Combustion Equilibrium Chemistry as a Teaching and a Research Tool in Hellenic Naval Academy: The Case of Oxy-Diesel Combustion

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Abstract. The present study presents the theoretical work, which was performed under a diploma thesis in Hellenic Naval Academy and it was based on the theoretical investigation of oxy-diesel combustion. The term “oxy-fuel” combustion corresponds to the combustion of a liquid or a gaseous fuel in the presence of high oxidative and high CO_2 availability. The primary motivation of this study was the diesel combustion equilibrium simulation in the case of combination of intake air oxygen-enrichment and cooled exhaust gas recirculation (EGR) for identifying the pertinent effects on diesel combustion products and pollutants. According to published studies, the increase of the oxygen content in the intake air of diesel engines through the installation of separation membranes in the engine intake results in reduction of ignition delay, increase of peak cylinder pressure, dramatic reduction of particulate emissions and reduction of CO and HC emissions. Oppositely, intake air oxygen-enhancement results in serious deterioration of diesel-emitted NOx. On the other hand, EGR has been widely acknowledged as one of the most effective methods for significant NOx reduction in diesel engines with however, detrimental effects on soot emissions and on brake specific fuel consumption (BSFC). Hence, it emerges as a serious challenge the combination of intake air oxygen-enrichment and EGR with primary target the simultaneous reduction of soot and NOx emissions with beneficial or in worst case, non-detrimental effects on brake efficiency of diesel engines. Recirculated exhaust gas stream contains primarily carbon dioxide (CO_2), water (H_2O), oxygen (O_2) and nitrogen (N_2). In addition, the engine inducted air contains nitrogen, which reacts with oxygen at high combustion temperatures resulting thus, in NO generation inside the cylinder of a diesel engine. Hence, it is of high interest the investigation of diesel combustion and gaseous pollutant generation in the case of minimization or even of complete depletion of nitrogen in the inducted gaseous mixture through high oxygenation of intake air and the use of high rates of cooled EGR. Hence, in the present study, a preliminary theoretical investigation was performed for examining the effect of increased oxygenation of intake air stream and cooled EGR as well as the effect of diesel combustion with pure oxygen (inexistence of nitrogen) in the presence of carbon dioxide on the formation of diesel combustion equilibrium concentrations and particulate and gaseous emissions concentrations under combustion conditions close to actual diesel ones. Towards this aim the NASA combustion equilibrium solver was used for predicting the equilibrium mole fractions of the most important combustion-released gaseous constituents and through them to estimate on a qualitative basis the gaseous and particulate emissions.

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INTRODUCTION

The implementation of continuously stringent environmental regulations for four-stroke diesel engines has led to the development of various technologies for the curtailment of diesel-emitted gaseous and particulate pollutants [1-3]. These pollutant-reduction technologies can be divided into two main categories [4]: (a) In those which aim to the in-cylinder curtailment of gaseous and particulate pollutants and they are often called as “Internal Measures” and (b) in those which focus on the suppression of diesel-emitted pollutants in the engine exhaust and they are called as “External Measures”. Nitrogen oxides (NOx) and soot particulates are the most important atmospheric pollutants, which are emitted from diesel engines [1-3]. One of the most prominent methods for diesel combustion improvement and reduction of soot emissions is the increase of in-cylinder available oxygen mass. There are three main ways to enhance in-cylinder oxygen availability [4-9]:

1. The increase of air mass supplied to the engine cylinders by increasing boost pressure through advanced turbocharging [5,6].
2. The local increase of available for combustion oxygen mass through the increase of oxygen molar fraction in engine inducted air [7-11].
3. The combustion of oxygenated fuels either as pure fuels or as mixtures with conventional fuels [12-20].

According to existing experimental and theoretical investigations [12-20] the increase of intake air oxygen mole fraction in diesel engines results in the increase of peak cylinder pressure and in the dramatic decrease of particulate emissions. It results also in reduction of carbon monoxide (CO) emissions, unburned hydrocarbons (HC), brake specific fuel consumption (BSFC), ignition delay and diesel-emitted noise. The increase of intake air oxygen mole fraction can be attained using air separation membranes, which separate the air mixture of oxygen and nitrogen aiming to the production of air mass with higher oxygen content compared to the one air having at the entrance of the separation membrane [13,14,21-23]. The operational principle of the air separation membrane is based on the selective penetration of molecules through elements constructed from polymeric membranes. Previously published study [14] has shown that the increase of intake air oxygen fraction results in the increase of diesel engine power and in particular, the potentiality of diesel engine power generation comparable to brake power produced by turbocharged diesel engines. Hence, it has been proposed [14] the possibility of the replacement of a diesel engine turbocharging and intercooling system by a smaller and less demanding turbocharging system and air seperation membrane modules for the air supply of a diesel engine with increased oxygen mole fraction. This will result in the reduction of weight and development of a turbocharged diesel engine. Finally, previously published studies [24-28] have demonstrated that the intake air oxygen-enrichment may result in improvement of ignitability and the combustion efficiency of low grade and emulsified fuels compensating thus, their considerably lower heating value compared to conventional diesel oil. Despite the aforementioned advantages, the intake air oxygen-enhancement results in severe increase of NOx emissions and for this reason the specific in-cylinder oxygen-enrichment method should be combined with other techniques, which will aim to the simultaneous curtailment of the most important diesel-emitted pollutants: soot and NOx.

One of the most effective methods used in diesel engine technology for curtailing NOx emissions is the partial recirculation of exhaust gases and their mixing with intake air, which is commonly known as “Exhaust Gas Recirculation – EGR”. According to existing literature [29-37], EGR results in reduction of in-cylinder generated NOx concentrations due to the reduction of in-cylinder temperatures and to the reduction of engine-inducted oxygen. The suppression of in-cylinder gas temperatures is ascribed to the increase of intake gaseous mixture specific heat capacity and the intake oxygen reduction is attributed to the partial replacement of intake air by exhaust gases. According to the literature [31-37] the reduction of in-cylinder gas temperature with EGR results in deterioration of BSFC compared to conventional diesel operation whereas, both the reduction of combustion chamber temperatures and in-cylinder available oxygen has detrimental effects on diesel-emitted soot compared to non-EGR diesel operation. In general, EGR affects diesel engine performance characteristics and pollutant emissions through three different physical and chemical mechanisms [31-33,35-37]:

- **Thermal mechanism**: The mixing of recirculated gases with inducted air leads to the increase of the charge mixture heat capacity mainly due to the higher specific heat capacities of recirculated CO_2 and H_2O compared to O_2 and N_2. The increase of intake heat capacity results in reduction of in-cylinder gas temperatures downplaying thus, in-cylinder NOx formation rate [29-32].
- **Dilution mechanism**: The partial replacement of inlet charge by carbon dioxide and water steam, which are the primary constituents of recirculated exhaust gases, result in reduction of inlet O_2 concentration. This results in reduction of local combustion rates contributing thus, to the curtailment of local gas temperatures in addition to the aforesaid thermal effect. The reduction of local oxygen mole fraction inside fuel jet due to its lower in-cylinder availability results in suppression of kinetically-controlled local NOx formation rate [31,32]
- **Chemical dissociation mechanism**: The recirculated water steam and carbon dioxide are dissociated during combustion process affecting thus, the NOx formation inside the combustion chamber [31,32].

The aforementioned effects of EGR on local fuel oxidation rate and local gas temperature inside fuel jet have detrimental consequences on brake specific fuel consumption (BSFC) and exhaust particulate matter of diesel engines, which vary with EGR rate, composition and thermodynamic conditions (i.e. pressure and temperature) [33,34]. Ladommatos et al. [35-37] in their fundamental work managed successfully to isolate the three aforementioned major effects of EGR on diesel engine combustion characteristics and NOx emissions revealing that, under constant inlet pressure, dilution of charge mixture is the most influential mechanism on the reduction of engine-out NOx.

From the aforementioned thorough examination of available literature in the fields of intake air oxygen-enrichment and EGR the following conclusions were derived: Intake air oxygen-enrichment results in reduction of BSFC under constant fuelling rate or in diesel engine power boosting under increased fuelling rate. In addition, the increase of intake air oxygen mole fraction results in dramatic reduction of diesel-emitted soot and in some cases in soot-free diesel operation. Intake air oxygen-enhancement results also in substantial reduction of diesel-emitted CO and HC whereas; it has serious detrimental effects on NOx emissions compared to conventional diesel operation. On the other hand, EGR results in serious suppression of diesel-emitted NOx with detrimental, however, effects on BSFC and soot emissions.

Hence, the main objective of the present study, which was performed under a diploma thesis in Hellenic Naval Academy, was the theoretical investigation of the potentiality of combining the positive effects on intake air oxygen-enrichment on BSFC and soot reduction and the corresponding beneficial effect of EGR on NOx suppression. Though that literature contains published theoretical and experimental studies [38-41] regarding the combined effect of intake air oxygen-enhancement and EGR on four-stroke diesel engine performance and pollutant emissions, it has not been examined the combination of the two aforementioned techniques for minimizing and potentially eliminating the presence of nitrogen in intake gaseous mixture, which is expected to result in elimination of diesel-emitted NOx.

