4 + HO2 = CH3 + H2O2; C2H5 + O2 = C2H4 + HO2; C2H4 + O2 = CH2HCO + O; and CH3OH + O2 = CH3OH + HO2) were identified by applying adjoint sensitivity analysis43 in the ignition delay simulations of the 205-reactions mechanism; the Arrhenius rate constant parameters for these reactions were optimized within an order of magnitude. It was also verified that HO2 chemistry is significant for ethanol combustion.

### 2.2. Simulations

#### 2.2.1. Ignition Delay times

Simulated ignition delay times can be defined by the time interval to reach the maximum rate of pressure or temperature rise, a specific temperature change delta (ΔT), and either the maximum or the start of specific species concentration. The time interval for a specific temperature change delta is usually chosen for the numerical prediction of ignition delay times due to its strong temperature dependence. Ignition delay times were simulated with a 0-D tool in CONVERGE,36 which are defined as the time necessary to achieve a temperature of 400 K greater than the initial value. The air–fuel mixtures react exothermically in a constant volume bomb. It solves the ordinary differential equations (ODEs) by CVODE with a dense solver for smaller reaction sets, CVODE with an iterative solver for reaction sets with more than 100 species, and CVODE with the SuperLU iterative solver for reaction sets with more than 500 species. Furthermore, the derivatives of the Jacobian matrix can be calculated numerically or analytically.45 The same solvers and methods of Jacobian derivative calculations were available in all 0-D simulations. Ignition delay times of ethanol were simulated with all reaction mechanisms in the temperature and pressure ranges of 770–1430 K and 20–50 bar, respectively, for both ultra-lean (Φ = 0.3 and 0.5) and stoichiometric (Φ = 1.0) conditions, as shown in Table 1.

#### 2.2.2. Laminar Flame Speed

A 1-D combustion utility from CONVERGE36 was applied on the premixed laminar flame speed calculation to model a free-flame propagation at constant pressure within a channel of fixed cross-sectional area. The stand-alone steady-state solver was chosen for solving the species- and energy-conservation equations using Newton’s method to obtain the temperature and composition of the burned mixture. The implicit species diffusion within the Newton—Raphson loop, sparse solver, and central difference scheme can be used for discretization by utilizing Newton’s method.35 Laminar flame speeds at 358 K within 1–12 bar and the equivalence ratio ranging between 0.5 and 1.0 were calculated.

#### 2.2.3. Virtual Piston Engine

Owing to the limited market of rotary engines, no commercial software has been developed for the simulation of these engines. Although the available variety of commercial software for simulation of piston engines has not made it possible to directly use the Wankel engine dimensions in the simulations.46 Thus, the dimensions of the virtual piston engine for 0-D simulations were defined using mainly the similarity criteria that are described by characteristic equations based on the geometric parameters of these engines.36 Table 3 shows the parameters of the virtual piston engine used in 0-D simulations.

| type                                      | 4-stroke                  |
|-------------------------------------------|---------------------------|
| bore × stroke                             | 80 × 200 mm               |
| connecting rod length                     | 350 mm                    |
| displacement volume                       | 1.005 L/combustion event   |
| compression ratio                         | 16.15:1                   |
| engine speed                              | 3600–7200 rpm             |
| effective compression ratio               | 30–50:1                   |
| boost pressure                            | 2–3 bar                   |

ACS Omega 2021, 6, 206–216
The engine reactor from CONVERGE simulated a single-cycle for HCCI engines by 0-D calculation of a volume at every time-step as a function of engine geometric parameters.\(^9,45\)

\[
\frac{V}{V_C} = 1 + \frac{r_c - 1}{2} \left[R_{\text{engine}} + 1 - \cos \theta \right.
\]

\[
- \sqrt{R_{\text{engine}}^2 + \sin^2 \theta} \right] \sin \theta
\]

\(V_C\) is the clearance volume, \(r_c\) is the compression ratio, \(\theta\) is the crank angle, and \(R_{\text{engine}}\) is the ratio of the connecting rod length (\(l\)) to the crank radius (\(a\)). The clearance volume is defined as \(V_C = \frac{r_c - 1}{V_d}\) and the maximum displaced volume is calculated as \(V_d = \pi/2D^2a\), where \(D\) is the cylinder bore diameter.

In engine simulations, the time-derivative of the clearance volume is calculated as follows

\[
\frac{dV/V_c}{dt} = \frac{1}{2} \left[(r_c - 1) \sin \theta \sqrt{R_{\text{engine}}^2 - \sin^2 \theta} \right] \frac{d\theta}{dt}
\]

\(st\) is the engine cylinder stroke (twice the crank radius).

As it was necessary to define the heat-transfer correlation to calculate the heat loss from the gas to the walls, the widely used empirical heat-transfer correlations from Woschni\(^47\) and Chang\(^48\) were chosen for the 0-D HCCI engine simulations. Table 4 shows the conditions for 0-D HCCI engine simulations.

