Reactivity enhancement of natural gas/diesel RCCI engine by adding ozone species

Author(s): Gharehghani, Ayat; Salahi, Mohammad Mahdi; Andwari, Amin Mahmoudzadeh; Mikulski, Maciej; Könnö, Juho

Title: Reactivity enhancement of natural gas/diesel RCCI engine by adding ozone species

Year: 2023

Version: Accepted manuscript

Please cite the original version:

Gharehghani, A., Salahi, M. M., Andwari, A. M., Mikulski, M. & Könnö, J. (2023). Reactivity enhancement of natural gas/diesel RCCI engine by adding ozone species. *Energy* 274, 127341. https://doi.org/10.1016/j.energy.2023.127341

Reactivity Enhancement of Natural Gas/Diesel RCCI Engine by Adding Ozone Species

Ayat Gharehghani[a*], Mohammad Mahdi Salahi[b], Amin Mahmoudzadeh Andwari[b*], Maciej Mikulski[c], Juho Könnö[b]

[a] School of Mechanical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran
[b] Machine and Vehicle Design (MVD), Materials and Mechanical Engineering, University of Oulu, P.O. Box 4200, FI-90014 Oulu, Finland
[c] School of Technology and Innovation, Energy Technology, University of Vaasa, Wolffintie 34, FI-65200 Vaasa, Finland

ABSTRACT

Reactivity controlled compression ignition (RCCI) is an alternative combustion strategy with the potential of significant advantages in terms of increasing thermal efficiency together with reduction of NOx and soot emissions. The RCCI engines have been encountered not to be applicable broadly since they suffer from some difficulties mainly contributed to the controllability of combustion and limited operating ranges. The difficulties become even worse where low-reactivity fuels like natural gas (NG) are applied. Ozone gas, a chemical species with an extreme level of reactivity, can improve the combustion efficiency along with the advancement of combustion phasing in the RCCI engine. In this study a multidimensional computational fluid dynamic (CFD) which is coupled with proper detailed chemical kinetic mechanisms is employed to investigate the influence of ozone addition (i.e., 10, 100 and 1000 ppm) to air-fuel mixture with different initial conditions (e.g., intake temperature and equivalence ratio), on the performance and emissions characteristics of the RCCI engine. The results imply that the addition of even low concentrations of ozone (10 ppm) have considerable influences on the RCCI combustion characteristics. Addition of ozone by a distinct quantity not only can enhance the combustion phasing controllability, but also can extend the operating range of the RCCI engine in both lower intake air temperature and the lower fraction of the high-reactive fuel. From the results it is conceived that by adding 1000 ppm ozone into the air-fuel mixture, it is possible to reduce the diesel fuel fraction from 20 % to 10 % and intake air temperature from 355 K to 335 K, respectively.

Keywords: RCCI Engine, Numerical Simulation, Detailed Chemistry, Natural Gas, Ozone Species

1. Introduction

Based on the recent emission regulations, the level of NOx and particulate matter (PM) pollutions should be reduced drastically and RCCI combustion strategy would be a promising solution to reach this restricted emission levels [1]. Although, the RCCI mode of operation could manage simultaneously the emissions level (i.e., NOx and PM) and fuel consumption as well as reach high thermal efficiency [2,3], but the low reactivity fuel (i.e., NG) characteristics causes restrictions in application of this combustion strategy [4-6]. Cetane number of NG is low and as result, it is necessary to preheat the intake charge and/or use turbocharger to avoid long ignition delay in NG/diesel RCCI engines [7-10]. Long ignition delay will cause to

[*] Corresponding authors:
Ayat Gharehghani, E-mail: Ayat_Gharehghani@iust.ac.ir, Tel: +98 21 73228953
Amin Mahmoudzadeh Andwari, Email: Amin.Mahmoudzadehandwari@oulu.fi, Tel: +358 50 347 5131

instable combustion (i.e., misfire) and as result, high level of CO and HC emissions will be produced during the combustion process [11,12]. To overcome this concern, some researchers varied the cetane number of mixtures by combination of two or more fuels with distinct properties. Rahnama et al. [13-15] numerically investigated the combustion and emission characteristics of a NG/diesel RCCI engine enriched with reformer gas. They reported that reformer gas addition could enhance the combustion efficiency and decrease CO emission. Gharehghani et al. [16] experimentally investigated the effect of using biodiesel instead of diesel fuel in enhancing the reactivity of the mixture in a NG/diesel (biodiesel) RCCI engine. Their revealed results showed that CO emission for CNG/biodiesel case reduced drastically, and the HC emission level was 32.5 % lower than compared to CNG/diesel RCCI engine. Replacing the high reactivity fuel was also reported by other researchers and showed the same trend for emissions behavior [17-20]. Kakoee and colleagues tried to improve the lean combustion condition in a NG/diesel RCCI engine by using hydrogen [21]. They used a 3D numerical model coupled with reduced chemical kinetics to explore the effect of various hydrogen concentrations on the lean burning (i.e., low load) conditions of RCCI engine. Their results showed that that 30 % H_2 addition to the intake mixture causes that the amount of UHC and CO lower by 29.8 % and 35.5%, respectively. Using pre-combustion chamber as an effective tool to improve the lean burning condition and reducing the CO and HC emissions was reported by some researchers [22]. Using other low reactivity fuels (i.e., ethanol) instead of NG is the other solution which was investigated numerically and experimentally by the researchers [23, 24]. Some investigators used variable valve timing strategy together with RCCI combustion mode to reach the better performance and enhanced emission treatments of engine [25,26]. Changing the injection timing of high/low reactivity fuels as well as changing the reactivity of mixture by varying the portion of each fuel reported as effective ways to reach lower CO and HC emissions levels [27-30]. The results of an experimental study which investigated the various direct-injected fuels with cetane number (CN) ranging from 34 to 100 revealed that for cetane number higher than 56, the high level of EGR (~ 45 %) is suitable regarding stable combustion [31]. The role of low reactivity fuel stratification on the performance of NG/diesel RCCI engine was investigated numerically by Mikulsi and Bekdemir [32]. They concluded that NG stratification leads to higher combustion efficiency and lower HC and CO emissions.

Although the above-mentioned efforts are interesting for researchers, but employment of them is difficult for the automotive engines. Other interesting and applicable strategy which has been used to control the premixed/homogeneous charged compression ignition (PCCI/HCCI) combustion is to take advantage of minor species with high oxidation levels to improve the combustion of the main fuel [33,34]. One of the remarkable oxidant species that could impact the start of combustion and its phasing and as result, HC and CO emissions level, in HCCI/PCCI engines is the Ozone species [35-37]. Researchers have shown that with existence of ozone, oxygen atoms which are produced by decomposition of ozone molecules can help initiating the oxidation process of the methane fuel [38, 39]. Also, ozone leads to higher burning velocity of methane/air mixture and can help extending the stable combustion range in HCCI engines [40,41].

Even though ozone addition for engines with HCCI combustion mode has been numerically and experimentally investigated, to the best of authors knowledge, this study is the first of its kind undertaken developing a 3-D simulation model to investigate the effect of ozone addition on the combustion characteristics of NG/diesel RCCI engine. Accordingly, the combustion process of a NG/diesel RCCI engine is modeled by employing a 3-D CFD simulation code which works in conjunction with a set of reduced chemical kinetics mechanisms. Moreover, for the first time, NG/diesel chemical kinetics is modified and upgraded by adding the ozone species together with its reactions to study the influence of ozone addition on required intake temperature as well as optimal NG/diesel ratio for combustion stability (i.e., no misfire). Numerical simulation results are validated by the experimental data acquired from a single-cylinder Ricardo engine. Furthermore, for the constant intake temperature and NG/diesel ratio, the effect of ozone addition is swept and for each case, the optimal ozone concentration is determined.

2. Procedure of numerical investigation

2.1. Simulation methods and tools

The numerical simulation tools employed in the present work, is AVL Fire software. This software has a 3-D CFD solver, based on finite volume method, and has the ability to solve in-cylinder flow field equations with fuel injection and the chemical processes. To model the turbulence effects, a version of the standard k–ω turbulence model is used that can account for flow compressibility. To simulate heat transfer between flow boundary layers and in-cylinder walls, a standard wall function with modifications for variation of fluid density and turbulent Prandtl number is employed [42]. Chemical kinetics phenomena control the combustion procedure in RCCI engines and therefore, appropriate modeling of the chemical kinetics is an essential part in the simulation of NG/diesel RCCI engine. The solver of the AVL Fire is internally coupled with the CHEMKIN solver for chemical kinetics. In conjunction with the CFD solver, the chemical kinetics solver, undertakes the equations of generation (and destruction) rates for all chemical species and computes the according released heat [42].

To model the combustion in the NG/diesel RCCI engine, a reduced chemical kinetics mechanism which was developed by Hockett [43] and consists of 141 species and 709 reactions, is used. In this numerical study, methane (CH4) is employed as a chemical surrogate for natural gas (NG), while normal heptane (nC7H16) is used as a representative of diesel fuel. To consider the effect of ozone species on the combustion characteristics, the mentioned mechanism is combined with the Sub-mechanisms for Kinetics Reactions of Ozone, that are presented in Table 1[35]. The reactions set contain such reactions as formation and decomposition processes of ozone (O3 +M → O2 + O + M), oxidation by ozone (O3 + X→O2 + XO), and HO_2 species production (O3 + XH → HO2 + product). The finally resulted mechanism that is used for the simulations has 726 reactions (709 for dual fuel mechanism and 17 for ozone processes) and 142 chemical species.