For this reason, a preliminary theoretical investigation is performed in the present study to examine the effect of intake air oxygen-enhancement and EGR on the chemical equilibrium products on oxy-heptane combustion. N-heptane has been used in numerous simulations of diesel combustion as one of the primary combustion surrogates of conventional diesel oil. The results of a such preliminary study will be quite useful since will allow the examination of the effect of air oxygen-enrichment in combination with the dilution mechanism of EGR and the effect of diesel combustion with pure O_2 and CO_2 without the presence of N_2 on chemical equilibrium products concentration and especially to those ones which controlling the formation of gaseous (i.e. NO and CO) and the oxidation of diesel-generated soot (i.e. O_2 and OH). The results of this preliminary analysis will be also quite fruitful and helpful in the case of diesel combustion with pure O_2 and CO_2 before performing an overall diesel engine simulation since will allow the estimation of the impact of oxy-diesel combustion (i.e. pure O_2 and CO_2 without the presence of N_2) on combustion-generated soot oxidizers and CO concentration in the case of inexistence of NO. N-heptane combustion equilibrium analysis was performed with NASA chemical equilibrium solver [42,43] whereas, Zeldovich mechanism was used to assess the impact on NO formation rate [1,44] and CO formation – oxidation mechanism was used to estimate the effect of equilibrium CO on net CO formation rate [45]. Under the present preliminary theoretical study, three different scenarios of oxygen-enriched diesel combustion were investigated: (a) Conventional diesel combustion without EGR and without intake air oxygen-enrichment: This case was simulated by n-heptane combustion with a gaseous mixture comprised of 21%v/v O_2 and 79%v/v N_2, (b) Diesel combustion with intake air oxygen-enrichment and EGR: This case was simulated by n-heptane combustion with a gaseous mixture comprised of 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2 and (c) Diesel combustion with pure O_2 and CO_2 without the presence of N_2 (i.e. oxy-heptane or oxy-diesel combustion): This combustion case was simulated by n-heptane combustion with a gaseous mixture comprised of 40%v/v O_2 and 60%v/v CO_2. For the three aforementioned cases of n-heptane combustion, calculations were made under conditions occurring inside diesel engine cylinder (a) in areas with high oxygen availability (oxygen excess ratio: $\lambda_{O2} = 2$), (b) in areas inside the combustion chamber, which are close to the stoichiometry (i.e. close to flame boundaries) (oxygen excess ratio: $\lambda_{O2} = 1$) and (c) in areas of the combustion chamber, which indicate high fuel to oxygen availability (i.e. inside fuel jet core) (oxygen excess ratio: $\lambda_{O2} = 0.5$).

BRIEF DESCRIPTION OF NASA CHEMICAL EQUILIBRIUM SOLVER AND POLLUTANTS FORMATION MECHANISM

The knowledge of combustion equilibrium concentrations of a chemically reactive system offers the potentiality of calculating the thermodynamic properties of the system and most importantly, offers the ability to use the chemical equilibrium concentrations as initial values for estimating the actual concentrations of gaseous pollutants (i.e. NO and CO), which are primarily controlled by chemical kinetics rather than chemical equilibrium. In addition, the calculation of chemical equilibrium concentrations of primary soot oxidizers (i.e. O_2 and OH) provides the opportunity to estimate soot oxidation rate, which is the primary destruction mechanism of the soot generated inside a combustion chamber. For more than 40 years the NASA Lewis research center [42,43] has been involved in the development of methods and computer programs for calculating complex chemical equilibrium concentrations and for estimating also thermodynamic properties of equilibrium mixtures. It is worth to mention that NASA's chemical equilibrium solver [42,43] has been implemented successfully in several engineering combustion applications. NASA's chemical equilibrium computational code [42,43] can calculate the combustion equilibrium concentrations for predefined thermodynamic conditions of the combustible mixture. These thermodynamic conditions can be defined by two thermodynamic properties as follows [42,43]:

- Temperature and pressure, t-p
- Enthalpy and pressure, h-p
- Entropy and pressure, s-p
- Temperature and volume, u-v
- Internal energy and volume, u-v
- Entropy and volume, s-v

Chemical equilibrium is usually describes either by chemical equilibrium constants of individual combustion reactions or by the minimization of free energy. McBride and Gordon [42], which compared the two chemical equilibrium solution methods, have shown that if a generalized solution method is used the two equilibrium solution approximations (i.e. equilibrium constants and minimization of free energy) are reduced to the same number of iteration equations. However, with the application of free energy minimization method, each chemical constituent can be treated independently with requiring the determination of the chemical equilibrium reactions, which is necessary in the method of chemical equilibrium constants. For this reason, the revised chemical equilibrium applications (CEA) program of NASA uses as a solution method for chemical equilibrium problems the minimization of Gibbs free energy [42,43]. A detailed description of the NASA's CEA program can be found in ref. [42].

NO Formation Mechanism

As well-described in [1-3,44], NO formation is predominantly controlled by chemical kinetics rather than chemical equilibrium. For the description of NO formation rate has been used in a vast number of theoretical investigations the extended Zeldovich mechanism, which comprised of the following three reactions [1,44]:

$$\left.\begin{aligned} N + NO &\rightleftharpoons N_2 + O \\ N + O_2 &\rightleftharpoons NO + O \\ N + OH &\rightleftharpoons NO + H \end{aligned}\right\} \tag{10}$$

The forward reactions constants are the following:

$$\begin{aligned} K_{f1} &= 1.6 \times 10^{10} \\ K_{f2} &= 6.4 \times 10^{6} T \exp(-3125/T) \\ K_{f3} &= 4.2 \times 10^{10} \end{aligned} \tag{11}$$

Upon mathematical manipulation, the combustion-generated NO concentration is calculated by solving the following ordinary differential equation [1-3,44]:

$$\frac{d(NO)}{dt} = \frac{2R_1\left\{1 - a^2\right\}}{1 + \left\{a \dfrac{R_1}{R_2 + R_3}\right\}} \tag{12}$$

where: $a = \dfrac{(NO)}{(NO)_e}$.

As observed, the chemical equilibrium concentration NO, which is necessary for the solution of the aforementioned ODE, is determined by the solution of the chemical equilibrium problem and as it can be shown has a profound effect on the calculation of actual NO formation rate.

Soot Formation – Oxidation Mechanism

One of the most widely accepted soot formation and oxidation models, which it has been implemented successfully in a vast number of diesel combustion computational simulations, is the Hiroyasu's soot formation and oxidation model [46]. According to this model, soot concentration is the net different between two competing mechanisms: One describing the soot formation rate and one depicting the soot oxidation rate. According to Hiroyasu's model [46], soot formation and soot oxidation rates are described by the two following Arrhenius-type relations:

$$\left.\begin{aligned} \frac{dm_{sf}}{dt} &= A_{sf} m_{f,ev} p^{0.5} \exp\left(-\frac{E_{act,sf}}{R_{mol} T_i}\right) \\ \frac{dm_{sox}}{dt} &= A_{sox} m_s \left(\frac{p_{ox}}{p}\right) P^{1.8} \exp\left(-\frac{E_{act,sox}}{R_{mol} T_i}\right) \end{aligned}\right\} \tag{13}$$

where the index "f" denotes soot formation and the index "ox" denotes soot oxidation, $m_{f,ev}$ is the evaporated fuel mass and p_{ox} is the partial pressure of the oxidative inside burning zone. As witnessed, soot formation rate is primarily controlled by the local availability of evaporated fuel mass, pressure and local temperature. Soot oxidation rate is predominantly controlled by the local availability of oxidizer through its partial pressure. In most studies [1-3,44] this soot oxidizer has been considered to be only chemical equilibrium O_2. However, Hountalas et al [47] have proposed the utilization of equilibrium-derived hydroxyl (OH) radicals in conjunction with O_2 chemical equilibrium concentration for the estimation of soot oxidizer partial pressure for better describing the effect of burning zone oxidizers on soot oxidation rate. In most of the theoretical investigations of diesel combustion conducted in the literature [1-3,44,47] constants A_f and A_{ox} are selected for matching theoretical and experimental results for soot at a certain engine operating condition. Hence, according to Hiroyasu's model [44] the net soot formation rate is expressed through the following equation:

$$\frac{dm_s}{dt} = \frac{dm_{sf}}{dt} - \frac{dm_{sox}}{dt} \tag{14}$$

CO Formation Mechanism

The primary cause of CO formation in conventional diesel engines is the fuel – air over mixing phenomenon, which can be appear in cases of high ignition delay since CO is primarily formed during diesel premixed combustion phase. One of the widely used CO formation models in reciprocating engines is the one of Arsie et al. [45], according to which CO formation rate inside combustion chambers is described by the two following reactions:

$$\begin{aligned} &CO + OH \leftrightarrow CO_2 + H \quad && k_{1f}\left(m^3/kmole \cdot s\right) = 6.76x10^{10} \exp\left(T/1102\right) \\ &CO_2 + O \leftrightarrow CO + O_2 \quad && k_{2f}\left(m^3/kmole \cdot s\right) = 2.51x10^{10} \exp\left(-22041/T\right) \end{aligned} \tag{15}$$

According to Arsie et al. [45] CO formation rate is described by the following differential equation:

$$\frac{d[CO]}{dt} = \left(R_1 + R_2\right)\left[1 - \frac{[CO]}{[CO]_e}\right] \tag{16}$$

where R_1 and R_2 is the rates of the two chemical reactions of Eq. (6). As evidenced from Eq. (7) the CO formation rate is predominantly be controlled by the pertinent chemical equilibrium concentration of CO (i.e. $[CO]_e$).