### Table 4. Conditions for Zero-Dimensional HCCI Engine Simulations

| start time | end time | initial temperature \((T_i)\) | initial pressure \((P_i)\) | hydrous ethanol composition | equivalence ratio \((\Phi)\) | engine speed | wall temperature | heat transfer correlation |
|------------|----------|-------------------------------|--------------------------|-----------------------------|--------------------------|--------------|-------------------|-------------------------|
| -240 CAD/\(-180\) CAD | 240 CAD/180 CAD | 400 K/435 K/443 K/450 K/500 K | 1 bar/2 bar/3 bar | 94.5% C\_2H\_5OH; 4.9% H\_2O; 0.6% CH\_3OH | 0.50/0.55 | 3600 rpm/4000 rpm/7200 rpm | 500 K | Woschni/Chang |

### 3. RESULTS AND DISCUSSION

#### 3.1. Simulated and Experimental Ignition Delay times

The ignition delay time is an essential parameter for the combustion process, related to the fuel reactivity. It affects the combustion initiation, propagation, and efficiency in internal combustion engines. Therefore, it is of central importance for the validation and optimization of chemical kinetics models. Ignition delay times measured in shock tubes and rapid compression machines (RCM) have been normally applied to these purposes. However, recent studies have reported small ignition inhomogeneities in the shock tube experiments that can lead to local pre-ignition and result in shorter experimental ignition delay times at low temperatures.\(^27,29,41,49\) On the contrary, the heat transfer to the combustion chamber wall reduces the temperature and reactivity in the RCM, which results in slightly longer ignition delay times at low temperatures.\(^29\) These issues create difficulty in capturing the behavior of ignition delay times at low temperatures and high pressures through the chemical kinetics models. For this reason, deviations of the experimental data from the simulated ignition delay times are expected at low temperatures.

Otherwise, a single methodology based on a specific temperature change delta to predict ignition delay times from all reaction mechanisms was applied to avoid any deviations related to the calculation method.

Figures 1–4 show the simulated ignition delay times of the different reaction mechanisms with comparison to the experimental ignition delay times.

From these figures, the simulated ignition delay times of the 188-reactions chemical kinetics model are found to fit well with the experimental ignition delay times under ultra-lean ethanol/air conditions \((\Phi = 0.30 \text{ and } \Phi = 0.50)\) for all pressures. The model simulations were in agreement with the experimental data for shock tubes at high temperatures and RCMs at low temperatures for 20 and 40 bar \((\Phi = 0.50)\). In addition, this model was in better agreement with the experimental data for 30 bar \((\Phi = 0.30)\) and 40 bar \((\Phi = 0.50)\) than other reaction sets. Moreover, this reaction set simulated the ignition delay times in a slightly better agreement than others for the RCM experimental data at low temperatures for 20 bar \((\Phi = 0.5)\).
In contrast, the 205-reactions chemical kinetics model simulated ignition delay times in good agreement with those experiments for the stoichiometric ethanol/air mixtures at high temperatures and 30 bar, and at intermediate and low temperatures with 40 bar. Particularly, this model simulated ignition delay times significantly better than other chemical kinetics models for these ranges of temperatures and pressures. However, the ignition delay times measured in the shock tube and RCM were very different for stoichiometric ethanol/air condition at low temperatures and 40 bar.
The simulated ignition delay times from detailed reaction mechanisms were in poor agreement only with experimental data at low temperatures, except for the 50 bar ultra-lean condition where they are quite similar.

The most recent chemical kinetics from San Diego simulated the ignition delay times with better fit to the experimental data than that obtained by Saxena. Although the reaction mechanism from Saxena was the single set evaluated with NOx chemistry, CONVERGE includes simplified and detailed emission modeling options, which can be added to the reaction set for CFD multidimensional simulation purposes.

3.2. Simulated and Experimental Laminar Flame Speed. Laminar flame speed has an important role in engines mainly due to its effect on turbulent flame speed, flame propagation, and stability. Consequently, the chemical kinetics models were also validated using laminar flame speeds. In this study, only laminar flame speeds with temperatures above the normal boiling point of ethanol were simulated with the different reaction mechanisms for comparison to experiments, since vapor ethanol will be employed in the combustion chamber of the Wankel test engine. There are few experimental data of laminar flame speeds at high temperatures and pressures for ethanol/air mixtures, relevant to engine operation. Moreover, the new reaction sets proposed in this work simulated laminar flame speeds similarly in poor agreement with the experimental data at 358, 453, and 600 K under atmospheric pressure. Therefore, only the results of laminar flame speeds at 358 K are shown. Figure 5 shows the simulated and experimental laminar flame speeds with different pressures at 358 K. Although the experimental data of Egolfopoulos and Guelder correspond to different temperatures, they were closer to the current simulation data. This pointed out a probable and small temperature error in the published chemical kinetics models. The simulations from these reaction sets were almost similar to each other and over-predicted the experimental laminar flame speeds in all conditions, except for those at a higher temperature (363 K) from the Egolfopoulos data at 1 atm.