Table 1. Sub-mechanisms for Kinetics Reactions of Ozone ($k = AT^n\exp[-E/(1.9872T)]$) (cal/mol)[35]

Reactions	A (mol/cm.s)	n	E (cal/mol)
O3 + N2→ O2 + O + N2	4.00×10^{14}	0.0	22667
O2 + O + N2→ O3 + N2	1.60×10^{14}	-0.4	-1391
O3 + O2→ O2 + O + O2	1.54×10^{14}	0.0	23064
O2 + O + O2→O3 + O2	3.26×10^{19}	-2.1	0
O3 + O3→ O2 + O + O3	4.40×10^{14}	0.0	23064
O2 + O + O3→ O3 + O3	1.67×10^{15}	-0.5	-1391
O3 + H ↔ O2 + OH	8.43×10^{13}	0.0	934
O3 + O ↔ O2 + O2	4.82×10^{12}	0.0	4094
O3 + OH ↔ O2 + HO2	1.85×10^{11}	0.0	831
O3 + HO2↔ O2 + OH + O2	6.09×10^{09}	0.0	938
O3 + H2O ↔ O2 + H2O2	6.62×10^{01}	0.0	0
O3 + CH3 ↔ O2 + CH3O	3.07×10^{12}	0.0	417
O3 + NO ↔ O2 + NO2	8.43×10^{11}	0.0	2603
O3 + N ↔ O2 + NO	6.03×10^{07}	0.0	0
O3 + H ↔ O + HO2	4.52×10^{11}	0.0	0

$O3 + H2 \leftrightarrow OH + HO2$	6.00×10^{10}	0.0	19840
$O3 + CH4 \leftrightarrow CH3O + HO2$	8.13×10^{10}	0.0	15280

2.2. Grid generation

In the present investigation, the simulation is done on an engine closed cycle, from intake valve close (IVC) to exhaust valve open (EVO) time. In addition, the simulated geometry can be considered symmetrical. Therefore, Fame Engine Plus module from the AVL-Fire software is used to generate a moving mesh of half of the in-cylinder geometry with a symmetry plane on a closed cycle. To get more accurate results, finer computational cells should be generated in the zone of the pre-chamber and its connecting part to the main chamber.
A view of the generated grid in the TDC position is shown in Figure 1. The generated moving grid has 75493 cells in the TDC and 180118 cells in the BDC position.

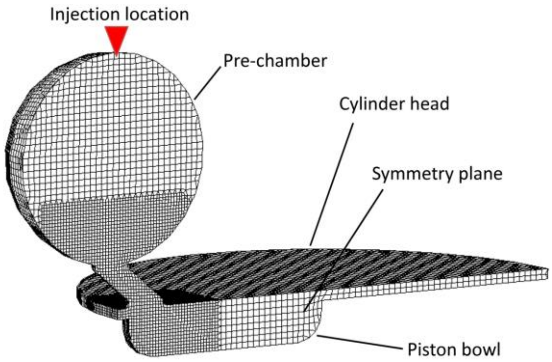


Figure 1: Generated grid at TDC position

3. Experimental test setup and simulation validation

3.1. Experimental test setup and methods

Figure 2 shows the schematic (a) and real test setup (b) of RCCI engine experimental test rig and employed measurement instrumentation. The test engine is a single-cylinder diesel engine manufactured by Ricardo company that has been modified to operate in the RCCI mode. Natural gas, which is the fuel with low reactivity, is added to intake air throughout the intake manifold and diesel fuel, the highly reactive fuel, is injected directly into the cylinder. To control the torque and speed of the engine, an electric 22 kW dynamometer is exploited.

AVL QC43D water cooled, piezo-electric type pressure transducer was used for measurement of the in-cylinder pressure. A Fotek MES-2500 D-T magnetic rotary encoder with the resolution of 2500 PPR was installed near to the crankshaft to monitor the crank angle. To regulate the intake air temperature, an electrical air heater is installed on the intake manifold.
A high-pressure CNG reservoir tank was used with a gas regulator to provide the NG fuel with a controlled constant pressure. To monitor the natural gas fuel flow rate, a Yamatake flow meter was utilized, and a Lambda sensor was installed on the engine exhaust to monitor the air-fuel ratio (AFR). K-type thermocouples with accuracy of ± 1°C were used for measuring the temperature of intake air and exhaust gas. The intake charge and exhaust gas temperatures were measured by using K-type thermocouples with an accuracy of ± 1°C.
To monitor the flow rate of the diesel flow, An AVL-735 fuel meter was used. The diesel injector nozzle has four holes of diameter 0.25 mm, and the liquid fuel rail pressure can be varied from 150 to 200 bars. The uncertainty values of experimental measurements are presented in Table 2 and Table 3 presents the engine specifications data. To record the engine

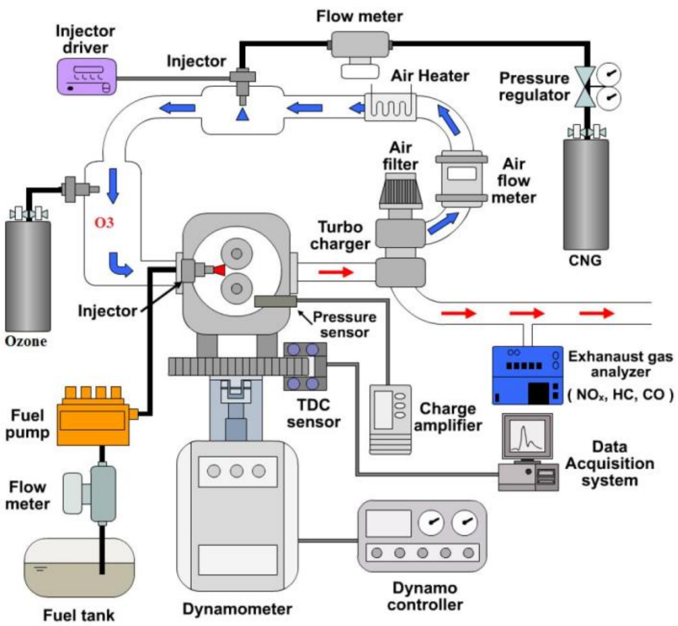
pressure curve, in each operating state, the in-cylinder pressure data for 200 consecutive cycles were gathered and their averaged values were exploited.

Table 2: Experimental uncertainty values

Parameter	Uncertainty (%)
Temperature	<2
Pressure	<2
Engine speed	<1
Fuel flow rate	<1
Air flow rate	<1

Table 3 :Engine specifications

Parameter	Specification
Engine type	Single cylinder E6/MS
Bore	76.2 (mm)
Stroke	110 (mm)
Displacement	507 (cc)
Compression Ratio	17.2:1
IVC	144° BTDC
IVO	7° BTDC
EVC	7° ATDC
EVO	144° ATDC
Injector hole diameter	0.25 (mm)
Injection Pressure	180 (bar)



(a) Schematic diagram

(b) Real test bed

Figure 2: RCCI engine test rig and instrumentation; (a) Schematic view of test facilities and instrumentation, (b) Real stance of engine test bed

3.2. Model validation

The experimental results of engine operation in RCCI mode were used to validate the numerical model simulation data.

In experiments, the engine was operated on was 800 rpm speed, the intake temperature was 355 °K and the intake pressure was 1.2 bars. Total equivalence ratio of fuel was adjusted to a constant value of 0.3 and the ratio of NG and diesel fuels is 80 % and 20 % of total energy content, respectively.

The calculated and measured in-cylinder pressure are compared in Figure 3. It is seen that the simulation properly predicts the start of combustion as well as combustion phasing and there is a good agreement between the experimental and numerical results, specially throughout the combustion process.

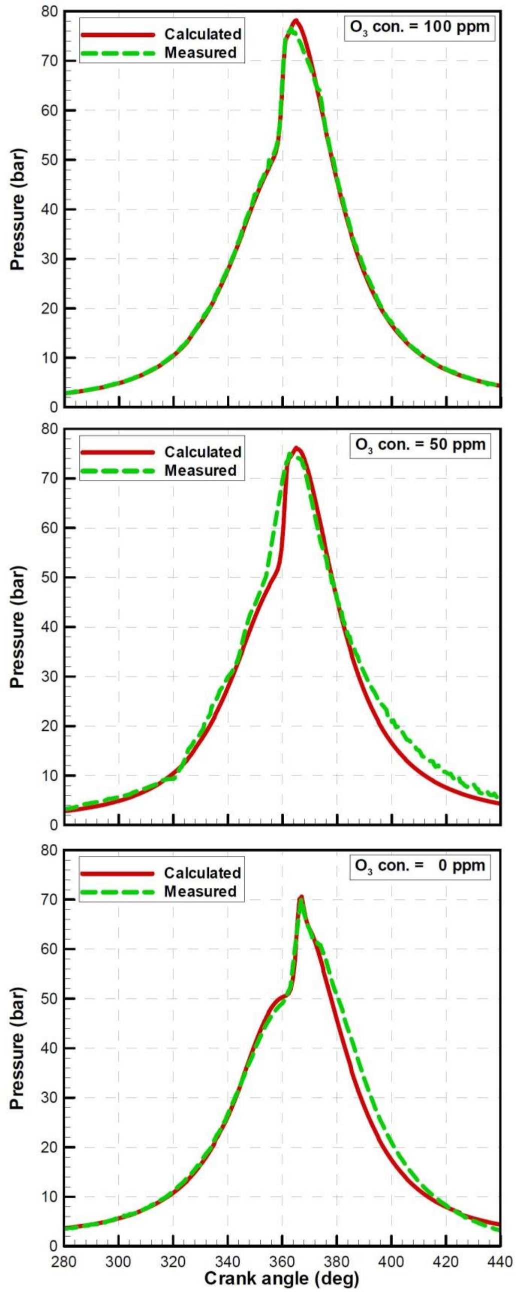


Figure 3: Comparison of measured and calculated pressure and heat release rate curves

4. Results and discussion

Various different concentrations of ozone are chosen to investigate the influence of ozone species on the combustion process and performance of NG/diesel RCCI engines.

To simulate the engine operation with ozone addition, it is supposed that a premixed charge of air+O3+NG enters the cylinder. In the experiments, air is ozonized by passing through an ozonizer (Fig. 2 (b)). Four concentration amounts for ozone addition are investigated in the present work: no addition (0 ppm), low (10 ppm), medium (100 ppm) and high amounts (1000 ppm). To achieve the RCCI combustion mode in the present work, there is early injection of the secondary fuel (diesel fuel) in the engine pre-chamber. In all of the presented cases, the start of injection (SOI) time is 45° BTDC.

4.1. Ozone addition effects on combustion progress and engine performance

OH ion is known to be the most affecting among the species on the high temperature combustion process to take place [44]. To investigate the ozone addition effect on generating OH ion in the RCCI combustion mode, the state with initial temperature of 355 K, initial pressure of 1.2 bars and initial equivalence ratio of 0.3, i.e., the baseline state, is considered. Similar to the validation case, the ratio of NG and diesel fuels is also 80 % and 20 % of total energy content. In the present section, simulations are done with consideration of making the mixture with four above mentioned concentrations of ozone.

Mass fraction contours for distribution of OH species in the combustion chamber are shown in figure 4. In this figure, in-cylinder distribution of the OH ion in five successive crank angles near the piston TDC for the four mentioned values of ozone concentration are compared. Presented sections in this figure are colored contours on the middle vertical section of the combustion chamber and the illustrated crank angles are: -7°, 0°, 2°, 6° and 14° ATDC. It is evident that addition of higher amounts of ozone causes earlier start in generation of OH which results in earlier start of the high temperature combustion phase.