THEORETICAL STUDY ASSUMPTIONS – TEST CASES EXAMINED

In the literature there have been proposed various approximations for the solution of combustion chemical equilibrium equations [1,48-50]. The common reference point of all these solution methods of chemical equilibrium equations is that they focus on the 11 most important combustion gaseous products (N_2, O_2, CO_2, H_2O, CO, H_2, NO, OH, N, H, O) neglecting all other equilibrium constituents which their overall number is quite high (more than 300 chemical constituents). Most of chemical equilibrium solution methods already proposed in the literature and they have focused on the calculation of the chemical equilibrium concentrations of the aforementioned 11 species are based on the development of an 11x11 non-linear system of equations. For the development of the non-linear system the following 7 chemical equilibrium reactions are utilized [48-50]:

$$\left.\begin{array}{l}
1/2\,H_2 \xrightleftharpoons{K_{p1}} H \\
1/2\,O_2 \xrightleftharpoons{K_{p2}} O \\
1/2\,N_2 \xrightleftharpoons{K_{p3}} N \\
2H_2O \xrightleftharpoons{K_{p4}} 2H_2 + O_2 \\
H_2O \xrightleftharpoons{K_{p5}} OH + 1/2\,H_2 \\
H_2 + CO_2 \xrightleftharpoons{K_{p6}} H_2O + CO \\
H_2O + \dfrac{1}{2}N_2 \xrightleftharpoons{K_{p7}} H_2 + NO
\end{array}\right\} \qquad (17)$$

where K_{pir} are the chemical equilibrium constants (ir = 1,2,…7).

In addition the C, H, O and N atom balances between the reactants and products of perfect combustion are used for the development of the 11x11 non-linear system of equations. The proposed chemical equilibrium solution methods differ in terms of the algorithmic process adopted for the arithmetic solution of the non-linear system of equilibrium equations. For example, Way [49] transformed the 11x11 non-linear system of equations into a 3x3 linear system of equations by expressing all equilibrium species concentrations as function of molar oxygen (O_2) equilibrium concentration. Unfortunately, Way's method [49] even quite innovative for its time it was algorithmically time-consuming regarding its convergence due to the fact that at each time step necessitates the application of an internal procedure for the estimation of the main species concentrations as function of which all other concentrations are expressed. More effective in terms of rapid convergence compared to Way's method [49] is attained with the computational method for the solution of chemical equilibrium and the calculation of the aforementioned 11 species equilibrium concentrations, which was proposed initially by Olikara and Borman [50] and its significantly improved version suggested by Rakopoulos et al. [48]. According to this method, perfect combustion is used to estimate the mole fractions of fuel, oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2) and water (H_2O). Then these estimated values are used as initial approximation to the solution method of the 11x11 non-linear system of chemical equilibrium equations.

Unfortunately this computational method has been developed for the solution of chemical equilibrium equations in the presence of oxygen and nitrogen contained in the oxidative mixture (i.e. air) and thus it cannot be used for the solution of chemical equilibrium problem in the case of combustion with pure oxygen without the presence of nitrogen. The main purpose of the present computational investigation is the examination of the combined effect of intake air oxygen-enrichment and EGR on diesel combustion equilibrium products. Towards this aim, NASA chemical equilibrium solver was used, which has been developed by McBride and

Gordon [42,43]. The specific chemical equilibrium solver in contrast to the aforementioned solution methods [48-50] offers the potentiality of rapid solution of chemical equilibrium equations for the combustion of a vast number of organic species under different thermodynamic conditions. The NASA chemical equilibrium solver may predict the equilibrium concentrations of a large number of gaseous products (i.e. more than 300). In addition, NASA program offers the ability of the combustion simulation of organic species, which are considered as diesel fuel surrogates with pure oxygen (i.e. oxy-diesel combustion). As known, real diesel oil comprised of thousands of organic species of different molecular structure (paraffins, olefins, natphenes and aromatic hydrocarbons). For this reason, in most of the computational simulations of diesel combustion, surrogate hydrocarbons are used. The sequence of the combustion reactions of these surrogate hydrocarbons approximates the combustion chain reactions of diesel fuel. One of the most commonly used hydrocarbons in diesel combustion simulations is the n-heptane (C_7H_{16}), which has combustion chain reactions closed to the ones of conventional diesel fuel and for this reason is used in the present computational simulation. In the specific study the diesel combustion simulation was performed for various pressures and temperatures as well as oxygen to fuel equivalence ratios, which appear inside a diesel engine combustion chamber. The primary target of the present investigation was the calculation of chemical equilibrium species concentrations under thermodynamic conditions (pressures and temperatures) appearing inside diesel engine cylinder under the following cases of n-heptane combustion:

- **Case 1:** N-heptane combustion with air (21%v/v O_2 and 79%v/v N_2). This simulation case corresponds to conventional diesel combustion with air.
- **Case 2:** N-heptane combustion with oxygen-enriched air and recirculated exhaust gases. In this case it was assumed that the diesel engine cylinder-induced gaseous mixture comprised of oxygen, nitrogen and carbon dioxide as a result of the mixing of air stream with cooled EGR stream. The aforementioned assumption is based on the consideration that the EGR cooler absorbs the entire quantity of water vapor from the recirculated exhaust gases. Hence, in this simulation case it was assumed that the oxidative gaseous mixture comprised of 40%v/v O_2 due to air oxygen-enrichment, 30%v/v N_2 and 30%v/v CO_2.
- **Case 3:** N-heptane combustion with pure O_2 in the presence of CO_2 (i.e. oxy-heptane combustion). This simulation case is coming up from the following diesel engine operational scenario: An air separation membrane has been installed in the intake of a diesel engine for enriching the intake air stream with oxygen from 21%v/v to 40%v/v. Oxygen-enriched diesel combustion results in reduction of N_2 in the products of perfect combustion and thus, to a significant reduction of N_2 in the stream of recirculated cooled exhaust gases, which is comprised primarily of CO_2, N_2 and O_2 after the EGR cooler. The partial replacement of intake air from recirculated exhaust gases lowers the capacity demands from the air separation membrane and thus, the specific membrane under the same pressure differential may generate an air stream with oxygen content higher than 40%v/v resulting thus, in dramatic reduction of nitrogen in the generated air stream. Hence, the combination of a high capacity air separation membrane with high cooled EGR rate may result in the production of a diesel engine-inducted gaseous mixture comprised only of O_2 and CO_2 formulating thus, a combustion environment with pure oxygen without the presence of nitrogen, which is the primary cause for the generation of nitrogen oxides (NOx) inside diesel engine combustion chamber. For the simulation of this combustion case it was assumed in the present study that the intake gaseous mixture contains 40%v/v O_2 and 60%v/v CO_2.

For each one of the aforementioned combustion simulation cases, three different oxygen/fuel equivalence ratios (i.e. oxygen excess ratios) were assumed, which they typically appear in different points of a diesel engine cylinder. Specifically, for each one of the aforementioned cases 1-3, chemical equilibrium simulations of n-heptane combustion were performed for the following stoichiometry cases:

- **Case A:** Oxygen/fuel equivalence ratio $\lambda_{O2} = 2$ (Combustible mixture rich in oxygen): This stoichiometry case may appear in diesel combustion chamber areas outside of the flame zone, where there is high oxygen availability compared to other in-cylinder areas.
- **Case B:** Oxygen/fuel equivalence ratio $\lambda_{O2} = 1$ (Combustible mixture stoichiometric in oxygen): This stoichiometry case may appear in diesel combustion chamber areas close to the flame zone, where the combustible mixture is close to the stoichiometry.
- **Case C:** Oxygen/fuel equivalence ration $\lambda_{O2} = 0.5$ (Combustible mixture lean in oxygen): This stoichiometry case corresponds to diesel combustion chamber areas, where there is high availability of evaporated fuel and low availability of oxidizer (either air or pure oxygen) due to the limited penetration of the oxidizer inside diesel fuel jet.

It is worth to mention that oxygen/fuel equivalence ratio (i.e. oxygen excess ratio) was used as mean for characterizing the stoichiometry of the combustible mixture instead of air/fuel equivalence ratio (i.e. air excess ratio), which is commonly used. This selection was made since the air/fuel equivalence ratio is not suitably for characterizing stoichiometry in the case of n-heptane combustion with pure O_2.

For each one of the aforementioned cases (1.A-1.C, 2.A-2.C and 3.A-3.C) the NASA chemical equilibrium solver was implemented for calculating n-heptane combustion equilibrium concentrations for constant initial pressure and temperature values (problem t-p). Specifically, chemical equilibrium calculations were performed for three different values of reactants pressure namely 50, 100 and 200atm. For each one of the aforementioned pressures, a temperature range from 1000K to 2800K with step 100K was considered. These thermodynamic conditions cover (case by case) the corresponding conditions appearing inside the cylinders of modern diesel engines during the stages of combustion and expansion. The calculation cases of chemical equilibrium products during n-heptane combustion with air, with oxygen-enriched air and cooled EGR and with pure O_2 and CO_2 are presented in Table 1.

The combustion stoichiometry factors shown in Table 1 were calculated based on the following perfect combustion reaction of a hydrocarbon C_nH_m (for the case of n-heptane: n = 7 and m = 16).

Hydrocarbon C_nH_m perfect combustion reaction:

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 + 3.773\left(n + \frac{m}{4}\right)N_2 \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.773\left(n + \frac{m}{4}\right)N_2 \tag{18}$$

Stoichiometric oxygen/fuel ratio:

$$OF_{st} = \frac{\left(n + \frac{m}{4}\right)MW_{O2}}{MW_{fuel}} \tag{19}$$

where MW_{O2} is the oxygen molecular weight and MW_{fuel} is the fuel molecular weight.

