Oxy-fuel HCCI combustion in a CFR engine with carbon dioxide as a thermal buffer

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Abstract

Global warming and the increasingly stringent emission regulations call for alternative combustion techniques to reduce CO₂ emissions. Oxy-fuel combustion is one of those techniques since the combustion products are easily separated by condensing the water and storing CO₂. A problem associated with the burning of fuel using pure oxygen as an oxidant is that it results in high adiabatic flame temperature. This high flame temperature is decreased by introducing a thermal buffer to the system. A thermal buffer in this context is any gas that does not participate in combustion but at the same time absorbs some of the released heat and thus decreases the temperature of the medium. Many experiments have been conducted to study oxy-fuel combustion in ICE using noble gases as thermal buffers. However, those experiments focused on using hydrogen as a fuel to avoid any build-up of CO₂ in the system. On the contrary, the work presented in this paper investigates using CO₂ as a thermal buffer for oxy-fuel combustion in HCCI engines. Experiments were performed on a standard Waukesha variable compression ratio cooperative fuel research CFR engine, modified to run in HCCI mode. Emissions were measured using an AVL SESAM-60 FTIR spectrometer. As expected, results showed that the CO₂ mixture degraded engine efficiency. The relatively lower engine temperature also decreased NOₓ emissions, simultaneously increasing CO and unburned hydrocarbon (UHC) emissions.

Introduction

Global warming is most likely anthropogenic, necessitating a reduction in greenhouse gas (GHG) emissions [1]. Although some doubts exist about the credibility of models that predict the future of the earth under climate change [2], the scientific community is pushing decision makers to impose cuts to carbon dioxide emissions. The response from the international community of IC engine research is to accelerate improvement of engine efficiency and reduce these emissions [3].

There are three intuitive ways to decrease carbon dioxide emitted by internal combustion engines [4]. The first obvious solution is enhancing engine efficiency to lower the amount of fuel consumed and as a consequence the amount of carbon dioxide emitted to the atmosphere. The second solution is to use a fuel with a low carbon-to-hydrogen ratio, such as methane in order to decrease the emitted carbon dioxide per energy produced. Finally, the third way is to use biofuels. Biofuels have a short carbon cycle meaning that any emitted carbon dioxide will be retrieved from the atmosphere. A problem associated with biofuels is that they are extracted from edible crops raising many concerns about the effect of such fuels on the food security [5].

Another challenging solution could involve non-carbon fuels like hydrogen and ammonia. The use of hydrogen as fuel is probably as old as the engine itself. In 1822 Cecil developed a vacuum engine based on hydrogen fuel [6]. In 1978 Boer et. al argued that the practicality of hydrogen fuel is justified, since its specific heat ratio is higher than gasoline, increasing overall thermodynamic efficiency [7]. A car run on liquid hydrogen has been developed by a group of researchers at the Musashi Institute of Technology in Japan. Their prototype car has shown both increased efficiency and better emissions [8]. However, hydrogen has a much lower volumetric energy density compared to other liquid fuels, making it less practical. Its volatility and low flash point also raises important questions about the safety of its distribution infrastructure. Having a reasonable volumetric energy density and safer characteristics, ammonia is another non-carbon fuel that could easily be used in an ICE. The main problem associated with ammonia is that its production from methane is not a carbon-free process. In fact, it has been suggested that ammonia production could produce more carbon dioxide emissions than directly combusting hydrocarbon fuels [9].

The carbon battle is now experiencing a paradigm shift towards capturing carbon dioxide before its release into the environment. Oxy-fuel combustion, which produces mainly CO₂ and water as combustion products, could be a viable solution for carbon capture and storage (CCS) since the combustion products are easily separated by condensing the water and storing the emitted carbon dioxide [10], but oxygen separation from air makes oxy-fuel combustion difficult to implement in light-duty vehicle engines. Oxygen separation from air using ceramic-based membranes is a rising technology [11]. However, oxygen separation is still far from being implemented for engine application, mainly due to the limited flow rates required. One more practical consideration is the elevated adiabatic flame temperature associated with oxy-fuel combustion. The best way to reduce this temperature is to recirculate carbon dioxide back to the combustion chamber. In this case, CO₂ acts as a thermal buffer and absorbs some of the released energy, resulting in acceptable temperatures.