In contrast, the simulated laminar flame speeds of the new reaction sets proposed here under-predict those from the experiment at low pressures (1 and 5 bar) but fit very well with the experimental data at high pressures (10 and 12 bar).

Except at 1 bar, the simulated values from the different reaction mechanisms are very similar under ultra-lean ethanol/air conditions (up to Φ = 0.55), which are of interest to Wankel engine operation.

3.3. Engine Simulation. The Wankel test engine fueled with ethanol will run at high temperature and pressure under ultra-lean conditions. Misfire and problems in flame propagation may appear and CFD multidimensional simulations can help to verify more suitably the combustion initiation and
propagation. Thereby, a reliable reaction mechanism with a low computational cost is required, which can properly simulate ignition delay times and laminar flame speeds to capture accurately the combustion characteristics. Furthermore, combustion engines used for electric power generation usually operate near the stoichiometric condition (Φ = 1.0) or lean-burn conditions (Φ = 0.3–0.8). It is important to note that the proposed reaction mechanisms were optimized to be useable in a limited range of ethanol combustion conditions, in which they resulted in predictions well-fitted to the experimental data.

Therefore, the proposed reaction mechanisms and the reaction set from San Diego42 were selected for 0-D HCCI engine simulations. The San Diego chemical kinetics model showed quality results for ignition delay times under ultra-lean conditions at high pressures and laminar flame speed at atmospheric pressure, but it failed to predict laminar flame speeds at high pressures. The reaction sets proposed in this work showed comparatively better results for both ignition delay times and laminar flame speeds at high pressures, but they failed to appropriately predict laminar flame speeds at atmospheric pressure. In addition, a reference detailed reaction mechanism from Mittal27 was applied to the HCCI engine simulations for comparison.

For engine operating conditions, the 0-D HCCI engine simulations can help to predict the maxima temperatures and pressures and verify the knock susceptibility. Engine simulations with heat transfer correlation from Chang48 resulted in better pressure profiles closer to the top dead center (TDC) at higher engine speeds, and they were considered here.

At first, pressure profiles for initial temperatures of 400, 450, and 500 K with start time at −240 CAD were simulated for HCCI engine under ultra-lean ethanol/air mixtures. The results showed higher pressure peaks for the initial temperature of 450 K. At 400 K, the ethanol/air mixtures were not adequately ignited by all reaction mechanisms, as reported earlier by Marinov58 and recently demonstrated for HCCI engine simulations.59

The initial temperature of 443 K and the start time at −180 CAD, which resulted in better ethanol ignition and higher pressure peaks for the ultra-lean engine conditions were established after running numerous simulations with reaction set from Mittal.27

Figure 6 shows the simulated temperature profiles for hydrous ethanol under ultra-lean conditions in the HCCI engine at 3600 rpm. The temperature profiles for higher engine speeds are very similar to those displayed in Figure 6; they became only narrower with the increasing engine speed and for that reason, are not presented here.

All reaction sets simulated approximately the same temperature peaks, but they achieved the peaks at different rates, except for the current chemical kinetics models, which showed lower temperature peaks, but only for the engine condition without turbocharging (P_i = 1 bar). The 188-reactions mechanism showed a temperature rise time quite similar to that from Mittal.27 The 205-reactions mechanism exhibited the fastest temperature rise time and those from San Diego the slowest. Overall, all reaction sets simulated faster temperature rise times for higher boost pressures. All models manifested slower temperature rise times for higher engine speeds.

The maxima temperatures simulated for hydrous ethanol fueled HCCI engines were approximately 2500 K (Φ = 0.50) and 2580 K (Φ = 0.55).

The chemical kinetics begins to change around 670 K (−53 CAD) within the range of autoignition temperatures for ethanol (638–696 K).60 The reaction initiations (−53 CAD) observed from the simulated pressure profiles were at approximately 6 bar without turbocharging, 12 bar with 2 bar of boost pressure, and 18 bar with 3 bar of boost pressure. Afterward, an abrupt change occurs next to TDC and results in different simulated pressure rise rates from the reaction sets.

Figure 7 shows the simulated pressure profiles of the different reaction mechanisms for hydrous ethanol under ultra-lean conditions in the HCCI engine, where a similar behavior between the pressure rise rate and the temperature rise time was observed.

The reaction mechanisms applied to the 0-D HCCI engine simulations with hydrous ethanol/air mixtures showed similar pressure profiles at 3600 rpm for all initial pressure conditions and the equivalence ratios (Φ = 0.50 and Φ = 0.55). In addition, all reaction sets showed higher pressure rise rates with an increase in the boost pressure for all engine speeds. The higher the engine speed, the lower the simulated pressure rise rate from all reaction mechanisms. Nevertheless,
it is more significant for San Diego and 188-reactions mechanisms and decreases the reactivity and exhibits poor ethanol ignition, mainly for the engine conditions without turbocharging. In these cases, a higher initial temperature is required for these reaction mechanisms to properly simulate the pressure profiles.