Stoichiometric air/fuel ratio:

$$AF_{st} = \frac{\left(n + \frac{m}{4}\right)MW_{O2} + 3.773\left(n + \frac{m}{4}\right)MW_{N2}}{MW_{fuel}} \tag{20}$$

Oxygen/fuel equivalence ratio (i.e. oxygen excess ratio):

$$\lambda_{O2} = \frac{N_{O2} MW_{O2}}{OF_{st}\left(N_{fuel} MW_{fuel}\right)} \tag{21}$$

where N_{O2} is the molar quantity of oxygen and N_{fuel} is the fuel moles.
Air/fuel equivalence ratio (i.e. air excess ratio):

$$\lambda_{\alpha} = \frac{N_{O2} MW_{O2} + N_{N2} MW_{N2}}{AF_{st}\left(N_{fuel} MW_{fuel}\right)} \tag{22}$$

TABLE 5. Calculation cases of chemical equilibrium concentrations of n-heptane combustion with air, with oxygen—enriched air stream and recirculated exhaust gases and with pure oxygen in the presence of carbon dioxide

CASE 1.A		**CASE 2.A**		**CASE 3.A**	
n-Heptane (C_7H_{16}) combustion with air (O_2 and N_2) (Oxygen/Fuel Equivalence Ratio = 2)		**n-Heptane (C_7H_{16}) combustion with O_2, N_2 and CO_2 (Oxygen/Fuel Equivalence Ratio = 2)**		**n-Heptane (C_7H_{16}) combustion with O_2 and CO_2 (Oxygen/Fuel Equivalence Ratio = 2)**	
N_{O2} (mole O_2)	0.21	N_{O2} (mole O_2)	0.4	N_{O2} (mole O_2)	0.4
N_{N2} (mole N_2)	0.79	N_{N2} (mole N_2)	0.3	N_{N2} (mole N_2)	0
N_{CO2} (mole CO_2)	0	N_{CO2} (mole CO_2)	0.3	N_{CO2} (mole CO_2)	0.6
N_{fuel} (mole n-heptane)	0.0096	N_{fuel} (mole n-heptane)	0.0182	N_{fuel} (mole n-heptane)	0.0182
Stoichiometric oxygen/fuel ratio OF_{st}	3.52	Stoichiometric oxygen/fuel ratio OF_{st}	3.52	Stoichiometric oxygen/fuel ratio OF_{st}	3.52
Stoichiometric air/fuel ratio AF_{st}	15.14	Stoichiometric air/fuel ratio AF_{st}	15.14	Stoichiometric air/fuel ratio AF_{st}	15.14
Air/fuel equivalence ratio λ_{α}	1.996	Air/fuel equivalence ratio λ_{α}	0.770	Air/fuel equivalence ratio λ_{α}	0.465
CASE 1.B		**CASE 2.B**		**CASE 3.B**	
n-Heptane (C_7H_{16}) combustion with air (O_2 and N_2) (Oxygen/Fuel Equivalence Ratio = 1)		**n-Heptane (C_7H_{16}) combustion with O_2, N_2 and CO_2 (Oxygen/Fuel Equivalence Ratio = 1)**		**n-Heptane (C_7H_{16}) combustion with O_2 and CO_2 (Oxygen/Fuel Equivalence Ratio = 1)**	
N_{O2} (mole O_2)	0.21	N_{O2} (mole O_2)	0.4	N_{O2} (mole O_2)	0.4
N_{N2} (mole N_2)	0.79	N_{N2} (mole N_2)	0.3	N_{N2} (mole N_2)	0
N_{CO2} (mole CO_2)	0	N_{CO2} (mole CO_2)	0.3	N_{CO2} (mole CO_2)	0.6
N_{fuel} (mole n-heptane)	0.019	N_{fuel} (mole n-heptane)	0.036	N_{fuel} (mole n-heptane)	0.036
Stoichiometric oxygen/fuel ratio OF_{st}	3.52	Stoichiometric oxygen/fuel ratio OF_{st}	3.52	Stoichiometric oxygen/fuel ratio OF_{st}	3.52
Stoichiometric air/fuel ratio AF_{st}	15.14	Stoichiometric air/fuel ratio AF_{st}	15.14	Stoichiometric air/fuel ratio AF_{st}	15.14
Air/fuel equivalence ratio λ_{α}	0.998	Air/fuel equivalence ratio λ_{α}	0.385	Air/fuel equivalence ratio λ_{α}	0.232
CASE 1.C		**CASE 2.C**		**CASE 3.C**	
n-Heptane (C_7H_{16}) combustion with air (O_2 and N_2) (Oxygen/Fuel Equivalence Ratio = 0.5)		**n-Heptane (C_7H_{16}) combustion with O_2, N_2 and CO_2 (Oxygen/Fuel Equivalence Ratio = 0.5)**		**n-Heptane (C_7H_{16}) combustion with O_2 and CO_2 (Oxygen/Fuel Equivalence Ratio = 0.5)**	
N_{O2} (mole O_2)	0.21	N_{O2} (mole O_2)	0.4	N_{O2} (mole O_2)	0.4
N_{N2} (mole N_2)	0.79	N_{N2} (mole N_2)	0.3	N_{N2} (mole N_2)	0
N_{CO2} (mole CO_2)	0	N_{CO2} (mole CO_2)	0.3	N_{CO2} (mole CO_2)	0.6
N_{fuel} (mole n-heptane)	0.038	N_{fuel} (mole n-heptane)	0.072	N_{fuel} (mole n-heptane)	0.072
Stoichiometric oxygen/fuel ratio OF_{st}	3.52	Stoichiometric oxygen/fuel ratio OF_{st}	3.52	Stoichiometric oxygen/fuel ratio OF_{st}	3.52
Stoichiometric air/fuel ratio AF_{st}	15.14	Stoichiometric air/fuel ratio AF_{st}	15.14	Stoichiometric air/fuel ratio AF_{st}	15.14
Air/fuel equivalence ratio λ_{α}	0.5	Air/fuel equivalence ratio λ_{α}	0.192	Air/fuel equivalence ratio λ_{α}	0.116

RESULTS AND DISCUSSION

Effect of Intake Air Oxygen-Enrichment and Cooled EGR on n-Heptane Chemical Equilibrium Concentrations for Constant Thermodynamic and Stoichiometric Conditions

The investigation of the combined effect of conventional intake air oxygen-enrichment and cooled EGR and the diesel combustion in pure oxygen environment in the presence of CO_2 on the chemical equilibrium concentrations of n-heptane combustion initiates with the case at which the thermodynamic conditions (pressure and temperature) and the stoichiometric conditions (oxygen/fuel equivalence ratio) remain unchanged. The main purpose of this theoretical investigation is the assessment of the effect of n-heptane combustion with oxygen-enriched air in the presence of CO_2 (approximation of the engine operational case, which is based on the combination of intake air oxygen-enrichment and cooled EGR) and the effect of n-heptane combustion with pure O_2 and CO_2 (approximation of the engine operational case, which is based on the high oxygenation of intake air stream and high cooled EGR rate) on the chemical equilibrium concentrations in contrast to conventional n-heptane combustion with air (approximation of the conventional diesel engine operation).

In Figures 1-5 are presented the effect of oxidative gaseous mixture composition during n-heptane combustion under constant initial thermodynamic conditions (pressure and temperature) and constant stoichiometric conditions (i.e. oxygen/fuel equivalence ratio) on the variation of chemical equilibrium mole fraction of various gaseous species, which as expressed as function of temperature. Specifically, theoretical results for chemical equilibrium molar fractions are given for the following equilibrium species: CO_2 (Figure 1), O_2 (Figure 2), NO (Figure 3), CO (Figure 4) and OH (Figure 5). NASA's program [38,39] predictions, which are given in Figures 1-5 concern computations, which were performed under constant pressure (100 atm) and for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to: (a) 2, (b) 1 and (c) 0.5. In each one of the figures (a), (b) and (c) of Figures 1-5 comparative predictions are presented for the following cases of n-heptane combustion: Case 1.A ($O_2/N_2/CO_2$ = 0.21/0.79/0.0), Case 1.B ($O_2/N_2/CO_2$ = 0.4/0.3/0.0) and Case 1.C ($O_2/N_2/CO_2$ = 0.4/0.0/0.6).

According to Figures 1(a)-(c), for all cases of oxygen/fuel equivalence ratio examined, CO_2 equilibrium concentration is slightly reduced with increasing temperature for the cases of conventional n-heptane combustion and for the case of n-heptane combustion with 40%v/v O_2, 30%v/v N_2 και 30%v/v CO_2. In the case of n-heptane combustion with 40%v/v O_2 and 60%v/v CO_2 the rate of CO_2 equilibrium concentration reduction with temperature is higher compared to the two aforementioned cases.

Observing Figures 2(a)-(c) it becomes evident that for the case of conventional n-heptane combustion with air the O_2 equilibrium mole fraction is slightly reduced with increasing temperature for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to 2 and to 1 whereas it remains constant for temperatures up to 2400K and then it increases slightly in the case of oxygen/fuel equivalence ratio equal to 0.5. According also to Figures 2(a)-(c), the chemical equilibrium mole fraction of O_2 remains constant and close to zero for temperatures up to 2200K and then it increases for all the cases of oxygen/fuel equivalence ratio examined. It is also characteristic that in the case of n-heptane combustion with 40%v/v O_2 and 60%v/v CO_2 the equilibrium concentration of O_2 remains constant and close to zero independently of the values of temperature and oxygen/fuel equivalence ratio.