Introducing CO₂ to the combustion chamber is not a novel idea: one technique for decreasing NOₓ emissions in engines is recirculating the exhaust gas (EGR) with carbon dioxide concentrations. Ladommatos et al. isolated EGR effects in a direct injection diesel engine and concluded that only the dilution effect of replacing oxygen with carbon dioxide compared significantly to the chemical and thermal effects [12]. The introduction of EGR in compression ignition engines decreases NOₓ emissions, but at the same time it increases smoke, CO emissions and unburned hydrocarbons (UHC). It also decreases thermodynamic efficiency, all of which result in deteriorated brake efficiency [13]. Cinar et al. [14] reported similar results.

EGR is used in HCCI engines for a different purpose. HCCI engines are characterized by high efficiency and low NOₓ emissions, but their problem is low indicated mean effective pressure (IMEP). In this case, EGR was used to decrease the rate of combustion that enabled the use of higher fuel/air ratio to gain higher IMEP [15,16]. Pure CO₂ was injected in an HCCI engine, with different
concentrations, and as expected, temperature rise delays were observed, since CO₂ decreases the overall specific heat ratio [17]. However, decreasing the combustion rate and the in-cylinder temperature resulted in higher CO emissions and unburned hydrocarbons [18].

This work investigates the possibility of oxy-fuel combustion in HCCI engines with carbon dioxide dilution. Oxy-fuel combustion in automobile engines is not entirely feasible given the technological status quo. However, this concept could be implemented for stationary power applications especially in renewable energy production. Storage of energy in renewable plants is required when the production is higher than the demand. For example, the peak production of a solar power plant takes place during the day while the peak demand takes place during the night. In this case the excess energy can be used for electrolysis to separate oxygen from water. Then, oxygen is stored and used for oxy-fuel combustion in an ICE when energy is required. To the best of the authors’ knowledge, the study of oxy-fuel combustion in ICE has been focusing on diluting the mixture with noble gases to increase the specific heat ratio and hence the thermodynamic efficiency [19–22]. This paper in contrast studies the feasibility of diluting the charge with carbon dioxide. This work also paves the way for further studies involving the recirculation of CO₂ in oxy-fuel HCCI engines.

The experimental approach followed in this paper involves running the CFR engine with three different oxidizer mixtures: normal air, synthetic air (O₂ + N₂), and CO₂ + O₂. The first two mixtures should give similar results and represent a baseline for the tests. The CO₂+O₂ mixture (oxy-fuel combustion) is compared with the baseline to observe the behavior of the engine in terms of performance and emissions.

**Experimental Setup**

A cooperative fuel research (CFR) engine is a variable compression ratio engine that has been used for over 90 years to assess the performance of internal combustion engine fuels [23]. The standard engine is designed for spark ignition (SI) combustion and equipped with a carburetor to mix the fuel and air at stoichiometry. To run the engine under HCCI lean conditions, the carburetor was replaced by a port fuel injector that supplied the fuel at constant pressure. Injection duration controlled the amount of fuel injected to the engine to attain the required equivalence ratio. Table 1 shows specifications of the Waukesha CFR engine.

As discussed in the introduction, the engine was run with three different oxidizers to observe its performance as the specific heat ratio changes. For this purpose, four mass flow controllers were installed to control the flow of air, oxygen, nitrogen, and carbon dioxide. The different oxidizers are shown in Table 2. The three mixtures will be referred to here as case 1, case 2, and case 3: air, synthetic air, and CO₂/mixture (CO₂+O₂), respectively.

<table>
<thead>
<tr>
<th>Case</th>
<th>Oxidizer mixtures</th>
<th>O₂ (vol.%)</th>
<th>N₂ (vol.%)</th>
<th>Ar (vol.%)</th>
<th>CO₂ (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>20.95</td>
<td>78.09</td>
<td>0.93</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>Synthetic air</td>
<td>21.0</td>
<td>79.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>CO₂ + O₂</td>
<td>21.0</td>
<td>0.0</td>
<td>0.0</td>
<td>79.0</td>
</tr>
</tbody>
</table>

Thermocouples were also installed to measure intake and exhaust temperatures. Intake temperature was regulated by heaters, managed by a PID controller. In-cylinder pressure was measured with an AVL QC34D pressure transducer; the pressure signal was then amplified and digitized in an A/D converter. The crank encoder delivered an output pulse every 0.2 CAD. Intake and exhaust pressures were also measured using AVL water-cooled pressure transducers.