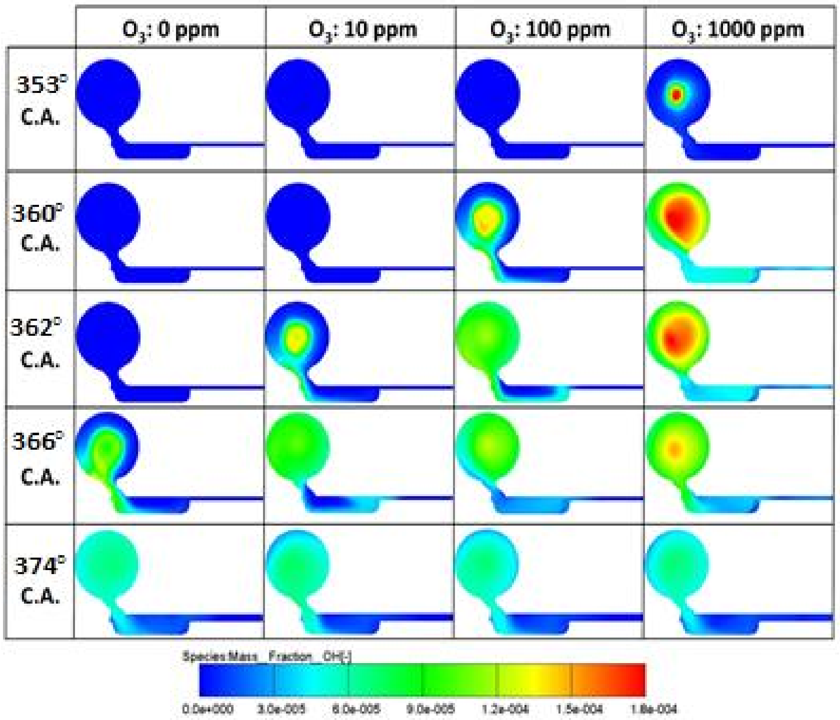


Figure 4: OH concentration for five successive crank angles near the piston TDC, for different amounts of ozone addition

To discuss the effect of ozone addition on engine performance characteristics, effect of adding various amounts of ozone to the baseline conditions on HRR and in-cylinder pressure is presented in Figure 5. The curves imply that adding ozone results in earlier rise of heat release rate and the pressure and consequently, causes higher heat release rate and pressure peaks. It is also seen that by increasing the amounts of added ozone, there will be more advancement in heat release phasing and as a result, expedition in pressure rise and higher peaks of HRR and pressure.

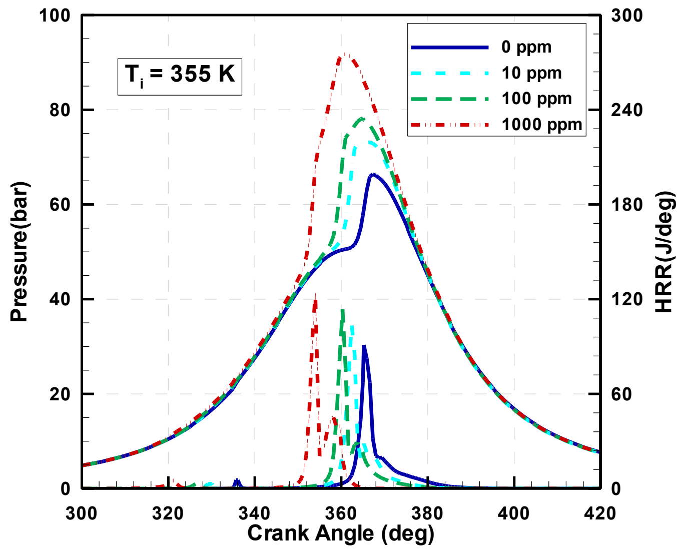


Figure 5: HRR and in-cylinder pressure for various amounts of ozone addition to the baseline conditions

By definition, combustion efficiency is calculated as the total combustion heat released divided to overall LHV energy of the consumed fuel [46]. This parameter can be considered as an indicator for the completeness and quality of the combustion process.
Figure 6 shows Combustion efficiency for various amounts of ozone addition to the baseline conditions. It can be seen that ozone addition takes the RCCI combustion process towards more completeness. The reason is enhancement in mixture reactivity and the consequent sooner start of combustion.

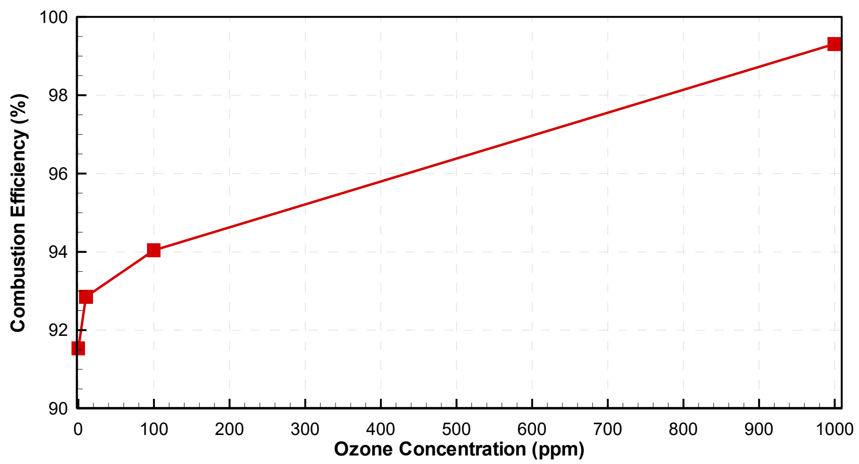


Figure 6: Combustion efficiency for various amounts of ozone addition to the baseline conditions

The parameter CA50 is defined as the engine crank angle in which 50% of the total introduced fuel is burned. For the baseline case, Figure 7 illustrates the result of adding various amounts of ozone on engine CA50. The figure shows that addition of 1000 ppm ozone can make an advancement of 12° in CA50 (from 6° ATDC for 0 ppm, to -6° ATDC for 1000 ppm ozone). It is clearly seen that ozone addition amount has a direct relation with the advancement of combustion phasing in the engine, which could be used to control the LTC engine combustion phasing.

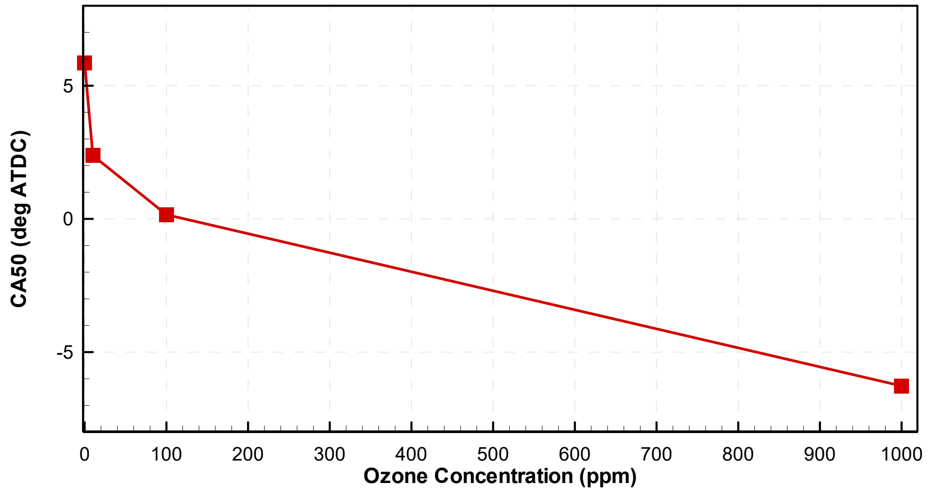


Figure 7: CA50 for various amounts of ozone addition to the baseline conditions

In the present work, indicated fuel conversion efficiency (IFCE) is the parameter that is used for comparing the engine efficiency in the studied cases. The definition of IFCE is as follows:

$$IFCE = \frac{Work_{gross}}{Fuel\ Energy} \tag{1}$$

In the present paper, $work_{gross}$ denotes the indicated work delivered in a closed cycle from engine IVC to EVO, therefore it doesn't account for intake and exhaust work losses. In addition, Fuel Energy is the total LHV energy of the fuel. Figure 8 presents a comparison of IFCE values for different ozone addition amounts to the baseline case is presented in. IFCE is seen to increase with ozone addition at first, which is because of combustion improvement and then decrease with ozone addition more than 100 ppm to 1000 ppm, which is because of the excessive advancement in the combustion phasing, that results in more negative work during the engine compression stroke and that can decrease the net engine work.

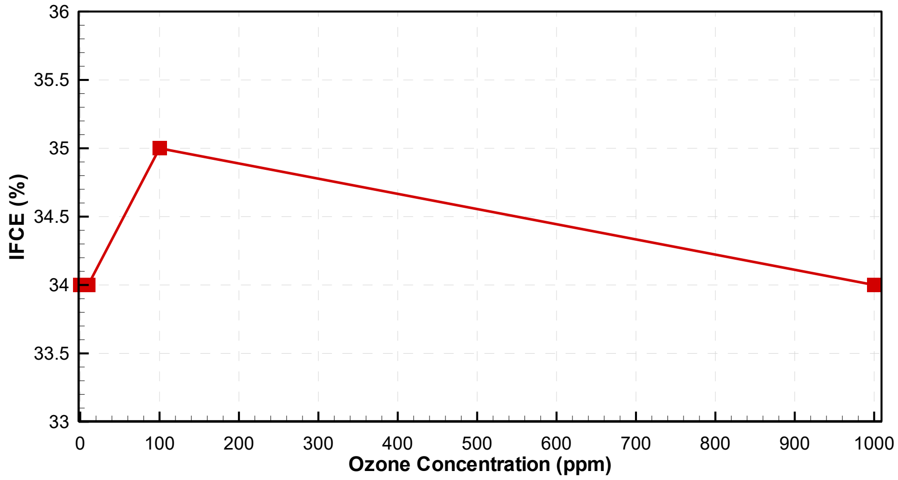


Figure 8: IFCE for different amounts of ozone addition to the baseline conditions

In the present work, besides engine performance characteristics, unburned hydrocarbons (uHC), Carbon monoxide (CO) and Nitrogen oxide (NO) emissions are considered. Emission contours on the middle vertical section of the combustion chamber, for different amounts of ozone addition to the baseline conditions, in the time of engine EVO are illustrated in Figure 9 and the averaged values (over the entire volume) of emissions are presented in Figure 10. It is clearly seen that the combustion improvement, which is the result of ozone addition, leads to emitting lower amounts of HC and CO emissions but it has increased the levels of NO emission.