As observed from Figures 3(a)-(b), NO equilibrium mole fraction increases almost exponentially with the increase of temperature for the cases of n-heptane combustion with air and with mixture of 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2 under oxygen/fuel equivalence

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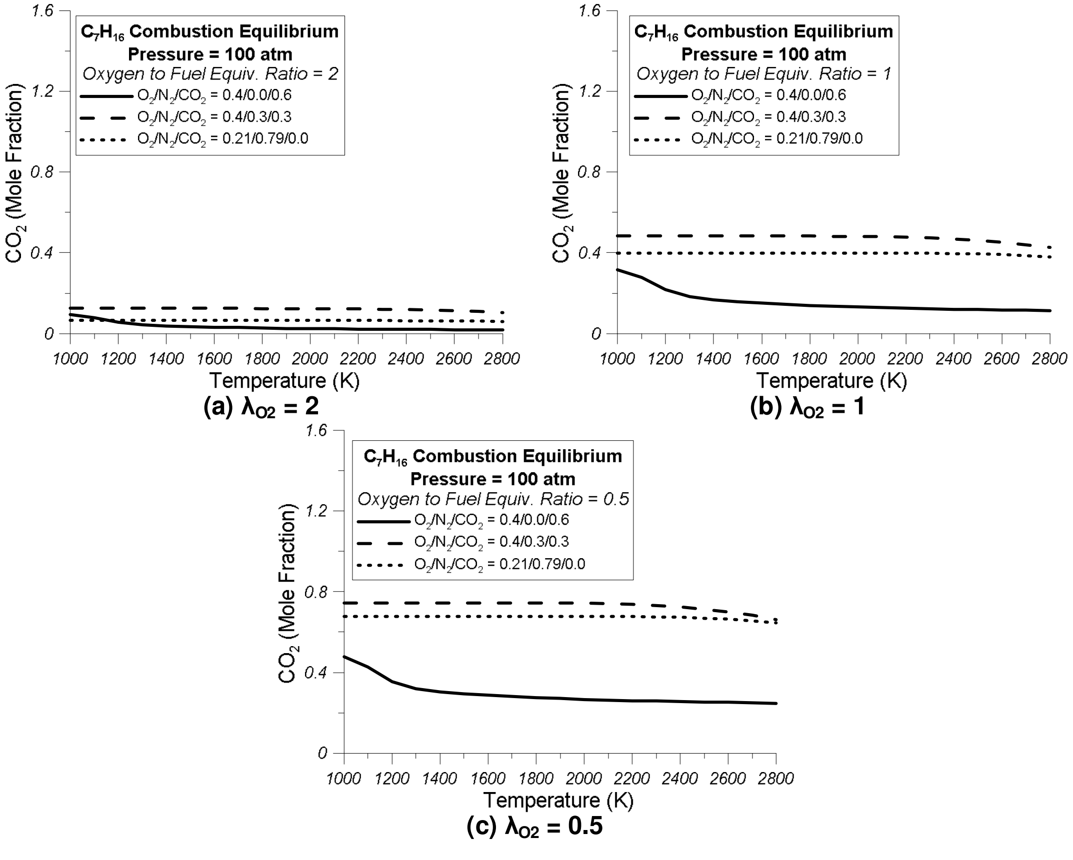
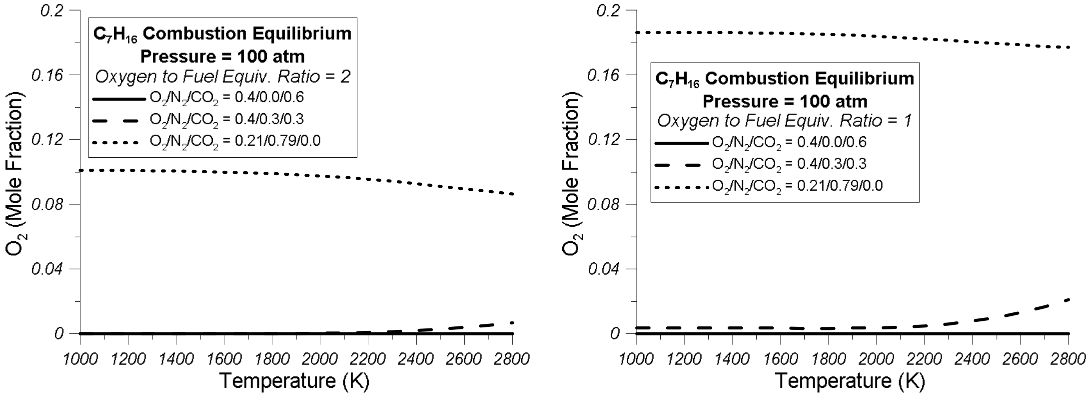
ratios equal to 2 and to 1. Oppositely, according to Figures 3(a) and (b), NO equilibrium concentration is zero as expected for the case of n-heptane combustion with 40%v/v O_2 and 60%v/v CO_2 independently of the value of oxygen/fuel equivalence ratio. As evidenced from Figure 3(c) NO equilibrium mole fraction values are zero for oxygen/fuel equivalence ratio equal to 0.5 independently of n-heptane combustion mode. NO equilibrium mole fractions found zero for this value of oxygen/fuel equivalence ratio since the corresponding N_2 equilibrium mole fractions are zero.

As observed from the examination of Figures 4(a)-(c), for all cases of oxygen excess ratio and for the cases of n-heptane combustion with air and n-heptane combustion with 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2, CO equilibrium mole fraction remain constant and equal to zero for temperatures up to 2200K whereas for higher temperatures they indicate a slight increase. Oppositely, in the case of n-heptane combustion with pure oxygen and CO_2, CO equilibrium mole fraction increases rapidly for temperatures ranging from 1000K to 1400K whereas for higher temperatures the rate of CO equilibrium concentration increase is substantially curtailed.

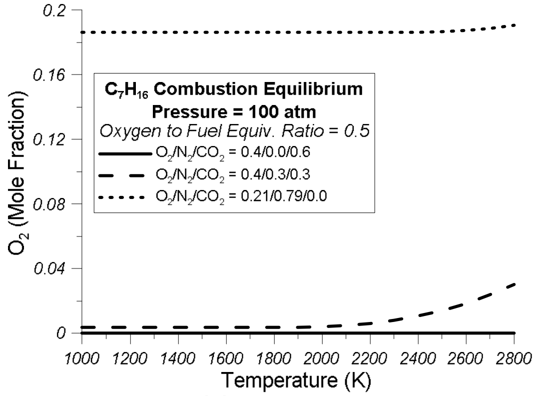


(a) λ_{O2} = 2 **(b) λ_{O2} = 1** **(c) λ_{O2} = 0.5**

FIGURE 6. Effect of composition of oxidation gaseous mixture during n-heptane combustion under constant initial thermodynamic conditions (pressure and temperature) and stoichiometric conditions (oxygen/fuel equivalence ratio) on the variation of chemical equilibrium CO_2 mole fraction as function of temperature. NASA chemical equilibrium [42,43] predictions are given under constant pressure (100 atm) and for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to (a) 2, (b) 1 and (c) 0.5. In each of figures (a), (b) and (c) comparative theoretical results are presented for the n-heptane combustion cases 1.A ($O_2/N_2/CO_2$ = 0.21/0.79/0.0), 1.B ($O_2/N_2/CO_2$ = 0.4/0.3/0.0) and 1.C ($O_2/N_2/CO_2$ = 0.4/0.0/0.6).



(a) $\lambda_{O2} = 2$ **(b) $\lambda_{O2} = 1$**



(c) $\lambda_{O2} = 0.5$

FIGURE 7. Effect of composition of oxidation gaseous mixture during n-heptane combustion under constant initial thermodynamic conditions (pressure and temperature) and stoichiometric conditions (oxygen/fuel equivalence ratio) on the variation of chemical equilibrium O_2 mole fraction as function of temperature. NASA chemical equilibrium [42,43] predictions are given under constant pressure (100 atm) and for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to (a) 2, (b) 1 and (c) 0.5. In each of figures (a), (b) and (c) comparative theoretical results are presented for the n-heptane combustion cases 1.A ($O_2/N_2/CO_2$ = 0.21/0.79/0.0), 1.B ($O_2/N_2/CO_2$ = 0.4/0.3/0.0) and 1.C ($O_2/N_2/CO_2$ = 0.4/0.0/0.6).