Exhaust emissions were measured by an AVL SESAM i60 FTIR analyzer. Emissions were measured here to estimate combustion efficiency from the total unburned hydrocarbons and to observe the difference in the emissions per se. Table 3 shows the accuracy of the different devices used experimentally.

<table>
<thead>
<tr>
<th>Device/System</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow controllers (MFCs)</td>
<td>± 0.5 % of the flow rate and ± 0.1 % of the full scale (1000 slpm)</td>
</tr>
<tr>
<td>Thermocouples</td>
<td>± 2 K</td>
</tr>
<tr>
<td>QC34D AVL pressure transducer</td>
<td>± 0.3% of the full scale (150 bar)</td>
</tr>
<tr>
<td>Intake and exhaust pressure transducers</td>
<td>± 0.1% of the full scale (10 bar)</td>
</tr>
<tr>
<td>FTIR analyzer</td>
<td>≤ 2% of the measured value</td>
</tr>
</tbody>
</table>

The CO₂ cooling effect in case 3 decreased the in-cylinder temperature which hinders the HCCI chemistry. For this reason, the fuel has to be a low octane number fuel that can easily auto-ignite. After trying different PRFs, n-heptane has been chosen as fuel for

### Table 2. Constituents of three different experimental mixtures

### Table 3. Accuracy of different devices used experimentally

![Figure 1. Experimental model schematic](image)

![Table 5. Waukesha single cylinder CFR engine specifications](image)
all the three different cases. Furthermore, n-heptane is assumed to be a surrogate that effectively describes the auto-ignition behavior of the diesel oil [24–26]. Table 4 summarizes the main characteristics of n-heptane.

**Table 4. characteristics of n-heptane**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>n-heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>RON</td>
<td>0</td>
</tr>
<tr>
<td>MON</td>
<td>0</td>
</tr>
<tr>
<td>Auto-ignition temperature [K]</td>
<td>488</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;16&lt;/sub&gt;</td>
</tr>
<tr>
<td>Molar mass [g/mol]</td>
<td>100.23</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>679.5</td>
</tr>
<tr>
<td>Boiling point [K]</td>
<td>371</td>
</tr>
</tbody>
</table>

Carbon dioxide absorbs released heat and decreases in-cylinder temperature; therefore, it was decided to increase the intake temperature to 80°C to enable combustion initiation. HCCI is a lean combustion technique with an equivalence ratio in the range of 0.2 to 0.4. A lower equivalence ratio will result in misfire, while higher equivalence ratios results in severe knock (higher dP/dCAD). However, this engine was run with a slightly richer mixture, having a fuel/oxygen equivalence ratio φ of 0.4 in order to enhance combustion stability especially when the oxidizer is an oxygen + carbon dioxide mixture. In all cases, the combustion was phased to have a CA50 at TDC. CA50 is the crank angle degree at which 50% of heat is released. Table 4 summarizes the testing conditions for the three different mixtures.

**Table 5. Testing conditions for the three different mixtures**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation speed</td>
<td>600 rpm</td>
</tr>
<tr>
<td>Intake temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Intake pressure</td>
<td>1 bar</td>
</tr>
<tr>
<td>CA50</td>
<td>TDC</td>
</tr>
<tr>
<td>Equivalence ratio φ (Fuel/Oxygen)</td>
<td>≈ 0.4</td>
</tr>
<tr>
<td>Fuel</td>
<td>n-heptane</td>
</tr>
</tbody>
</table>

It is worth mentioning that the conditions shown in table 5 are the conditions of the three different cases. The compression ratio was the tuning parameter to phase the combustion with CA50 at TDC. In cases 1 (air) and 2 (synthetic air) the compression ratio was 7.5 while for case 3 (CO<sub>2</sub>+O<sub>2</sub> mixture) the compression ratio was 16.5.

**Results and discussion**

The results first show and compare pressure traces obtained for the three different mixtures. Pressure is an important experimental outcome since it plays a vital role in the estimation of three important results: temperature trace, heat release rate, and efficiency analysis. The section concludes with the exhaust emissions measured using the FTIR spectrometer.

**In-cylinder pressure**

Figure 2 shows the pressure traces for the three different mixtures with CA50 phased at TDC.