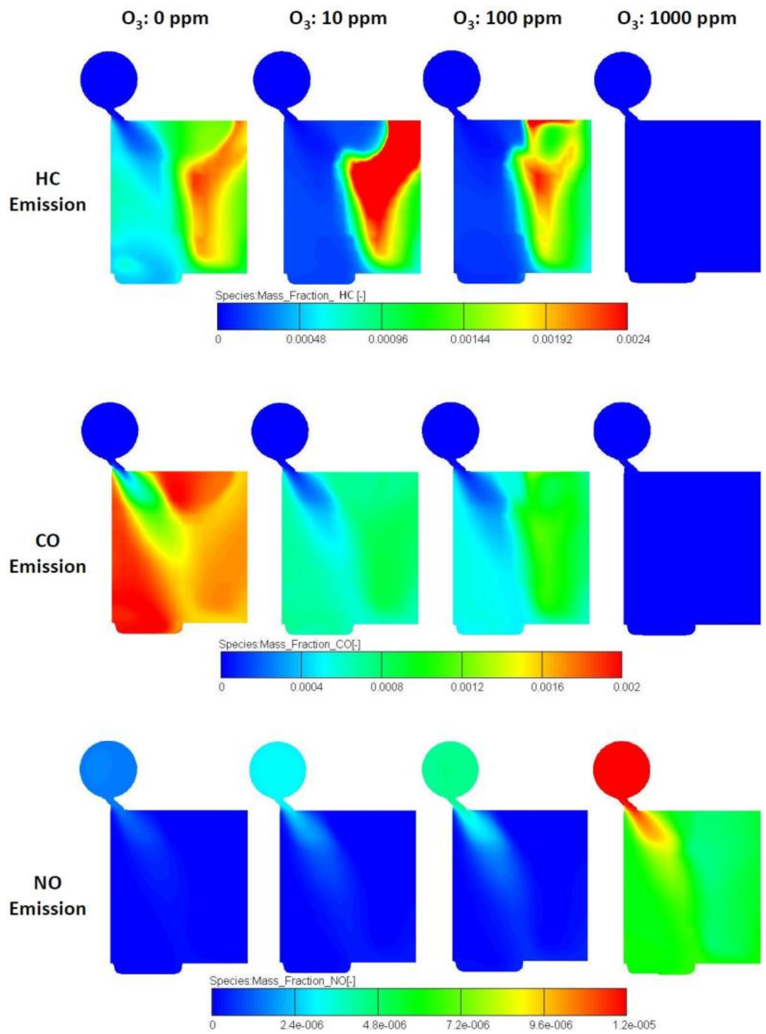


Figure 9: Emission contours for different amounts of ozone addition to the baseline conditions, EVO time

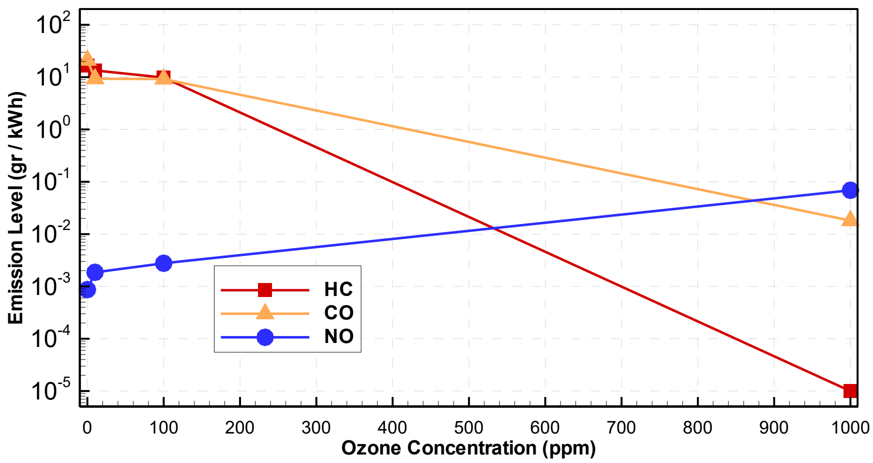


Figure 10: Emission Levels for different ozone addition amounts to the baseline conditions

4.2. Effect of ozone addition concentration on required initial temperatures

In the engines with RCCI combustion strategy, one of the parameters with the most significant effects on the engine combustion phasing is the temperature of intake air to the cylinder [45]. For mixtures with lower chemical reactivity, higher intake temperatures are required to have a complete combustion. To investigate the influence of added ozone amount on combustion process and performance characteristics in the RCCI engine, four cases with various intake temperatures are simulated: the baseline temperature, which is 355 K and in addition, three lower temperatures of 345 K, 335 K and 325 K. The other conditions are set the same as those for the baseline simulated case: initial pressure of 1.2 bar, overall fuel with equivalence ratio of 0.3 that is consisted of 80 % NG and 20 % diesel fuel (percentages of total energy content). In a range of zero to high amounts, ozone addition values of 0, 10, 100 and 1000 ppm (of the total in-cylinder mixture) to the intake air is investigated.

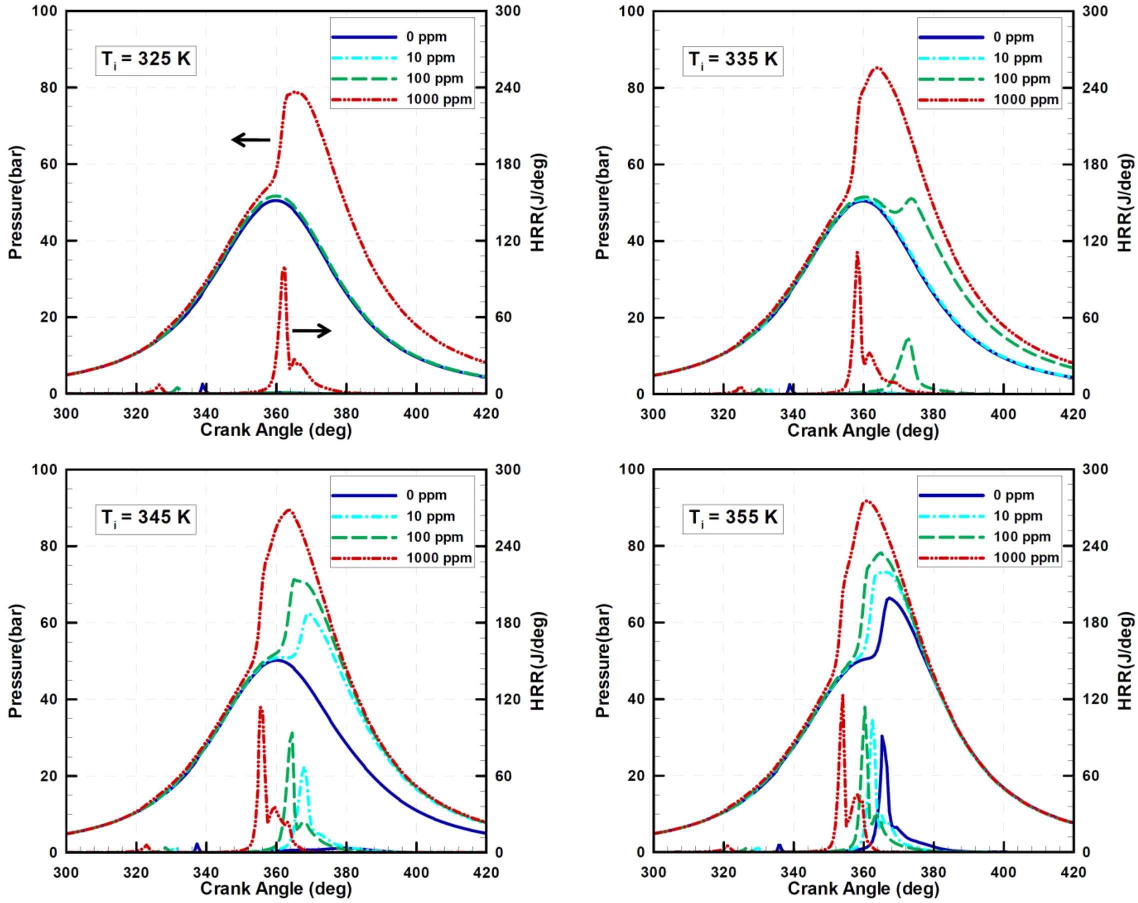


Figure 11: HRR and in-cylinder pressure for different initial temperatures and amounts of ozone addition

Influence of various ozone addition amounts on in-cylinder HRR and pressure is illustrated in Figure 11. Heat release rate and pressure curves for the previously mentioned cases, with different initial temperatures are depicted in this figure. As the first observation, it can be seen that for equal ozone addition amounts, increasing the initial temperature causes earlier heat release and as a result, earlier pressure rise and higher-pressure peaks. In all cases, it is seen that for equal conditions, as stated in the previous subsection, ozone addition causes earlier rise in heat release rate and the pressure curve and consequently, higher heat release rate and pressure peaks. It is seen that for the cases with zero ozone addition, reducing the T_i from 355 K to 345 K and less results in almost no combustion and heat release. For the mentioned cases, the figures show that adding ozone can make the combustion happen and so, extend the engine operating range to lower initial air temperatures. It can also be seen that for lower initial temperatures, more ozone is needed for the combustion process to occur properly, since higher mixture reactivity will be required where there are lower temperatures. It is worthy to note that for other performed simulations with lower temperatures (315 K and less) addition of no amount of ozone is useful to make the combustion happen. This means that there exists a limit for initial temperature range extension with ozone addition. One other fact that can be inferred from Figure 11 is that for higher initial temperatures (355 K and 345 K), even adding very low portions of ozone can intensively affect the combustion process and resulting heat release and in-cylinder pressure. This fact means that addition of proper amounts of ozone can be a promising means to control the combustion and operation in RCCI engine mode (and probably for other LTC strategies). For the discussed cases, values of combustion efficiency are compared in Figure 12. It can be seen that for initial temperatures lower than 355 K, ozone addition causes extreme growth in the combustion efficiency, which is a result of reactivity augmentation and consequently combustion improvement in the engine.