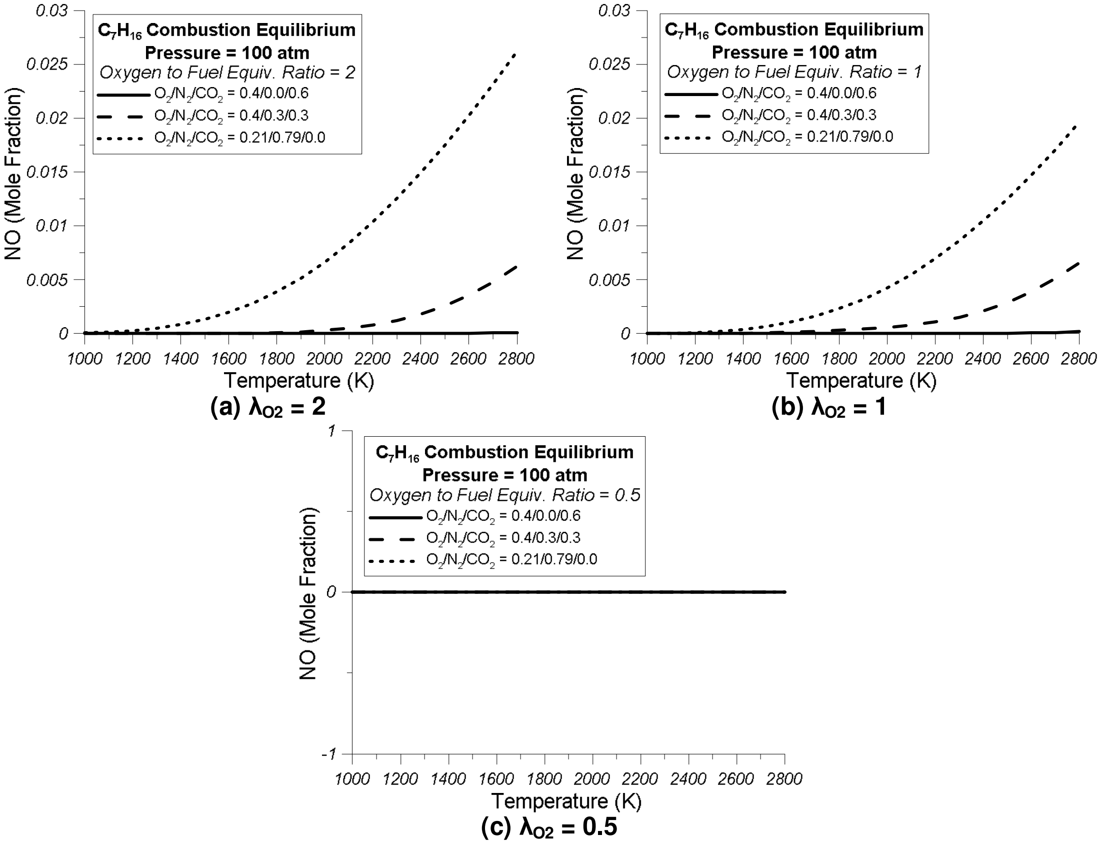
The observation of Figures 5(a)-(c) leads to the conclusion that for all cases of n-heptane combustion examined in the present study and for all values of oxygen/fuel equivalence ratio examined herein, OH equilibrium mole fraction remains constant and equal to zero for temperatures ranging from 1000K to 1600K whereas for higher temperatures the growth of OH equilibrium mole fraction is almost exponential.

From the overall examination of Figures 1-5 is becomes evident that n-heptane combustion with 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2 compared to conventional n-heptane combustion with air (21%v/v O_2 and 79%v/v N_2) results in:
Increase of CO_2 equilibrium mole fractions.

- Dramatic reduction of O_2 equilibrium mole fractions.
- Reduction of NO equilibrium concentrations (except of the case of lean mixture in terms of oxygen).
- Small increase of CO equilibrium mole fractions especially for temperatures higher than 2200K.
- Reduction of OH equilibrium concentrations.

In addition from the careful observation of Figures 1-5 it becomes obvious that n-heptane combustion with 40%v/v O_2 and 60%v/v CO_2 compared to conventional n-heptane combustion with air (21%v/v O_2 and 79%v/v N_2) results in:

- Substantial reduction of CO_2 equilibrium mole fractions.
- Elimination of O_2 equilibrium concentrations.
- Elimination of NO equilibrium mole fractions.
- Dramatic increase of CO equilibrium mole fractions.
- Drastic reduction of OH equilibrium concentrations.

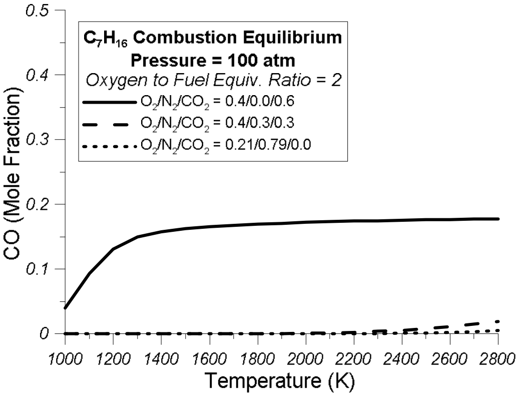


(a) $\lambda_{O2} = 2$

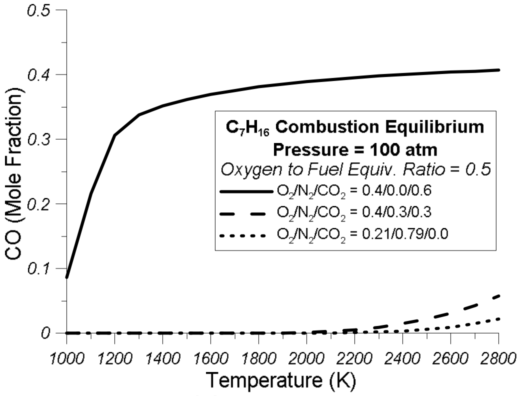
(b) $\lambda_{O2} = 1$

(c) $\lambda_{O2} = 0.5$

FIGURE 8. Effect of composition of oxidation gaseous mixture during n-heptane combustion under constant initial thermodynamic conditions (pressure and temperature) and stoichiometric conditions (oxygen/fuel equivalence ratio) on the variation of chemical equilibrium NO mole fraction as function of temperature. NASA chemical equilibrium [42,43] predictions are given under constant pressure (100 atm) and for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to (a) 2, (b) 1 and (c) 0.5. In each of figures (a), (b) and (c) comparative theoretical results are presented for the n-heptane combustion cases 1.A ($O_2/N_2/CO_2$ = 0.21/0.79/0.0), 1.B ($O_2/N_2/CO_2$ = 0.4/0.3/0.0) and 1.C ($O_2/N_2/CO_2$ = 0.4/0.0/0.6).

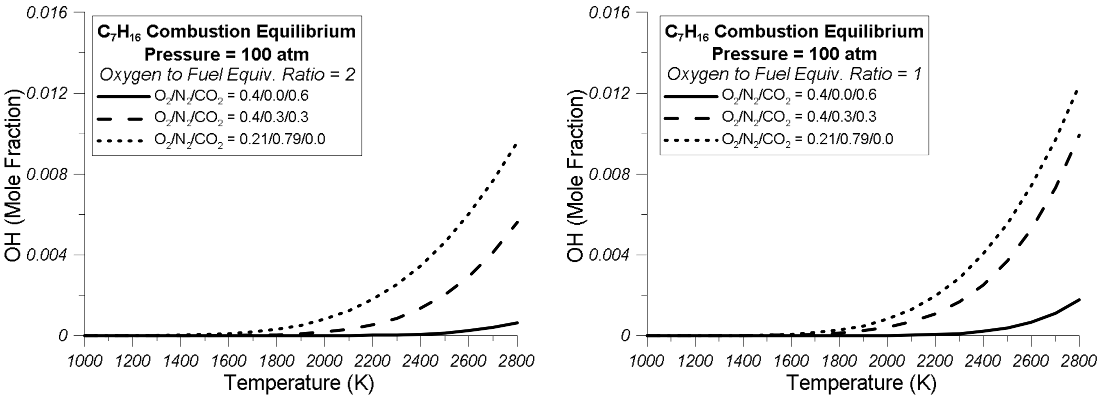


(a) $\lambda_{O2} = 2$ **(b) $\lambda_{O2} = 1$**

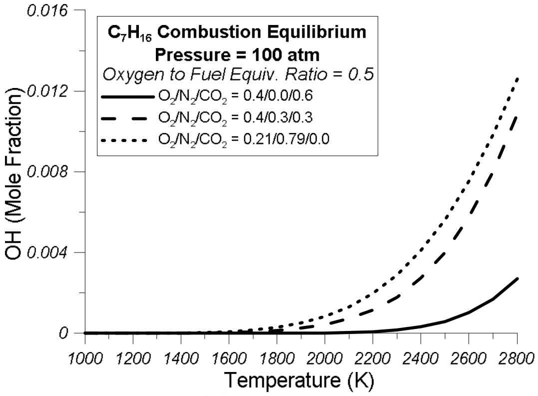


(c) $\lambda_{O2} = 0.5$

FIGURE 9. Effect of composition of oxidation gaseous mixture during n-heptane combustion under constant initial thermodynamic conditions (pressure and temperature) and stoichiometric conditions (oxygen/fuel equivalence ratio) on the variation of chemical equilibrium CO mole fraction as function of temperature. NASA chemical equilibrium [42,43] predictions are given under constant pressure (100 atm) and for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to (a) 2, (b) 1 and (c) 0.5. In each of figures (a), (b) and (c) comparative theoretical results are presented for the n-heptane combustion cases 1.A ($O_2/N_2/CO_2$ = 0.21/0.79/0.0), 1.B ($O_2/N_2/CO_2$ = 0.4/0.3/0.0) and 1.C ($O_2/N_2/CO_2$ = 0.4/0.0/0.6).