![Figure 2. Pressure traces for three different mixtures](attachment:image.png)

Two important observations are displayed in figure 2. First is that the low temperature heat release (LTHR) is prominent; this was expected since the fuel used was n-heptane. The second observation is that the pressure of the CO<sub>2</sub>+O<sub>2</sub> mixture was higher than that of air and synthetic air. This is attributed mainly to the higher compression ratio. The compression ratio was increased because the charge required a high temperature to establish the HCCI auto ignition chemistry. The CO<sub>2</sub> mixture had a lower specific heat ratio than the other mixtures in order to increase the compression ratio and reach the required temperature. The isentropic compression relations (equations 1 and 2) explain that behavior.

\[
P_2 = P_1 R_c^\gamma \quad (1) \\
T_2 = T_1 R_c^{\gamma - 1} \quad (2)
\]

Where

- \( P \) is the in-cylinder pressure
- \( T \) is the in-cylinder temperature
- \( R_c \) is the compression ratio
- \( \gamma \) is the specific heat ratio

Subscripts 1 and 2 denote the states before and after the compression stroke, respectively.

A previous publication by the authors showed the inverse of the previous behavior when a higher specific heat ratio mixture of argon and oxygen was used [20].

The air mixture (case 1) contains some argon (~1%) and consequently it has a slightly higher specific heat ratio than the
nitrogen – oxygen mixture (case 2). Thus, it is expected that the air mixture will have a higher pressure profile.

**Pressure-Volume diagram**

![Pressure-Volume diagram](image)

Figure 3. Pressure-Volume diagram for three different mixtures

Figure 3 shows the engine pressure-volume diagram. The difference in compression ratio among the three mixtures is apparent; and interesting observations can be made by enlarging two regions in the figure.

First is the heat addition region shown in figure 4. Two phases of heat release are apparent: the LTHR and the main heat release. It is obvious that only the main heat release was at constant volume; but LTHR developed as the piston moves. This behavior is best explained by the temperature that drives the reactions. In the LTHR region, the temperature was low and reactions developed slowly. Once the gas temperature increased in the cylinder, the heat was released quickly enough to achieve an almost isochoric heat addition.

![P-V diagram for three different mixtures, magnified at heat release region](image)

Figure 4. P-V diagram for three different mixtures, magnified at heat release region

The second region of interest is the enclosed area that represents gas exchange losses. While it is difficult to observe differences between the three mixtures in figure 5, the detailed efficiency analysis reveals that the CO₂ + O₂ mixture had lower gas exchange efficiency since CO₂ is a heavier molecule. The efficiency analysis is presented later in this paper.

**In-cylinder temperature**

![Temperature traces for three different mixtures](image)

Figure 5. Pressure-Volume diagram for three different mixtures, magnified at gas exchange region

Temperature plays a vital role in understanding combustion behavior in HCCI engines. The three cases in figure 6 have the same combustion phasing, but it is clear that reactions were initiated earlier in cases 1 and 2 than in case 3.

![Temperature traces for three different mixtures](image)

Figure 6. Temperature traces for three different mixtures

As mentioned earlier, the intake temperature (T_{in}) was 80°C. This temperature should not be confused with the intake valve closing temperature (T_{ivc}). Heat transfer with the cylinder wall and the hot residual gases increased the temperature of the charge. Thus, T_{ivc} was expected to be higher than T_{in}. Furthermore, T_{ivc} for the CO₂ mixture was expected to be lower than T_{ivc} of the other mixtures because of the lower specific heat ratio and the cooling effect of CO₂. Finally, it is worth mentioning that the temperature information was retrieved from the measured pressure trace using the ideal gas law.
**Heat release rate (HRR)**

The heat release rate can be estimated using the ideal gas law as follows:

\[
\frac{dQ_{hr}}{d\theta} = \frac{\gamma}{\gamma - 1} \frac{dp}{d\theta} + \frac{1}{\gamma - 1} V \frac{dV}{d\theta} + \frac{dQ_{ht}}{d\theta}
\]  

(3)

Where

- \(\frac{dQ_{hr}}{d\theta}\): the heat release rate (HRR) per crank angle degree (CAD)
- \(\gamma\): the specific heat ratio \(c_p/c_v\)
- \(p\): the in-cylinder pressure
- \(V\): the volume of the cylinder
- \(\frac{dV}{d\theta}\): the rate of volume change per crank angle degree
- \(\frac{dp}{d\theta}\): the rate of pressure change per crank angle degree
- \(\frac{dQ_{ht}}{d\theta}\): the rate of heat transfer losses per crank angle degree