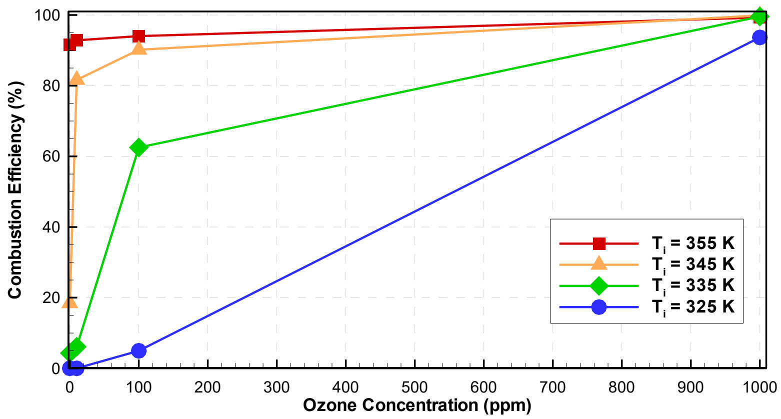


Figure 12: Combustion efficiency for different initial temperatures and different amounts of ozone addition

To investigate the effect of ozone addition on combustion phasing in the RCCI engine, CA50 parameter for the different discussed cases is presented in Figure 13. In this figure, the cases that face incomplete combustion and misfiring are omitted from the present phasing study. It is seen that higher initial temperature has resulted in more advancement in combustion phasing (earlier CA50crank angles). It also can be seen that for equal initial temperatures, adding ozone causes advancement in the combustion. It is also inferred that adding more ozone results in a more advanced combustion phasing.

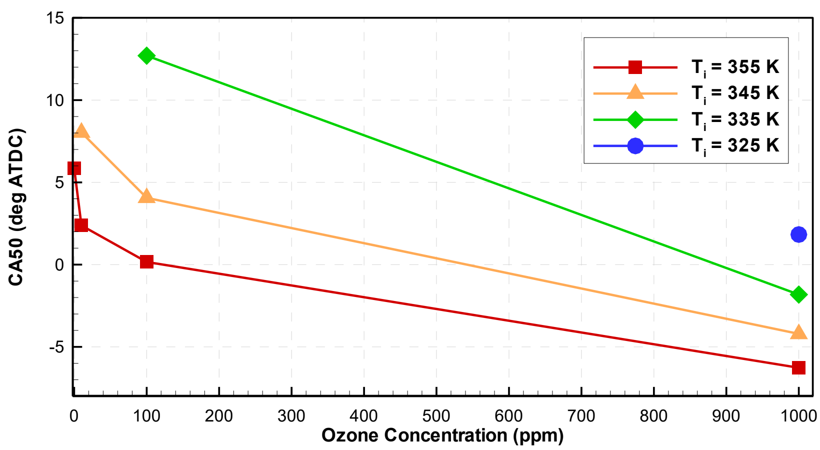


Figure 13:CA50 for different initial temperatures and different amounts of ozone addition

Values of IFCE for the discussed cases are compared in Figure 14. It can be seen that for highest simulated initial temperature, i.e., 355 K increase in ozone addition from 100 ppm to 1000 ppm results in decrease in engine efficiency. That is because, as seen from Figure 13, adding ozone results in too much advancement in combustion phasing and that leads to increasing engine negative work in the compression stroke and as a result, reduction in total engine work and IFCE. On the other hand, where there is a lower initial temperature, as can be inferred from Figure 12, addition of ozone addition improves the combustion process, and enhancement in engine efficiency can happen.

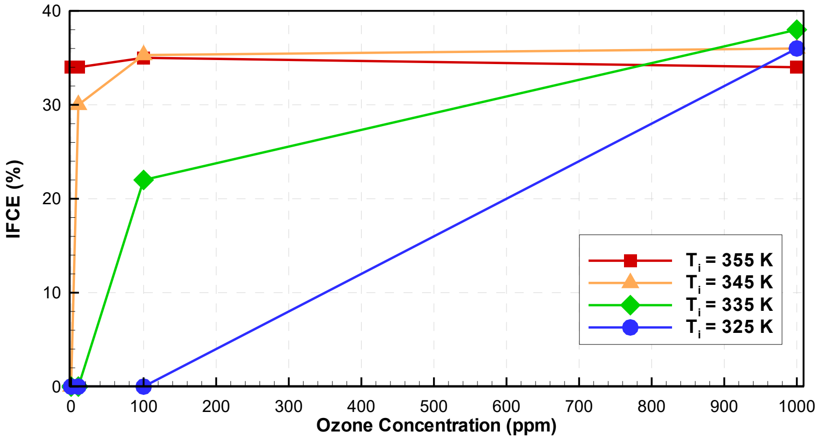


Figure 14: IFCE values for different initial temperatures and different amounts of ozone addition

It was seen that adding ozone can simultaneously make improvement in combustion and advancement in its phasing. Therefore, ozone addition amount should be set properly for each condition to improve the engine performance characteristics. For different values of initial temperature and different amounts of ozone addition, Curves of HC, CO and NO emissions are shown in Figure 15, Figure 16 and Figure 17 respectively. Emissions are presented in the gr per kWh unit and for the reason of big differences in magnitudes are shown with the logarithmic form in the vertical axis. It can be seen that for the cases with the same conditions, adding more ozone results in decrease in HC and CO emissions, which is due to the earlier discussed enhancement in combustion complement, which is resulted by the reactivity augmentation. It is also seen that adding more ozone increases NO emission, which is because more complete combustion and also earlier rise in engine in-cylinder pressure and temperature that leads to higher temperatures in the cylinder, which is the main source of NO emission generation. In addition, as expected, the figures show that because of the same reasons (more complete combustion) for the cases with equal conditions, increasing T_i decreases HC and CO emissions. Moreover, because of more in-cylinder temperatures, increasing T_i causes increase in NO emission.

Analyzing Figure 14 and Figure 17 together reveals a noteworthy conclusion. It is seen that the cases with T_i of 325 K and 335 K and 1000 ppm ozone, result rather high efficiencies and very low NO emission amounts. This means that with adding ozone it would be achievable to operate the engine with lower intake air temperatures and simultaneously increase the efficiency and remarkably reduce the NO emission.

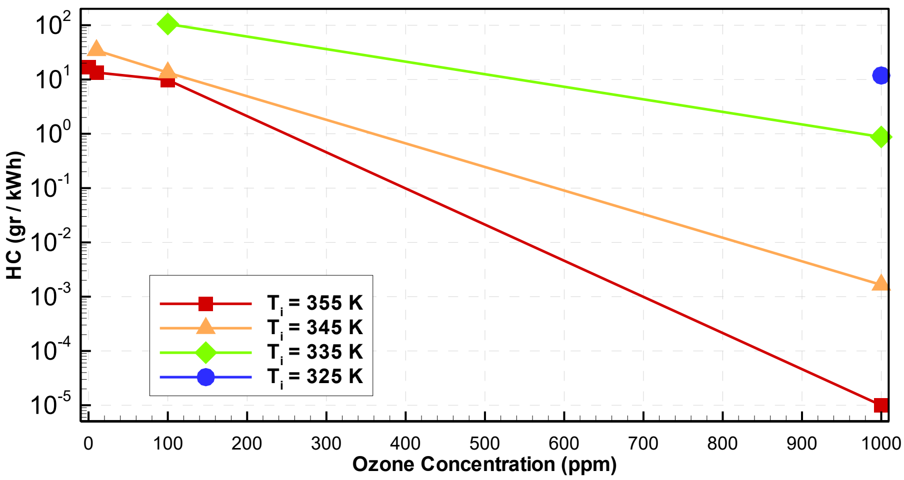


Figure 15: HC emission for different initial temperatures and different amounts of ozone addition

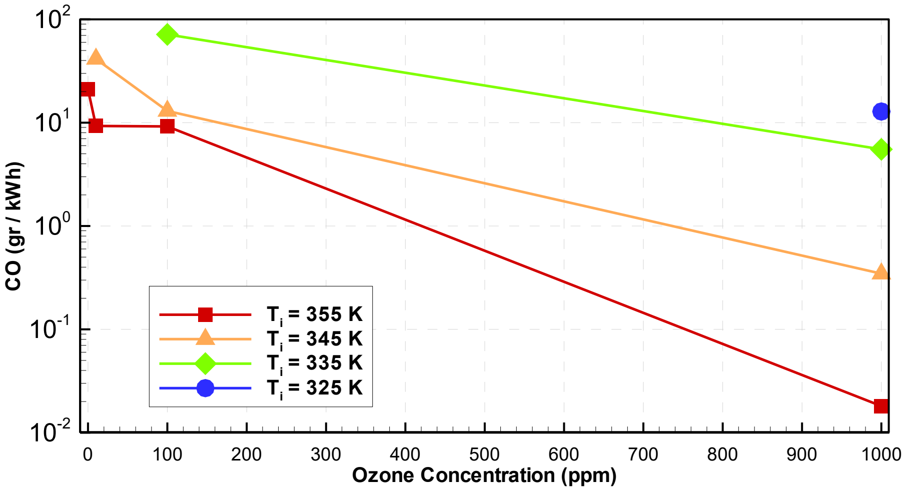


Figure 16: CO emission for different initial temperatures and different amounts of ozone addition

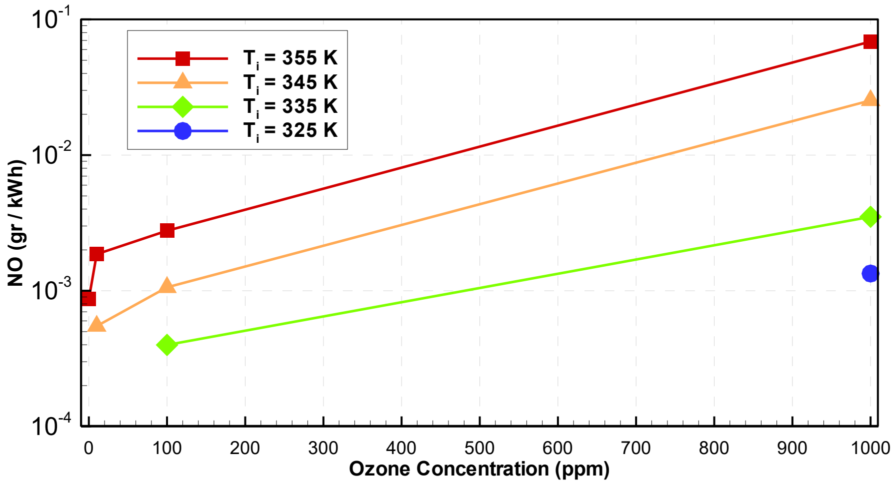


Figure 17: NO emission for different initial temperatures and different amounts of ozone addition

4.3. Decreasing diesel percentage by adding ozone

In the previous section it was shown that via increasing the mixture reactivity, ozone addition enables the RCCI engine to maintain a complete combustion with lower initial temperatures and it brings about advantages of higher efficiencies and lower emissions. In the present section, the main idea is to decrease the portion of the more reactive fuel and compensate the mixture reactivity reduction by adding ozone to the intake air. To do so, same as the previous section, initial temperature of 355 K, initial pressure of 1.2 bar and overall fuel equivalence ratio of 0.3 are set for the simulations. For energy portions of the two fuels are assumed: the baseline case of 20 % diesel and 80 % NG, the case with 15 % diesel and 85% NG, the case with 10 % diesel and 90 % NG, and finally the case with 5 % diesel and 95 % NG. Four ozone addition amounts of 0, 10, 100 and 1000 ppm are also assumed for the investigations. Influence of ozone addition on heat release rate and in-cylinder pressure is shown in Figure 18 for the four simulated fuel percentages. It can be seen that with equal ozone addition amounts, lowering the portion of the reactive fuel, i.e., diesel, results in later start in heat release and also decreases in-cylinder pressure and HRR. The pictures show that like in the previous section, addition of ozone causes advancement in heat release and RCCI combustion phasing and also the more the ozone addition is, the more the advancement in the combustion phasing will be.