(a) $\lambda_{O2} = 2$ **(b) $\lambda_{O2} = 1$**



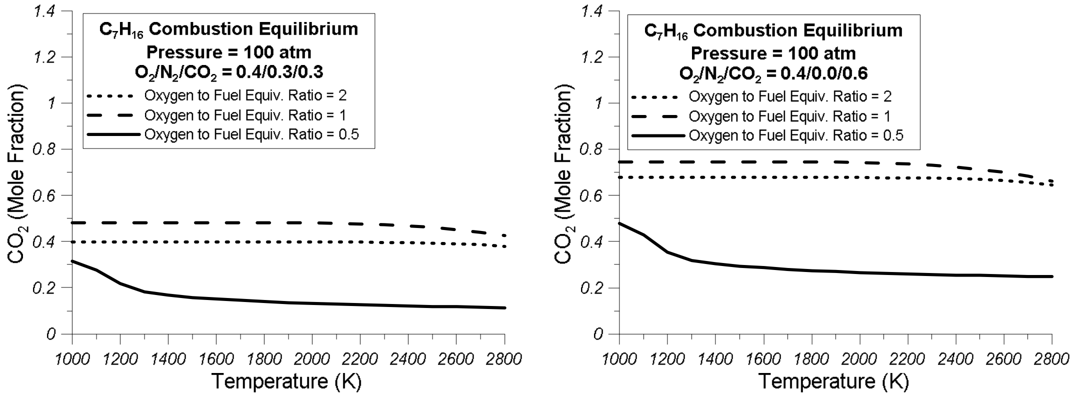
(c) $\lambda_{O2} = 0.5$

FIGURE 10. Effect of composition of oxidation gaseous mixture during n-heptane combustion under constant initial thermodynamic conditions (pressure and temperature) and stoichiometric conditions (oxygen/fuel equivalence ratio) on the variation of chemical equilibrium OH mole fraction as function of temperature. NASA chemical equilibrium [42,43] predictions are given under constant pressure (100 atm) and for values of oxygen/fuel equivalence ratio (λ_{O2}) equal to (a) 2, (b) 1 and (c) 0.5. In each of figures (a), (b) and (c) comparative theoretical results are presented for the n-heptane combustion cases 1.A ($O_2/N_2/CO_2$ = 0.21/0.79/0.0), 1.B ($O_2/N_2/CO_2$ = 0.4/0.3/0.0) and 1.C ($O_2/N_2/CO_2$ = 0.4/0.0/0.6).

Effect of Oxygen/Fuel Equivalence Ratio on n-Heptane Combustion with Increased Oxygen Availability in the Presence of CO_2

Figures 6-10 illustrate the effect of oxygen/fuel equivalence ratio on the variation of chemical equilibrium mole fractions of CO_2 (Figure 6), O_2 (Figure 7), NO (Figure 8), CO (Figure 9) and OH (Figure 10) as function of temperature. In Figures 6(a)-10(a) are given predictions of the NASA's chemical equilibrium solver [42,43] for the case of n-heptane combustion with 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2 under constant pressure (100 atm) for three different values of oxygen/fuel equivalence ratio (i.e. 2, 1 and 0.5). Correspondingly in Figures 6(b)-10(b) are given theoretical results of NASA's chemical equilibrium solver [38,39] for the case of n-heptane combustion with 40%v/v O_2 and 60%v/v CO_2 under constant pressure (100 atm) for the three values of oxygen/fuel equivalence ratio examined in this study.

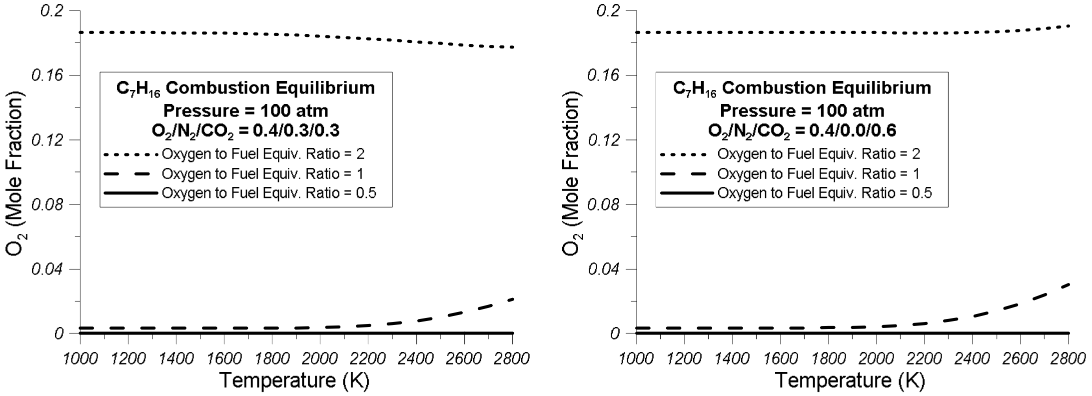
According to Figures 6(a)-(b) the increase of oxygen/fuel equivalence ratio from 0.5 to 1 results in the increase of CO_2 chemical equilibrium mole fraction whereas the further increase of oxygen/fuel equivalence ratio up to 2 leads in a slight reduction of CO_2 equilibrium concentrations. Hence, it is confirmed that CO_2 formation is favored in combustion chamber areas where the combustible mixture is stoichiometric or rich in terms of oxygen.



(a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 **(b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6**

FIGURE 11. Effect of oxygen/fuel equivalence ratio on the variation of CO_2 equilibrium mole fraction as function of temperature. NASA's program [42,43] chemical equilibrium predictions are given for the n-heptane combustion under constant pressure (100 atm) with (a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 and (b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6. In each of the cases (a) and (b) theoretical results are compared for values of oxygen/fuel equivalence ratio λ_{O2} = 0.5, 1 and 2.

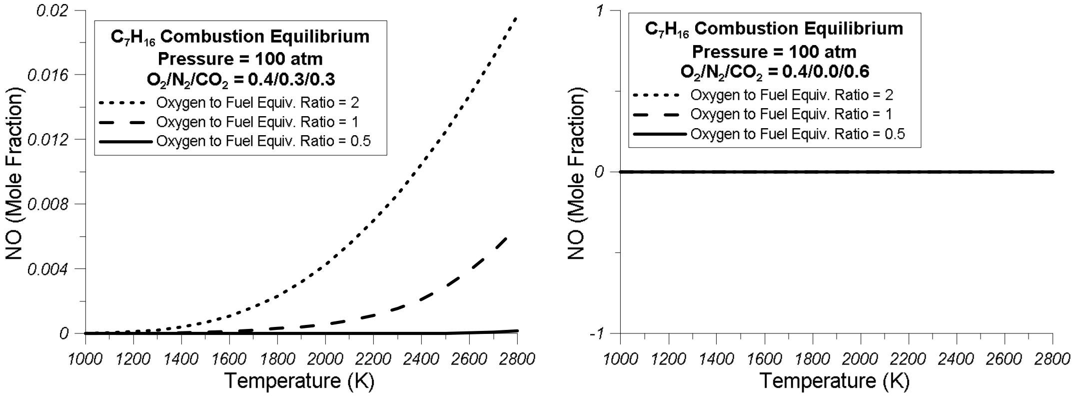
From the examination of Figure 7(a)-(b) is becomes evident that the increase of oxygen/fuel equivalence ratio from 0.5 to 1 does not cause substantial variation of O_2 equilibrium mole fraction. Oppositely, the further increase of oxygen/fuel equivalence ratio from 1 to 2 results as expected in substantial increase of O_2 equilibrium concentration.



(a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 **(b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6**

FIGURE 12. Effect of oxygen/fuel equivalence ratio on the variation of O_2 equilibrium mole fraction as function of temperature. NASA's program [42,43] chemical equilibrium predictions are given for the n-heptane combustion under constant pressure (100 atm) with (a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 and (b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6. In each of the cases (a) and (b) theoretical results are compared for values of oxygen/fuel equivalence ratio λ_{O2} = 0.5, 1 and 2.

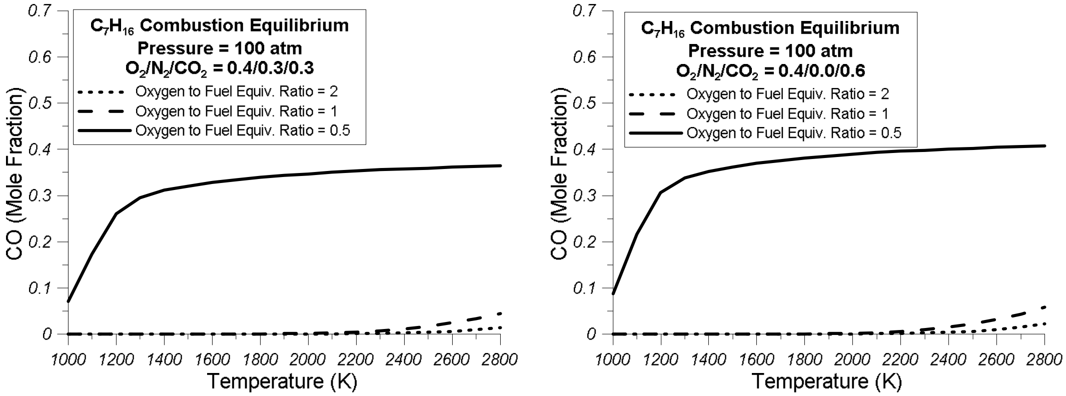
As observed from Figure 8(a) the increase of oxygen/fuel equivalence ratio from 0.5 to 1 and then up to 2 results in the increase of NO equilibrium concentration in the case of n-heptane combustion with 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2. This result was more or less expected since NO formation according to chemical equilibrium is favored in combustion chamber areas with increased local oxygen availability. In the case of n-heptane combustion with pure O_2 and CO_2, NO equilibrium mole fraction is zero independently of the value of oxygen/fuel equivalence ratio (Figure 8(b)).