The maxima pressure values in the ranges of 73−91 bar without turbocharging ($P_i = 1$ bar), 170−185 bar with $P_i = 2$ bar, and 270−280 bar with $P_i = 3$ bar were obtained from the engine simulations with the different reaction mechanisms on ethanol/air at 3600 rpm and $\Phi = 0.50$. The pressure peaks were slightly lower as engine speed increases to 5400 rpm, generally less than 5% within the ranges of 69−88 bar; 151−181 bar; and 258−278 bar. However, the San Diego reaction set, the 205-reactions mechanism for $P_i = 1$ bar, and the 188-reactions mechanism for $P_i = 2$ bar were exceptions from the above occurrence. The simulated values from the San Diego mechanism at 5400 and 7200 rpm for $P_i = 1$ bar, as well as those from the 188-reactions mechanism at 7200 rpm for $P_i = 1$ bar, were neglected owing to the inefficient ethanol ignition.

As the engine speed increased to 7200 rpm, an additional reduction in the pressure peaks was verified. Moreover, except...
for the 205-reactions mechanism, lower ethanol reactivity was observed by simulated pressure profiles for the engine conditions without turbocharging \((P_i = 1 \text{ bar})\), where the peaks were found farthest from the TDC. Maxima pressures in the ranges of 71–76 bar; 147–181 bar; and 228–272 bar were calculated for the HCCI engine at 7200 rpm.

As expected, the pressure peaks increased for the hydrous ethanol/air at \(\Phi = 0.55\) independent of the initial pressure, and they were normally up to 7% higher for all engine speeds. The same behavior of the leaner ethanol/air mixture (\(\Phi = 0.50\)) was verified, but in this case, the pressure peaks did not reduce as much when the engine speed increased.

The simulated pressure profiles did not exhibit knock characteristics, that is, pressure profiles with an initial pressure peak of thin triangular shape followed by a second minor pressure peak. However, high pressure rise rates were observed from the simulated pressure profiles.

The pressure rise rate \((\text{PRR} = \frac{dP}{dt}_{\text{max}})\) and ringing index \(\left(\text{RI} = \sqrt{\frac{d^2P_{\text{rms}}}{dP_{\text{max}}} \left(\frac{dP}{dt}\right)^2}\right)\), where \(\beta = 1/4f\), are usually applied to determine the knock limit for an engine. The ringing index is dependent on the first mode frequency (\(\beta\)) of the pressure wave, which is an experimental parameter.\(^6\)\(^1\)

Consequently, the pressure rise rates were adopted for the evaluation of the knock tendency.

Table 5 shows the pressure rise rates in bar/CAD and their equivalents in MPa/ms at 3600 rpm for the different simulated engine conditions from the reference detailed mechanism.\(^7\)

The maximum acceptable pressure rise rate is related to the size and type of engine and the operating conditions such as engine speed, compression ratio, and boost pressure.\(^6\) Moreover, several knock thresholds have been reported for different engine geometries and speeds.\(^6\)\(^1\) A diesel engine converted into a supercharged ethanol-fueled HCCI engine was operated without any deterioration at 15–20 bar/CAD or 9–12 MPa/ms for long periods and 40 bar/CAD or 24 MPa/ms for short periods.\(^6\)\(^2\)

Excluding the HCCI engine simulation without turbocharging \((P_i = 1 \text{ bar})\), all other simulated engine conditions showed pressure rise rates above the maximum observed value (24 MPa/ms) for this type of engine fueled with ethanol. Despite the slower temperature rise time and the slightly lower pressure rise rate values in bar/CAD at higher engine speeds, the equivalent values in MPa/ms were even higher and are not shown in Table 5.

As the Wankel engine is more resistant to knock owing to its engine geometry, it is supposed to be operated with hydrous ethanol fuel under a minimum PRR of 24 MPa/ms. The results indicate that the engine will be able to operate at the least speed of 2500 rpm up to 214 bar with this threshold PRR under ultra-lean conditions. Furthermore, the combustion control will be achieved with spark-assisted HCCI that lowers peak heat release rates and allows more temporally distributed heat release, therefore reducing the pressure rise rates and extending the knock limit with higher power outputs.\(^6\)\(^3\)

Engine optimization is required for higher power outputs by applying CFD multidimensional simulation based on chemical kinetics, after model calibration. The CFD model calibration should be carried out with experimental data from the test engine at 2500 rpm and 2 bar of boost pressure, taking into account the inherent errors in reaction mechanisms.

### 4. CONCLUSIONS

Reduced reaction mechanisms for ethanol under ultra-lean engine conditions were evaluated based on ignition delay times and laminar flame speeds. Furthermore, 0-D HCCI engine simulations were carried out with selected chemical kinetics models.