Equation 3 accounts only for heat transfer losses. Other losses (blow-by and crevice losses), are neglected in this analysis. Specific heat ratio \(\gamma = c_p/c_v\) depends on temperature, and assuming it to be constant is not quite realistic. To account for this dependence on temperature, a simple model was used to estimate the specific heat ratio of the charge (including the oxidizer and the fuel) as a function of crank angle degree. The model utilized Burcat’s thermodynamic data to estimate the specific heat of the species involved in the reactions, assuming complete combustion [27]. Figure 7 shows the results of this model; it is easily noticed that constant specific heat ratio assumption is not valid, especially at high temperatures close to TDC. This can be explained considering statistical thermodynamics, as high temperature enables the molecules to acquire more degrees of freedom.

![Figure 7. Specific heat ratio dependence on crank angle](image)

Heat release rates for the three different mixtures are shown in figure 8. As discussed earlier, the two peaks observed in each case represent two distinct reaction zones, i.e., LTHR and main heat release. The first peak corresponding to the LTHR appears as three parameters are decreased: RON of the fuel, intake temperature, and engine speed [28–30]. It can be noticed that the testing conditions of this experiment is the perfect match for such low temperature heat release. The fuel used to run the engine is n-heptane which has a zero RON. Also, the intake temperature is 80°C which is relatively low (motor octane test method requires an intake temperature of 149 °C). Furthermore, the engine speed is only 600 rpm which is also relatively low. All these conditions explain the prominent LTHR peak. Finally, the two peaks in case 3 (CO₂ mixture) are similar as a result of CO₂ cooling effect that decreases the in-cylinder temperature and gives more residence time for the LTHR to develop and match the high temperature main heat release.

![Figure 8. Heat release rates for three different mixtures](image)

Figure 9 shows the accumulated heat release for the three different mixtures. It can be noticed that 50% of the energy is already released at TDC, i.e, CA50 is at TDC.

![Figure 9. Accumulated heat for the three different mixtures](image)

**Exhaust emissions**

Unburned hydrocarbons (UHC), along with CO emissions, are indicators of degraded combustion efficiency. Figures 10–13 show the UHC and CO emissions. The reduced in-cylinder temperature in case 3 (CO₂ mixture) resulted in more fuel not being burned and less oxidation of CO. Thus, it is expected that the CO₂ mixture will have the highest UHC and CO emissions compared to the other two cases.

It should be noted that, unlike a conventional flame ionization detector (FID), the Fourier transform infrared radiation (FTIR) spectrometer does not provide a total hydrocarbon (THC) reading.
The following equation was used by Melo et al. to estimate the total unburned hydrocarbons (UHC) by the AVL SESAM i60 FTIR analyzer [31].

\[
\text{UHC} = \text{CH}_4 + 2\text{C}_2\text{H}_2 + 2\text{C}_2\text{H}_4 + 3\text{C}_3\text{H}_6 + 5\text{IC}_5 + 5\text{NC}_5 + 7.5\text{AHC}
\]

Where ICs, NCs, and AHC stand for iso-pentane, normal pentane, and total aromatics concentration, respectively.

Figure 10. Unburned hydrocarbon emissions for the three mixtures (ppm)

Figure 11. Unburned hydrocarbons for the three mixtures (g/kWh)

Another mechanism for NO\textsubscript{x} formation is prompt or Fenimore NO\textsubscript{x}. Prompt NO\textsubscript{x} is formed when the CH radical reacts with nitrogen to produce hydrocyanic acid (HCN), which in turn dissociates and reacts with oxygen to produce NO\textsubscript{x}. However, this reaction is predominant in rich mixtures and cannot precisely explain NO\textsubscript{x} formation in HCCI lean conditions. A precursor for CH radical is C\textsubscript{2}H\textsubscript{2}, which accumulates in fuel rich conditions due to CH\textsubscript{3} recombination [32].

NO\textsubscript{x} generated via nitrous oxide N\textsubscript{2}O could be the reason for NO\textsubscript{x} formation in these experiments. N\textsubscript{2}O is formed when nitrogen reacts with oxygen in the presence of a third molecule, M, as per the following equation:

\[
\text{N}_2 + \text{O} + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}
\]

Nitrous oxide N\textsubscript{2}O then reacts with O atoms to produce NO as follows:

\[
\text{N}_2\text{O} + \text{O} \rightarrow \text{NO} + \text{NO}
\]
The activation energy of the previous equation is relatively low and does not require as high a temperature as needed to initiate the aforementioned thermal mechanism.