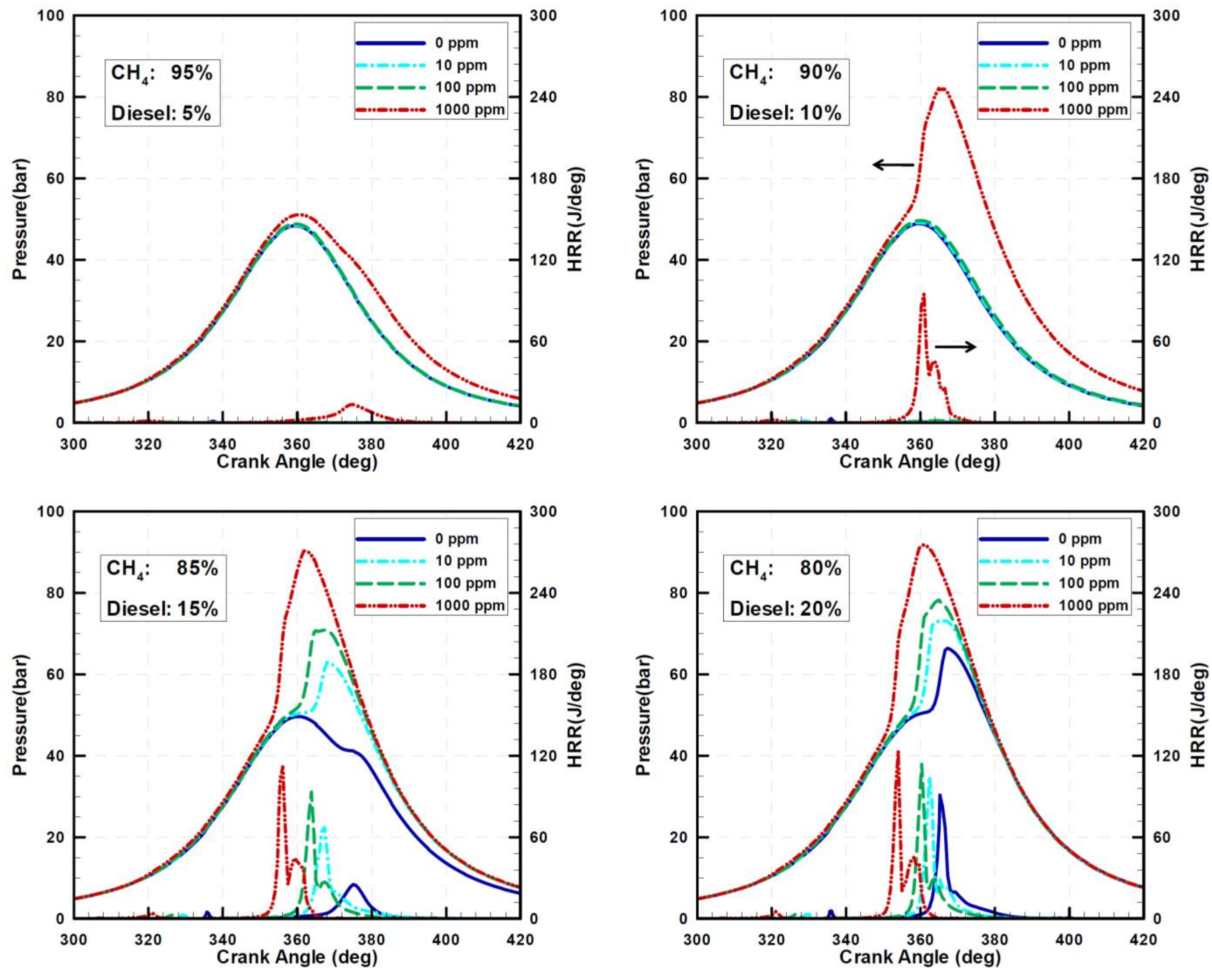


Figure 18: In-cylinder HRR and pressure for different diesel and NG ratios and amounts of ozone addition

For the RCCI cases with different portions of the two fuels with different reactivity levels, a comparison of combustion efficiencies is presented in Figure 19. It can be seen that because of incomplete combustion resulted from insufficient mixture reactivity, the cases with less amounts of the diesel fuel have lower combustion efficiencies. In all cases, as expected, adding more amounts of ozone is seen to increase the combustion efficiency. Figure 19 shows that the case with 10 % diesel fuel, have almost no combustion where no ozone is added, but with 1000 ppm ozone, this case experiences a perfect combustion process. On the other hand, for the case with only 5 % of diesel fuel, it seems that however ozone addition improves the combustion, but there is a limit for the improvement and 1000 ppm ozone can raise the combustion efficiency only to about 42 %.

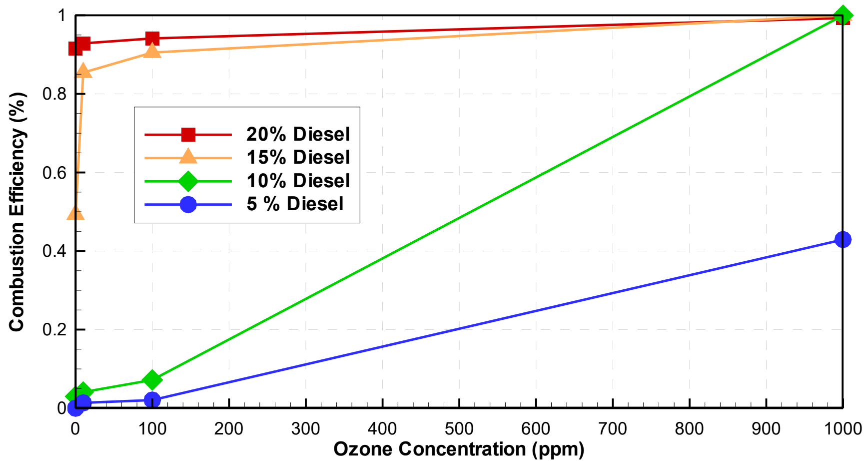


Figure 19: Combustion efficiency for different diesel and NG ratios and different amounts of ozone addition

The effect of ozone addition on combustion phasing (CA50) in the RCCI engine with various portions of the two fuels is depicted in Figure 20. It can be seen from the curves that higher portions of the more reactive fuel results in more advancement in combustion (earlier crank angles for CA50). The picture also shows that with the same fuel composition, addition of more ozone results in more advancement in combustion phasing.

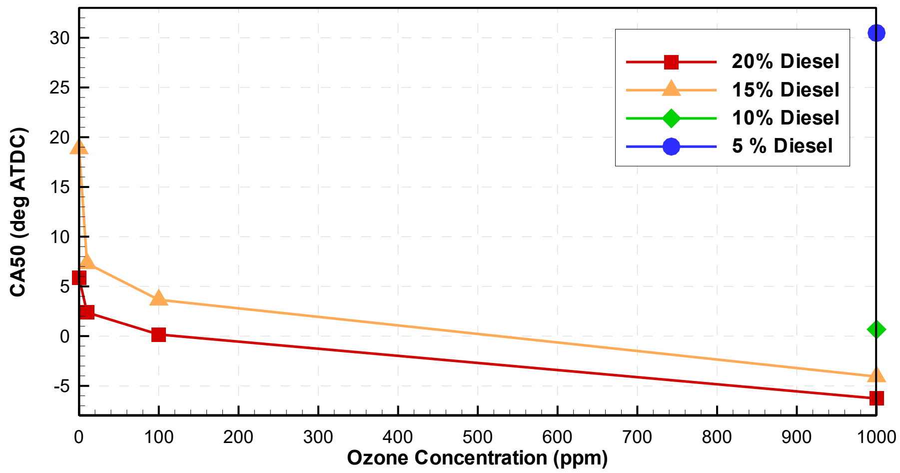


Figure 20: CA50 for different diesel and NG ratios and different amounts of ozone addition

In Figure 21, values of IFCE for the various portions of the two fuels are compared. As the picture shows, for the case with 20 % diesel fuel, ozone addition up to 100 ppm leads to a slight rise in the engine efficiency, but due to too advanced combustion phasing and the discussed increase in the negative work during the engine compression stroke, addition of 1000 ppm ozone has decreased the efficiency. One interesting result that Figure 19 shows is the case of 10 % diesel. This case is seen to have almost no combustion for up to 100 ppm ozone.

Nevertheless, adding 1000 ppm ozone to the case with 10 % diesel, as shown in Figure 21, results in a rather complete combustion and due to its late combustion phasing, the most engine efficiency in all of the studies cases.