The simulation results of the 188-reactions chemical kinetics model fitted considerably better to the experimental data of ignition delay times for ethanol under ultra-lean conditions \((\Phi = 0.30 \text{ and } \Phi = 0.50)\) in all pressures, especially at 30 and 40 bar, where this small reaction set simulated ignition delay times in excellent agreement with the experimental data. In addition, this reaction set could simulate high-temperature data from shock tubes and low-temperature data from RCM under ultra-lean ethanol/air conditions.

Although the reaction mechanisms presented in this work simulated results in poor agreement with the experimental laminar flame speeds at low pressures \((1–5 \text{ bar})\), the simulation results had a better fit to the experimental data of laminar flame speeds at high pressures \((10–12 \text{ bar})\). Nevertheless, all established chemical kinetics models simulated similar laminar flame speeds for ethanol under ultra-lean conditions at \(\Phi \leq 0.55\), except at 1 bar.

Moreover, HCCI engine simulations from the selected reaction mechanisms demonstrated that ultra-lean ethanol combustion initiated in the range of its autoignition temperature at 6 bar without turbocharging, at 12 bar with a boost pressure of 2 bar, and at 18 bar with a boost pressure of 3 bar. Ethanol-fueled engine simulations at 3600 rpm from the selected chemical kinetics resulted in similar temperature and pressure profiles with slightly different rise times. All reaction sets showed lower temperature and pressure rise rates as engine speed increased. This effect was more significant for the

| engine speed (rpm) | start time (CAD) | \(P_{\text{max}}\) (MPa) | pressure rise rate (bar/CAD) | equivalent \((dP/dt)_{\text{max}}\) (MPa/ms) |
|-------------------|-----------------|--------------------------|-----------------------------|----------------------------------|
| 3600              | 180             | 91                       | 10                          | 22                               |
|                   |                 | \(P_i = 1 \text{ bar})\) |                             |                                  |
|                   |                 | 182                      | 16                          | 35                               |
|                   |                 | \(P_i = 2 \text{ bar})\) |                             |                                  |
|                   |                 | 275                      | 26                          | 56                               |
|                   |                 | \(P_i = 3 \text{ bar})\) |                             |                                  |
| 3600              | 220             | 77                       | 8                           | 17                               |
|                   |                 | \(P_i = 1 \text{ bar})\) |                             |                                  |
|                   |                 | 164                      | 16                          | 35                               |
|                   |                 | \(P_i = 2 \text{ bar})\) |                             |                                  |
|                   |                 | 248                      | 22                          | 48                               |
|                   |                 | \(P_i = 3 \text{ bar})\) |                             |                                  |
| 3600              | 240             | 29                       | 1                           | 2                                |
|                   |                 | \(P_i = 1 \text{ bar})\) |                             |                                  |
|                   |                 | 140                      | 15                          | 32                               |
|                   |                 | \(P_i = 2 \text{ bar})\) |                             |                                  |
|                   |                 | 214                      | 16                          | 35                               |
|                   |                 | \(P_i = 3 \text{ bar})\) |                             |                                  |
| 3600              | 180             | 74                       | 8                           | 17                               |
|                   |                 | \(P_i = 1 \text{ bar})\) |                             |                                  |
|                   |                 | 148                      | 15                          | 32                               |
|                   |                 | \(P_i = 2 \text{ bar})\) |                             |                                  |
|                   |                 | 223                      | 18                          | 39                               |
San Diego and 188-reactions mechanisms, which resulted in inefficient ethanol ignition for the engine conditions without turbocharging.

However, overall the new 188-reactions mechanism had a better performance than the other reaction sets for ultra-lean and high-pressure ethanol/air combustion conditions. The simulation results pointed out maxima temperature between 2500 and 2580 K and maxima pressure between 280 and 289 bar for HCCI engine fueled with hydrous ethanol under ultra-lean conditions.

Despite the high pressure peaks and rise rates, the pressure profiles did not exhibit the characteristic shape related to knock combustion. Except for the engine conditions without turbocharging, all other engine conditions demonstrated larger maximum pressure rise rate (8–26 bar/CAD at 3600 rpm) than those measured for an ethanol-fueled HCCI engine. Therefore, the engine test should be performed at 2500 rpm with a boost pressure of 2 bar for CFD model calibration and further engine optimization.

■ ASSOCIATED CONTENT

References

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04170.

Mechanism, thermodynamic, and transport data files of the 188-reactions set in CHEMKIN format (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

Carla S. T. Marques – Porto Gestão de Tecnologia S.A., São Paulo, São Paulo 05443-002, Brazil; Department of Mechanical Engineering, Polytechnic School, University of São Paulo, São Paulo 05508-030, Brazil; orcid.org/0000-0002-5909-8837; Email: carla.tafuri@perto.org

Author

José R. M. da Silva – Porto Gestão de Tecnologia S.A., São Paulo, São Paulo 05443-002, Brazil

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04170

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Convergent Science for providing Converge v3.0 licenses and technical support. This work was funded by FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) through PIPE project (2017/17242-8).