(a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 **(b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6**

FIGURE 13. Effect of oxygen/fuel equivalence ratio on the variation of NO equilibrium mole fraction as function of temperature. NASA's program [42,43] chemical equilibrium predictions are given for the n-heptane combustion under constant pressure (100 atm) with (a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 and (b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6. In each of the cases (a) and (b) theoretical results are compared for values of oxygen/fuel equivalence ratio λ_{O2} = 0.5, 1 and 2.

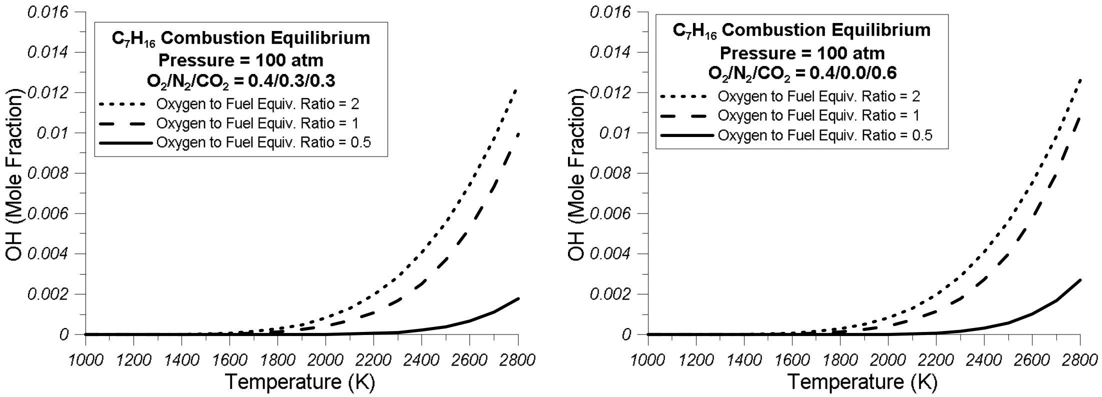
As evidenced from Figures 9(a)-(b) the increase of the oxygen/fuel equivalence ratio results in dramatic reduction up to elimination of CO chemical equilibrium mole fractions either in the case of reduced presence of N_2 (30%v/v N_2) or in the case without the presence of nitrogen in n-heptane combustion reactants. This finding is in accordance with observations made in diesel engines, which they mention that CO formation is favored in combustion chamber areas, where the combustible mixture is rich in fuel [1].



(a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 **(b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6**

FIGURE 14. Effect of oxygen/fuel equivalence ratio on the variation of CO equilibrium mole fraction as function of temperature. NASA's program [42,43] chemical equilibrium predictions are given for the n-heptane combustion under constant pressure (100 atm) with (a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 and (b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6. In each of the cases (a) and (b) theoretical results are compared for values of oxygen/fuel equivalence ratio λ_{O2} = 0.5, 1 and 2.

According to Figures 10(a)-(b) the progressive increase of oxygen/fuel equivalence ratio from 0.5 to 1 and then to 2 results in the increase of OH chemical equilibrium concentration over the entire range of temperature examined in this study and independently of the existence or the inexistence of nitrogen in the reactants of n-heptane combustion.



(a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 **(b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6**

FIGURE 15. Effect of oxygen/fuel equivalence ratio on the variation of OH equilibrium mole fraction as function of temperature. NASA's program [42,43] chemical equilibrium predictions are given for the n-heptane combustion under constant pressure (100 atm) with (a) $O_2/N_2/CO_2$ = 0.4/0.3/0.3 and (b) $O_2/N_2/CO_2$ = 0.4/0.0/0.6. In each of the cases (a) and (b) theoretical results are compared for values of oxygen/fuel equivalence ratio λ_{O2} = 0.5, 1 and 2.

CONCLUSIONS

The main objective of the present preliminary study, which was performed under a diploma thesis in Hellenic Naval Academy, was the theoretical investigation of the combined effect of intake air oxygen-enrichment and cooled EGR on diesel combustion equilibrium products and emitted pollutants. To attain this goal it was examined the chemical effect of intake air oxygen-enhancement and exhaust gas recirculation on the chemical equilibrium mole fraction of various gaseous combustion-released products of n-heptane combustion and through them it was evaluated qualitatively the repercussions on the formation of soot, NO and CO. It was also examined the effect of n-heptane combustion with pure oxygen in the presence of CO_2 (i.e. oxy-heptane combustion) on the chemical equilibrium concentrations of various gaseous chemical species. N-heptane combustion equilibrium calculations with different mixtures of oxygen, nitrogen and carbon dioxide were performed for various values of pressure and temperature and under different values of oxygen/fuel equivalence ratio using the free chemical equilibrium solver of NASA [42,43]. The assessment of the theoretical results of this preliminary theoretical investigation has led to the derivation of the following general conclusions:

The approximation of diesel combustion with oxygen-enriched intake air stream and cooled EGR (n-heptane combustion case with 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2) in contrast to the approximation of conventional diesel combustion (n-heptane combustion case with 21%v/v O_2 and 79%v/v N_2) resulted in:

- Reduction of NO equilibrium concentration in diesel combustion chamber areas where there is high availability of oxygen with respect to available fuel and in pertinent areas with oxygen to stoichiometric analogy i.e. flame zone. According to partial chemical kinetics Zeldovich mechanism, which describes more effectively actual NO formation inside a combustion chamber, the reduction of NO equilibrium mole fraction for specific values of pressure and temperature is anticipated to result in reduction of the actual NO formation rate, which is described by chemical kinetics rather than chemical equilibrium. Hence, it is concluded that the use of a diesel engine intake gaseous mixture comprised of oxygen-enriched air and cooled EGR, which it has substantially lower effect on in-cylinder gas temperature during compression compared to hot EGR, may result in the reduction of diesel in-cylinder generated NO and thus, to the reduction of diesel-emitted NO.

- Reduction of chemical equilibrium mole fractions of O_2 and OH. The reduction of equilibrium concentrations of these main soot oxidative chemical species is expected to result in the deterioration of diesel-emitted soot compared to conventional diesel engine operation due to suppression of soot oxidation rate for the same conditions of pressure and temperature.
- Increase of CO equilibrium mole fraction. This fact in conjunction with the fact of reduction of O_2 and OH equilibrium mole fractions is expected to affect negatively diesel-emitted CO, which are primarily controlled by partial chemical kinetics and they predominantly affected by chemical equilibrium concentrations of CO, O_2 and OH for constant values of pressure and temperature.

Further increase of CO_2 (from 40%v/v to 60%v/v) in the reactants gaseous mixture compared to the previous n-heptane combustion case (40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2) and the elimination of N_2 from the reactants it was found that result in:

- Elimination of NO equilibrium mole fraction as initially expected. In this case is expected that the actual combustion of a diesel fuel with pure oxygen and carbon dioxide will result in NOx-free diesel engine operation.
- Significant reduction of CO_2 equilibrium mole fraction. Hence, it is assessed that the feeding of a diesel engine with a gaseous mixture comprised of 40%v/v O_2 and 60%v/v CO_2 is expected to serious reduction of diesel-emitted CO_2, which are primarily controlled by chemical equilibrium, compared to conventional diesel operation and diesel operation with a intake gaseous mixture comprised of 40%v/v O_2, 30%v/v N_2 and 30%v/v CO_2. The reduction of CO_2 equilibrium mole fraction is a profound indicator of fuel conversion efficiency improvement. The substantial reduction of CO_2 equilibrium concentrations, which were observed in the case of oxy-heptane combustion, is of utmost importance since CO_2 is the predominant gas contributing to the deterioration of greenhouse effect. Μηδενισμό των συγκεντρώσεων ισορροπίας O_2 και δραματική μείωση των συγκεντρώσεων ισορροπίας OH. Στην περίπτωση αναμένεται ιδιαίτερα σημαντική επιβάρυνση της αιθάλης από την εφαρμογή της αντίστοιχης περίπτωσης καύσης με καθαρό O_2 και CO_2 σε ένα κινητήρα diesel λόγω ιδιαίτερα σημαντικής υποβάθμισης του ρυθμού οξείδωσης σε σχέση με ένα συμβατικό κινητήρα diesel.
- Substantial increase of CO chemical equilibrium concentrations. In this case and in conjunction with the dramatic reduction of the chemical equilibrium mole fractions of the predominant oxidative chemical species (O_2 and OH) it is anticipated a significant deterioration of diesel-emitted CO in the case of diesel operation with intake mixture comprised of pure oxygen and carbon dioxide.

Overall this preliminary study has provided the opportunity to examine different scenarios of diesel combustion with oxygen-enriched air stream and cooled EGR as well with pure oxygen and carbon dioxide and through them to develop qualitative predictions about the pertinent effects on actual diesel-emitted soot, NO and CO values. Hence, such preliminary studies can be proven quite useful before performing complex diesel engine simulations to understand certain effects on diesel combustion.

Another important aspect of this preliminary study, which was performed under a diploma thesis in Hellenic Naval Academy, is that chemical equilibrium solvers can be used as teaching and research tools in the hands of teachers and students for better comprehension of diesel combustion.

Another important finding of this study is that combustion with pure oxygen (40%v/v) and carbon dioxide (60%v/v) in actual diesel engines is anticipated to result – compared to conventional diesel operation – in improvement of combustion efficiency, reduction of CO_2 emissions and elimination of NO emissions with parallel serious detrimental effects on diesel-emitted soot and CO values. Hence, it is necessary the investigation of different analogies of O_2, N_2 and CO_2 as well as of O_2 and CO_2 in order to derive the optimum reactants mixture composition for simultaneous reduction of NOx and CO_2 emissions without serious negative effects on soot and CO emissions.

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