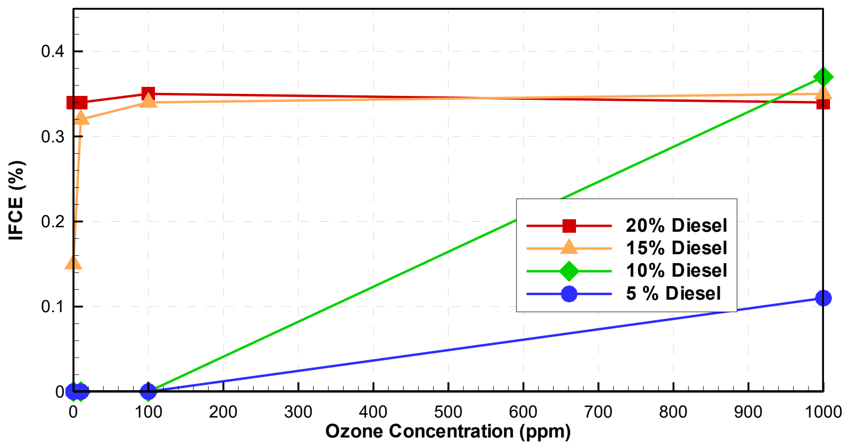


Figure 21: IFCE for different diesel and NG and different amounts of ozone addition

One of the most important issues about the engines that work in low temperature combustion modes (e.g., HCCI and RCCI engines) is their relatively high level of HC and CO emissions. The amounts of HC and CO emissions for different diesel fuel portions and different ozone amounts are shown in Figure 22 and Figure 23 respectively. For the cases with 20 % and 15 % diesel fuel, it can be seen that ozone addition can cause a drastic reduction in levels of HC and CO emissions, while according to Figure 21, their efficiency is increased or only slightly decreased.

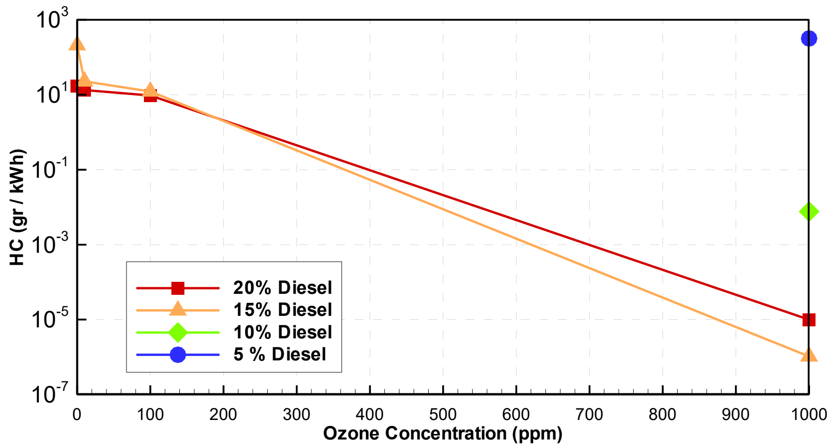


Figure 22: HC emission different diesel and NG ratios and different amounts of ozone addition

Amounts of NO emission for the discussed cases are depicted in Figure 24. Generally, engine NO formation is a function of in-cylinder temperature, oxygen concentration, and available time for reactions [47]. Because of the advanced combustion which causes higher in-cylinder temperatures, as the Figure 24 appears, ozone increment results more NO emission. However, for the presented cases, even after adding 1000 ppm ozone, despite the shown remarkable reduction in HC and CO emissions, NO level is still below the amount specified by the stringent regulations.

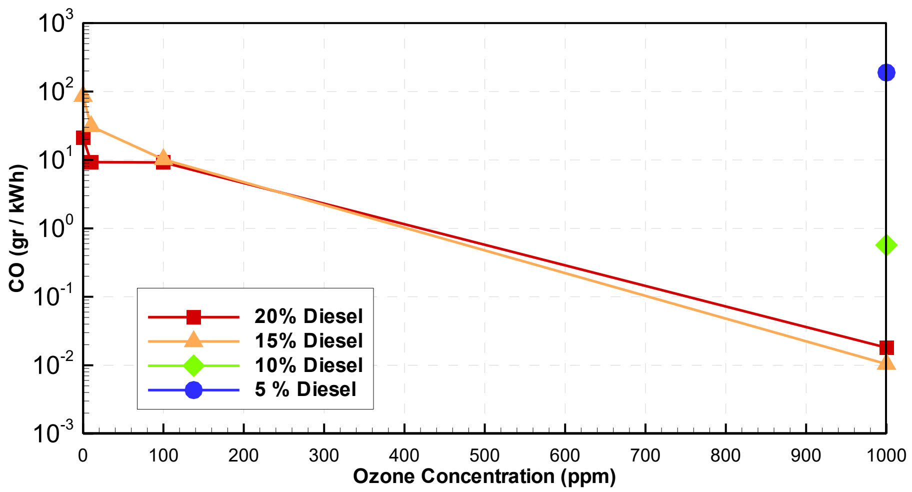


Figure 23: CO emission for different diesel and NG ratios and different amounts of ozone addition

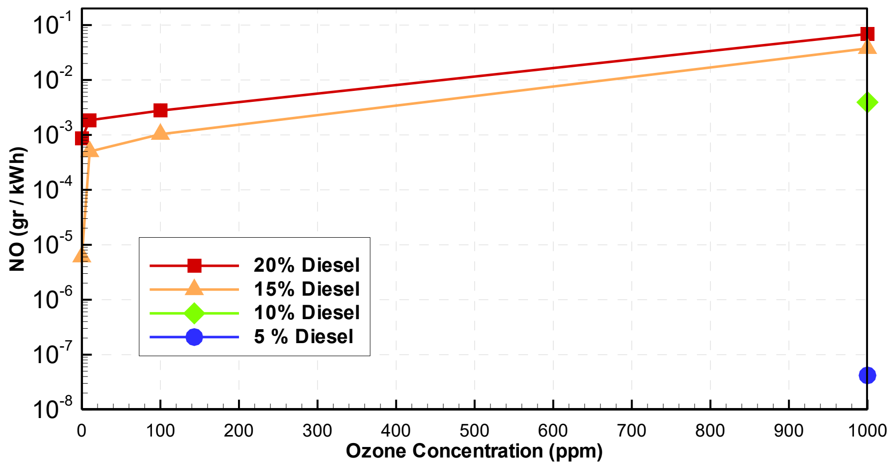


Figure 24: NO emission for different diesel and NG ratios and different amounts of ozone addition

5. Conclusion

The effects of adding various amounts of an extreme active species, ozone gas, to in-cylinder air-fuel mixture on combustion and performance characteristics of RCCI engine with NG and diesel fuels was numerically investigated. The numerical tool was a 3-D CFD model with consideration of appropriate chemical kinetic reactions. Firstly, experimentally obtained data was used to validate the numerical model and after that, the simulations were conducted with different values for ozone concentration, initial temperature, and the ratio of the two fuels, with the assumption of constant energy content. Throughout all investigated cases, engine speed considered at 800 rpm. The significant findings to emerge from the study can be concluded as follows:

- Adding ozone accelerates the formation of OH radical, and that causes advancement in high temperature heat release and combustion process. Adding more ozone leads to earlier start of RCCI combustion and consequently, more combustion efficiency.
- Since the occurrence of RCCI combustion requires a certain degree of initial temperature, ozone addition can help it to take place by having a lower initial temperature condition. It was observed that adding 1000 ppm ozone, required 20 K

lower initial temperature for RCCI combustion occurrence with a higher engine efficiency and lower emission levels.

- Ozone addition advances the combustion phasing therefore it can result in decreasing engine thermal efficiency. In order to gain optimum efficiencies, proper amount of ozone must be added to suitably adjust the combustion phasing.
- Given higher combustion completeness by adding ozone, will decrease the concentration of CO and HC emissions however it increases NO emission level. Addition of 1000 ppm ozone decreased the CO level 100 times while this amount is about 10^5 times for HC emission. Although, NO emission increased 100 times by 1000 ppm ozone addition, its amount is lower than NOx Euro 6 limit (i.e., 0.4 g/kWh).
- Addition of ozone enabled the engine to be operated under a different fuel share by having a lower amount of high-reactive fuel (i.e., diesel) combined with a higher amount of low-reactive fuel (i.e., NG) without encountering any delay in the start of combustion which causes misfiring. By adding 1000 ppm ozone into the mixture, it is possible to reduce the diesel fuel fraction from 20 % to 10 % by maintaining at the state of complete combustion (i.e., combustion efficiency ~ 100 %)

In general, ozone addition in the fuel mixture of RCCI engines resulted in a better combustion phasing adjustment, a decreased required initial intake air temperature, a lower consumption of diesel fuel (which is more costly and more pollutant) with lower initial temperature. Adding optimum amounts of a highly reactive species like ozone could be an effective means to address the controllability issue of the RCCI engine as well as the other premixed charge LTC engines in order to extend their operating range.

Acknowledgment

The authors would like to thank the thermodynamics laboratory of Amirkabir University of technology for providing the experimental facilities.

References

[1] Moradi J., Gharehghani A., Aghahasani M. Application of machine learning to optimize the combustion characteristics of RCCI engine over wide load range. Fuel 324 (Part A), 124494, 2022.
[2] Esfahanian V., Salahi M.M., Gharehghani A., Mirsalim M. "Extending the lean operating range of a premixed charged compression ignition natural gas engine using a pre-chamber", Energy, 119, pp. 1181-1194, 2017
[3] Xu Z., Jia M., Li Y., Chang Y., Xu G., Xu L., Lu X. Computational optimization of fuel supply, syngas composition, and intake conditions for a syngas/diesel RCCI engine. Fuel 234, 120-134, 2018.
[4] D.Z. Zhou, W.M. Yang, H. An, J. Li. Application of CFD-chemical kinetics approach in detecting RCCI engine knocking fuelled with biodiesel/methanol. Applied Energy 145, 255-264, 2015.
[5] R. Ahmadi, S. M. Hosseini. Numerical investigation on adding/substituting hydrogen in the CDC and RCCI combustion in a heavy-duty engine. Applied Energy 213, 450-468, 2018.
[6] K. Poorghasemi, R. Khoshbakhti Saray, E. Ansari, B. Khoshbakht Irdmousa, M. Shahbakhti, Jeffery D. Naber. Effect of diesel injection strategies on natural gas/diesel RCCI combustion characteristics in a light duty diesel engine, Applied Energy 199, 430-446, 2017.