■ REFERENCES

(1) Liao, S. Y.; Jiang, D. M.; Cheng, Q.; Huang, Z. H.; Wei, Q. Investigation of the cold-start combustion characteristics of ethanol-gasoline blends in a constant-volume chamber. Energy Fuels 2005, 19, 13–29.
(2) Dagaut, P.; Togbé, C. Experimental and modeling study of the kinetics of oxidation of ethanol-gasoline surrogate mixtures (E88 surrogate) in a jet-stirred reactor. Energy Fuels 2008, 22, 3499–3505.
(3) Roy, S.; Askari, O. A New Detailed Ethanol Kinetic Mechanism at Engine-Relevant Conditions. Energy Fuels 2020, 34, 3691–3708.
(4) Baêta, J. G. C.; Pontoppidan, M.; Silva, T. R. V. Exploring the limits of a down-sized ethanol direct injection spark ignited engine in different configurations in order to replace high-displacement gasoline engines. Energy Convers. Manage. 2015, 105, 858–871.
(5) Mathieu, O.; Pinzón, L. T.; Atherley, T. M.; Mulvihill, C. R.; Schoel, I.; Petersen, E. L. Experimental study of ethanol oxidation behind reflected shock waves: Ignition delay time and H2O laser-absorption measurements. Combust. Flame 2019, 208, 313–326.
(6) Noh, H. K.; No, S.-Y. Effect of bioethanol on combustion and emissions in advanced CI engines: HCCI, PPCI and GCI mode – A review. Appl. Energy 2017, 208, 782–802.
(7) Amrouche, F.; Erickson, P. A.; Varnhagen, S.; Park, J. W. An experimental study of a hydrogen-enriched ethanol fueled Wankel rotary engine at ultra lean and full load conditions. Energy Convers. Manage. 2016, 123, 174–184.
(8) Amrouche, F.; Erickson, P. A.; Park, J. W.; Varnhagen, S. An experimental evaluation of ultra-lean burn capability of a hydrogen-enriched ethanol-fueled Wankel engine at full load condition. Int. J. Hydrogen Energy 2016, 41, 19231–19242.
(9) Heywood, J. Internal Combustion Engine Fundamentals; McGraw Hill Ed., 1988; pp 1–37.
(10) Yamamoto, K. Rotary Engine; Toyo Kogyo Co. Ltd., 1981; pp 1–9.
(11) Ozcanli, M.; Bas, O.; Akar, M. A.; Yildizhan, S.; Serin, H. Recent studies on hydrogen usage in Wankel SI engine. Int. J. Hydrogen Energy 2018, 43, 18037–18045.
(12) Kagawa, R.; Okazaki, S.; Somyo, N.; Akagi, Y. A Study of a Direct-Injection Stratified-Charge Rotary Engine for Motor Vehicle Application. SAE Technical Paper Series, 1993; p 930677.
(13) Tashima, S.; Tsu’dokoro, T.; Okimoto, H.; Niwa, Y. Development of Sequential Twin Turbo System for Rotary Engine. SAE Technical Paper Series, 1991; p 910624.
(14) Fan, B.; Pan, J.; Tang, A.; Pan, Z.; Zhu, Y.; Xue, H. Experimental and numerical investigation of the fluid flow in a side-ported rotary engine. Energy Convers. Manage. 2015, 95, 385–397.
(15) Taskiran, O. O.; Calik, A. T.; Akin Kutlar, O. Comparison of flow field and combustion in single and double side ported rotary engine. Fuel 2019, 254, 115651.
(16) Ji, C.; Shi, C.; Wang, S.; Yang, J.; Su, T.; Wang, D. Effect of dual-spark plug arrangements on ignition and combustion processes of a gasoline rotary engine with hydrogen direct-injection enrichment. Energy Convers. Manage. 2019, 181, 372–381.
(17) Fanara, R. HCCI rotary engine with variable compression ratio control. U.S. Patent 9,435,2571B2, 2016.
(18) Resor, M. I. Computational Investigation of Rotary Engine Homogeneous Charge Compression Ignition Feasibility. Master Thesis, Wright State University, 2014.
(19) Amrouche, F.; Erickson, P.; Park, J.; Varnhagen, S. An experimental investigation of hydrogen-enriched gasoline in a Wankel rotary engine. Int. J. Hydrogen Energy 2014, 39, 8525–8534.
(20) Shi, C.; Ji, C.; Wang, S.; Yang, J.; Li, X.; Ge, Y. Numerical simulation on combustion process of a hydrogen direct-injection stratified gasoline Wankel engine by synchronous and asynchronous ignition modes. Energy Convers. Manage. 2019, 183, 14–25.
(21) Fan, B.; Pan, J.; Yang, W.; Zhu, Y.; Chen, W. Effects of hydrogen blending mode on combustion process of a rotary engine fueled with natural gas/hydrogen blends. Int. J. Hydrogen Energy 2016, 41, 4039–4053.
(22) Yontar, A. A. Effects of ethanol, methyl tert-butyl ether and gasoline-hydrogen blend on performance parameters and HC emission at Wankel engine. Biofuels 2020, 11, 377–388.
(23) Su, T.; Ji, C.; Wang, S.; Cong, X.; Shi, L.; Yang, J. Improving the lean performance of an n-butanol rotary engine by hydrogen enrichment. Energy Convers. Manage. 2018, 157, 96–102.
(24) Huang, Z.; Liu, B.; Zeng, K.; Huang, Y.; Jiang, D.; Wang, X.; Miao, H. Experimental study on engine performance and emissions for an engine fueled with natural gas-hydrogen mixtures. Energy Fuels 2006, 20, 2131–2136.
(25) Benvenutti, L. H.; Marques, C. S. T.; Bertran, C. A. Chemiluminescence emission data for kinetic modeling of ethanol combustion. Combust. Sci. Technol. 2005, 177, 1–26.
(26) Saxena, P.; Williams, F. A. Numerical and experimental studies of ethanol flames. Proc. Combust. Inst. 2007, 31, 1149−1156.
(27) Mittal, G.; Burke, S. M.; Davies, V. A.; Parajuli, B.; Metcalfe, W. K.; Curran, H. J. Autoignition of ethanol in a rapid compression machine. Combust. Flame 2014, 161, 1164−1171.
(28) Olm, C.; Varga, T.; Valkó, E.; Hartl, S.; Haase, C.; Turányi, T. Development of an Ethanol Combustion Mechanism Based on a Hierarchical Optimization Approach. Int. J. Chem. Kinet. 2016, 48, 423−441.
(29) Zhang, Y.; El-Merhibi, H.; Lefort, B.; Le Moine, L.; Curran, H. J.; Kéromnès, A. Probing the low-temperature chemistry of ethanol via the addition of dimethyl ether. Combust. Flame 2018, 190, 74−86.
(30) Hashemi, H.; Christensen, J. M.; Glarborg, P. High-pressure pyrolysis and oxidation of ethanol. Fuel 2018, 218, 247−257.
(31) Viggiano, A.; Magi, Y. A comprehensive investigation on the emissions of ethanol HCCI engines. Appl. Energy 2012, 93, 277−287.
(32) Boldaj, M. R.; Gainey, B.; Lawler, B. Thermally stratified compression ignition enabled by wet ethanol with a split injection strategy: A CFD simulation study. Appl. Energy 2019, 235, 813−826.
(33) Westbrook, C. K.; Dryer, F. L. Chemical kinetic modeling of hydrocarbon combustion. Prog. Energy Combust. Sci. 1984, 10, 1−57.
(34) Westbrook, C. K. Chemical kinetic modeling of hydrocarbon ignition in practical combustion systems. Proc. Combust. Inst. 2000, 28, 1563−1577.
(35) Boot, M. D.; Tian, M.; Hensen, E. J. M.; Mani Sarathy, S. Impact of fuel molecular structure on auto-ignition behavior − Design rules for future high performance gasolines. Prog. Energy Combust. Sci. 2017, 60, 1−25.
(36) Richards, K. J.; Senecal, P. K.; Pomranging. ENERGE 3.0; Madison, WI, 2020.
(37) Konnov, A. V. A Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism. Combust. Flame 2009, 156, 2093−2105.
(38) Cancino, L. R.; Fikri, M.; Oliveira, A. A. M.; Schulz, C. Measurement and chemical kinetics modeling of shock-induced ignition of ethanol-air mixtures. Energy Fuels 2010, 24, 2830−2840.
(39) Leplat, N.; Daguay, P.; Togbé, C.; Vandooren, J. Numerical and experimental study of ethanol combustion and oxidation in laminar premixed flames and in jet-stirred reactor. Combust. Flame 2011, 158, 705−725.
(40) Ranzi, E.; Frassoldati, A.; Grana, R.; Cuoci, A.; Faravelli, T.; Kelley, A. P.; Law, C. K. Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. Prog. Energy Combust. Sci. 2012, 38, 468−501.
(41) Lee, C.; Vranckx, S.; Heufer, K. A.; Khomik, S. V.; Uygun, Y.; Olivier, H.; Fernandez, R. X. On the chemical kinetics of ethanol oxidation: Shock tube, rapid compression machine and detailed modeling study. Zeitschrift Fur Phys. Chemie 2012, 226, 1−28.
(42) UC San Diego. Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism web page, Mechanical and Aerospace Engineering (Combustion Research); University of California at San Diego: USA, 2016, http://combustion.ucsd.edu (accessed 24 April 2020).