[7] Jamali, A., Ra, Y., Park, W., and Cho, G., "A Combustion Model for Multi-Component Fuels Based on Reactivity Concept and Single-Surrogate Chemistry Representation," SAE Technical Paper 2018-01-0260, 2018.
[8] G. Di Blasio, G. Belgiorno, C. Beatrice. Effects on performances, emissions and particle size distributions of a dual fuel (methane-diesel) light-duty engine varying the compression ratio, Applied Energy 204, 726-740, 2017.
[9] Jun Shu, Jianqin Fu, Jingping Liu, Lei Zhang, Zhichao Zhao. Experimental and computational study on the effects of injection timing on thermodynamics, combustion and emission characteristics of a natural gas (NG)-diesel dual fuel engine at low speed and low load. Energy Conversion and Management 160, 426-438, 2018.
[10] Mahmoudzadeh Andwari, A.; Aziz, A.A.; Said, M.F.M.; Latiff, Z.A. A Converted Two-Stroke Cycle Engine for Compression Ignition Combustion. Appl. Mech. Mater. 2014, 663, 331–335.
[11] Euijoon Shim, Hyunwook Park, Choongsik Bae. Intake air strategy for low HC and CO emissions in dual-fuel (CNG-diesel) premixed charge compression ignition engine. Applied Energy 225, 1068-1077, 2018.
[12] Srivatsa, C., Mattson, J., and Depcik, C., "Investigating Pre-Mixed Charge Compression Ignition Combustion in a High Compression Ratio Engine," SAE Technical Paper 2018-01-0900, 2018.
[13] Rahnama P., Paykani A., Bordbar V., Reitz R.D. A numerical study of the effects of reformer gas composition on the combustion and emission characteristics of a natural gas/diesel RCCI engine enriched with reformer gas. Fuel 209, 742-753, 2017.
[14] Rahnama P., Paykani A., Reitz R.D., “A numerical study of the effects of using hydrogen, reformer gas and nitrogen on combustion, emissions and load limits of a heavy-duty natural gas/diesel RCCI engine”. Applied Energy 193, 182–198, 2017.
[15] Gharehghani A. Hosseini R. Mirsalim M. Jazayeri A. Yusaf T., "An experimental study on reactivity controlled compression ignition engine fueled with biodiesel/natural gas," Energy, vol. 89, pp. 558-567, 2015.
[16] Andwari, A.M.; Said, M.F.M.; Aziz, A.A.; Esfahanian, V.; Salavati-Zadeh, A.; Idris, M.A.; Perang, M.R.M.; Jamil, H.M. Design, Modeling and Simulation of a High-Pressure Gasoline Direct Injection (GDI) Pump for Small Engine Applications. J. Mech. Eng. 2018, 1, 107–120
[17] J. Li, W.M. Yang, H. An, D. Zhao. Effects of fuel ratio and injection timing on gasoline/biodiesel fueled RCCI engine: A modeling study. Applied Energy 155, 59-67, 2015.
[18] Jing Li, Xiang Ling, Deng Liu, Wenming Yang, Dezhi Zhou. Numerical study on double injection techniques in a gasoline and biodiesel fueled RCCI (reactivity controlled compression ignition) engine. Applied Energy 211, 382-392, 2018.
[19] Jamshid Moradi, Ayat Gharehghani, Mostafa Mirsalim. Numerical investigation on the effect of oxygen in combustion characteristics and to extend low load operating range of a natural-gas HCCI engine. Applied Energy 276, 115516, 2020.
[20] Alireza Kakoee, Younes Bakhshan, Sattar Motadayen Aval, Ayat Gharehghani. An improvement of a lean burning condition of natural gas/diesel RCCI engine with a pre-chamber by using hydrogen. Energy Conversion and Management 166, 489-499, 2018.
[21] Salahi M.M., Esfahanian V., Gharehghani A., Mirsalim M. “Investigating the reactivity controlled compression ignition (RCCI) combustion strategy in a natural gas/diesel fueled engine with a pre chamber”. Energy Conversion and management 132, 40-53, 2017.
[22] A. M. Andwari, A. Pesiridis, V. Esfahanian, M. F. Muhamad Said. “Combustion and Emission Enhancement of a Spark Ignition Two-Stroke Cycle Engine Utilizing Internal and External Exhaust Gas Recirculation Approach at Low-Load Operation”, Energies, 2019, 12 (4), 609; 10.3390/en12040609

[23] Su Han Park, Dalho Shin, Jeonghyun Park. Effect of ethanol fraction on the combustion and emission characteristics of a dimethyl ether-ethanol dual-fuel reactivity controlled compression ignition engine. Applied Energy 182, 243-252, 2016.
[24] Yu, S., Dev, S., Yang, Z., Leblanc, S. et al., "Early Pilot Injection Strategies for Reactivity Control in Diesel-ethanol Dual Fuel Combustion," SAE Technical Paper 2018-01-0265, 2018.
[25] Guangfu Xu, Ming Jia, Yaopeng Li, Yachao Chang, Tianyou Wang. Potential of reactivity controlled compression ignition (RCCI) combustion coupled with variable valve timing (VVT) strategy for meeting Euro 6 emission regulations and high fuel efficiency in a heavy-duty diesel engine. Energy Conversion and Management 171, 683-698, 2018.
[26] Mikulski, M., Balakrishnan, P., Doosje, E., and Bekdemir, C., "Variable Valve Actuation Strategies for Better Efficiency Load Range and Thermal Management in an RCCI Engine," SAE Technical Paper 2018-01-0254, 2018.
[27] Gharehghani, A.; Kakoee, A.; Andwari, A.M.; Megaritis, T.; Pesyridis, A. Numerical Investigation of an RCCI Engine Fueled with Natural Gas/Dimethyl-Ether in Various Injection Strategies. *Energies* **2021**, *14*, 1638.
[28] Sedigheh Karami, Ayat Gharehghani. Effect of nano-particles concentrations on the energy and exergy efficiency improvement of indirect-injection diesel engine. Energy Reports, 7, 3273-3285, 202.
[29] J. Li, W.M. Yang, H. An, D.Z. Zhou, W.B. Yu, J.X. Wang, L. Li. Numerical investigation on the effect of reactivity gradient in an RCCI engine fueled with gasoline and diesel. Energy Conversion and Management 92, 342-352, 2015.
[30] Yaopeng Li, Ming Jia, Yachao Chang, Zhen Xu, Guangfu Xu, Hong Liu, Tianyou Wang. Principle of determining the optimal operating parameters based on fuel properties and initial conditions for RCCI engines. Fuel 216, 284-295, 2018.
[31] Hu Wang, Xumin Zhao, Laihui Tong, Mingfa Yao. The effects of DI fuel properties on the combustion and emissions characteristics of RCCI combustion. Fuel, 227, 457-468, 2018.
[32] Maciej Mikulski, Cemil Bekdemir. Understanding the role of low reactivity fuel stratification in a dual fuel RCCI engine – A simulation study. Applied Energy 191, 689-708, 2017.
[33] Masurier J.B, Foucher F, Dagaut P, Dayma G. “Investigation of iso-octane combustion in a homogeneous charge compression ignition engine seeded by ozone, nitric oxide and nitrogen dioxide”. Proceedings of the Combustion Institute 35, 3125–3132, 2015.
[34] Masurier J.B. Foucher F. Dayma G. Dagaut P. "Effect of Additives on Combustion Characteristics of a Natural Gas Fueled HCCI Engine," SAE Technical Pape, 2014-01-2662, 2014.
[35] Mohammad Mahdi Salahi, Ayat Gharehghani. Control of combustion phasing and operating range extension of natural gas PCCI engines using ozone species. Energy Conversion and Management 199, 112000, 2019.
[36] Nishida, H., and Tachibana, T., "Homogeneous charge compression ignition of natural gas/air mixture with ozone addition," Journal of propulsion and power 2006, 22 (1), 151-157.
[37] Mohammadi, A., Kawanabe, H., Ishiyama, T., Shioji, M. et al., "Study on Combustion Control in Natural-Gas PCCI Engines with Ozone Addition into Intake Gas," SAE Technical Paper 2006-01-0419, 2006.
[38] Rotzoll, G. Mass spectrometric investigation and computer modeling of the CH4-O2-O3 reaction from 480 to 830 K. J. Phys. Chem. 90 (4), 677–683, 1986.
[39] Nomaguchi, T., Koda S. Spark ignition of methane and methanol in ozonized air. Symp.(Int.)Combust., [Proc.], 22 (1), 1677–1682, 1989.
[40] Foucher F. Higelin P. Mounaim-Rousselle C. Dagaut P." Influence of ozone on the combustion of n-heptane in a HCCI engine," *Proceeding of the Combustion Institute*, vol 34, pp 3005-3012, 2013.

[41] Masurier J.B. Foucher F. Dayma G. Dagaut P. "Ozone applied to the homogeneous charge compression ignition engine to control alcohol fuels combustion," *Applied Energy*, vol. 160, pp 566-580, 2015.
[42] *AVL FIRE User Guide, Version 2011.*: AVL List Gmbh, 2012.
[43] Andrew Hockett, Greg Hampson, and Anthony J. Marchese. Development and Validation of a Reduced Chemical Kinetic Mechanism for Computational Fluid Dynamics Simulations of Natural Gas/Diesel Dual-Fuel Engines. *Energy & Fuels* **2016** *30* (3), 2414-2427
[44] Alireza Kakoee, Ayat Gharehghani, Mohsen Mostafaei. Development of a reduced chemical kinetic mechanism for biodiesel/natural gas mixture. Fuel 312, 122920, 2022.
[45] A. Kakoee, Y. Bakhshan, A. Gharehghani, M.M. Salahi. Numerical comparative study of hydrogen addition on combustion and emission characteristics of a natural-gas/dimethyl-ether RCCI engine with pre-chamber. Energy186, 115878, 2019.
[46] Heywood J. Internal combustion engine fundamentals. New York (USA): McGraw-Hill Publications; 1988.
[47] Gharehghani A, Hosseini R, Mirsalim M, Yusaf TF. A computational study of operating range extension in a natural gas SI engine with the use of hydrogen. Int J Hydrogen Energy 2015;40(17):5966–75.

Abbreviations List:

AFR	Air Fuel Ratio
ATDC	After Top Dead Center
BDC	Bottom Dead Center
BTDC	Before Top Dead Center
CA	Crank Angle
CFD	Computational Fluid Dynamics
CN	Cetane Number
CNG	Compressed Natural Gas
CO	Carbon Monoxide
EGR	Exhaust Gas Recirculation
EVC	Exhaust Valve Close
EVO	Exhaust Valve Open
HC	Hydro Carbon
HCCI	Homogeneous Charge Compression Ignition
HRR	Heat Release Rate
IFCE	Indicated Fuel Conversion Efficiency
IVC	Intake Valve Close
IVO	Intake Valve Open
LHV	Lower Heating Value
LTC	Low Temperature Combustion
NG	Natural Gas
NO	Nitrogen Oxide
O	Oxygen
PCCI	Premixed Charge Compression Ignition
PM	Particulate Matter
ppm	Parts Per Million

PPR	Pulses per Revolution
RCCI	Reactivity Controlled Compression Ignition
SOI	Start of Injection
T_i	Initial Temperature
TDC	Top Dead Center