(43) Zhou, C.-W.; Li, Y.; Burke, U.; Banyon, C.; Somers, K. P.; Ding, S.; Khan, S.; Hargis, J. W.; Sikes, T.; Mathieu, O.; et al. An experimental and chemical kinetic modeling study of 1,3-butadiene combustion: Ignition delay time and laminar flame speed measurements. Combust. Flame 2018, 197, 423−438.
(44) Marques, C. S. T.; Santos, L. R.; Shampato, M. E.; Barreta, L. G.; Santos, A. M. Temperature measurements by OH LIF and chemiluminescence kinetic modeling for ethanol flames. Quim. Nova 2009, 32, 2073−2077.
(45) Richards, K. J.; Senecal, P. K.; Pomranging, E. CONVERGE 3.0 Manual; Convergent Science: Madison, WI, 2020.
(46) Tartakovsky, L.; Baibikov, V.; Gutman, M.; Veinblat, M.; Reif, J. Simulation of Wankel engine performance using commercial software for piston engines. SAE Technical Paper Series, 2012; p 4.
(47) Woschni, G. A Universally Applicable Equation for the Instantaneous Heat Transfer Coefficient in the Internal Combustion Engine. SAE Technical Paper Series, 1967.
(48) Chang, J.; Guirald; O.; Filipi, Z.; Assanis, D.; Kuo, T. W.; Najt, P.; Rask, R. New heat transfer correlation for an HCCI engine derived from measurements of instantaneous surface heat flux. SAE Technical Paper Series, 2004.
(49) Heufer, K. A.; Olivier, H. Determination of ignition delay times of different hydrocarbons in a new high pressure shock tube. Shock Waves 2010, 20, 307−316.
(50) Aghsae, M.; Nativ, D.; Bozkurt, M.; Fikri, M.; Chaumeix, N.; Schulz, C. Experimental study of the kinetics of ethanol pyrolysis and oxidation behind reflected shock waves and in laminar flames. Proc. Combust. Inst. 2015, 35, 393−400.
(51) Bradley, D.; Lawes, M.; Mansour, M. S. Explosion bomb measurements of ethanol-air laminar gaseous flame characteristics at pressures up to 1.4 MPa. Combust. Flame 2009, 156, 1462−1470.
(52) Gílder, O. L. Laminar burning velocities of methanol, ethanol and isooctane-air mixtures. Symp. (Int.) Combust., [Proc.] 1982, 19, 275−281.
(53) Dirrenberger, P.; Glade, P. A.; Bounceau, R.; Le Gall, H.; Da Cruz, A. P.; Konnov, A. A.; Battin-Leclerc, F. Laminar burning velocity of gasolines with addition of ethanol. Fuel 2014, 115, 162−169.
(54) Egolfopoulos, F. N.; Du, D. X.; Law, C. K. A study on ethanol oxidation kinetics in laminar premixed flames, flow reactors, and shock tubes. Symp. (Int.) Combust., [Proc.] 1992, 24, 833−841.
(55) Liao, S. Y.; Jiang, D. M.; Huang, Z. H.; Zeng, K.; Cheng, Q. Determination of the laminar burning velocities for mixtures of ethanol and air at elevated temperatures. Appl. Therm. Eng. 2007, 27, 374−380.
(56) Esazadeh-Far, K.; Moghadass, A.; Al-Mulk, I.; Metghalchi, H. Laminar burning speeds of ethanol/air/diluent mixtures. Proc. Combust. Inst. 2011, 33, 1021−1027.
(57) Katoch, A.; Millán-Merino, A.; Kumar, S. Measurement of laminar burning velocity of ethanol-air mixtures at elevated temperatures. Fuel 2018, 231, 37−44.
(58) Marinov, N. M. A detailed chemical kinetic model for high temperature ethanol oxidation. Int. J. Chem. Kinet. 1999, 31, 183−220.
(59) Sharma, T. K.; Rao, G. A. P.; Murthy, K. M. Combustion Analysis of Ethanol in an HCCI Engine. Trends Mech. Eng. Technol. 2013, 3, 1−10.
(60) Chen, C.-C.; Liaw, H.-J.; Shu, C.-M.; Hsieh, Y.-C. Autioinignition temperature data for methanol, ethanol, propanol, 2-butanol, 1-butanol and 2-methyl-2,4-pentanediol. J. Chem. Eng. Data 2010, 55, 5059−5064.
(61) Andreae, M. M.; Cheng, W. K.; Kenney, T.; Yang, J. On HCCI engine knock. SAE Technical Paper Series, 2007.
(62) Christensen, M.; Johansson, B.; Annéus, P.; Mauss, F. Supercharged homogeneous charge compression ignition. SAE Technical Paper Series, 1998.
(63) Saxena, S.; Bedoya, I. D. Fundamental phenomena affecting low temperature combustion and HCCI engines, high load limits and strategies for extending these limits. Prog. Energy Combust. Sci. 2013, 39, 457−488.