Finally, it should be noted that in case 3 (CO₂ mixture) no nitrogen was supplied to the engine, nevertheless, there was almost 2 ppm of NOx. While this is a negligible concentration, it could be attributed to the nitrogen impurities in the O₂ and CO₂ cylinders.

**Efficiency analysis**

Indicated thermal efficiency \( \eta_{\text{ind,th}} \) is the product of three different efficiencies, as shown in equation 4. Those are combustion efficiency \( \eta_c \), gas exchange efficiency \( \eta_{\text{ge}} \), and thermodynamic efficiency \( \eta_{\text{th}} \). The details of efficiency calculations can be found in the appendix of a paper previously published by the authors [20].

\[
\eta_{\text{ind,th}} = \eta_c \eta_{\text{ge}} \eta_{\text{th}} \quad (4)
\]

Because of their composition similarity, cases 1 and 2 had almost the same efficiency. In contrast, in case 3 CO₂ decreased all efficiencies as a result of its properties.

**Combustion efficiency \( \eta_c \)**

Combustion efficiency is, by definition, the percentage of fuel energy released during the combustion process. Molecules with significantly lower heating value (LHV) in the exhaust are simply losses, since their energy could have been utilized.

The low in-cylinder temperature in case 3 (CO₂ mixture) decreased the rate of fuel oxidation, resulting in higher UHC concentration which decreased combustion efficiency. Deteriorated combustion efficiency was also a result of increased CO emissions which has a LHV of 10.1 MJ/kg. Furthermore, Hydrogen has a relatively high LHV of 120.0 MJ/kg, and it must be considered. However, hydrogen cannot be measured directly by the FTIR spectrometer since it is a diatomic molecule with zero dipole moment; therefore it does not respond to the IR radiation. A mass spectrometer is thus needed for accurate hydrogen measurement. Fortunately, hydrogen concentration can be estimated with fair accuracy using the water gas equation as follows:

\[
x_{\text{H}_2} = \frac{x_{\text{CO}} x_{\text{H}_2O}}{K x_{\text{CO}_2}} \quad (5)
\]

Where \( x \) stands for the molar concentration of the molecule and \( K \) is the water gas constant that is usually assumed to be 3.5 [4].

The combustion efficiency can then be estimated as follows:

\[
\eta_c = \frac{\sum M_i x_i Q_{LHV,i}}{M_p A/F Q_{LHV,f}} \quad (6)
\]

Where
- \( M_i \) is the molar mass of species i (UHC, CO, H₂)
- \( M_p \) is the molar mass of fuel
- \( x_i \) is the mole fraction of species i (UHC, CO, H₂)
- \( Q_{LHV} \) is the lower heating value of fuel \( f \) or species \( i \)
- \( A/F \) mass air fuel ratio.

As expected, the low in-cylinder temperature in case 3 (CO₂ mixture) resulted in low combustion efficiency, as shown in figure 16.

**Thermodynamic efficiency \( \eta_{\text{th}} \)**

Thermodynamic efficiency increases monotonically as the specific heat ratio of the charge increases. Case 3 (CO₂ mixture) had a relatively low specific heat ratio compared to the other two cases.
(air and synthetic air). This low specific heat ratio is a result of the nine degrees of freedom present in the CO$_2$ molecule. In addition to the three translational movements, it has only two rotational movements because CO$_2$ is a linear molecule and the third rotation does not change the position of the atoms. CO$_2$ also has four vibrational modes that are activated at high temperatures. Figure 17 shows the thermodynamic efficiency for the three different cases where, as expected, the CO$_2$ mixture had the lowest efficiency.

Figure 17. Experimental thermodynamic efficiency for three mixtures

The real efficiency shown in figure 17 differs from the ideal Otto efficiency, which depends on both compression ratio $R_C$ and specific heat ratio $\gamma$, as shown in equation 7.

$$\eta_{otto} = 1 - \frac{1}{R_C^{\gamma - 1}} \quad (7)$$

The reason for this deviation is neglecting the heat transfer losses. One more reason is that the previous formula assumes isochoric heat addition which is not the case in reality (figure 4). Table 6 shows a comparison between the experimental and theoretical efficiencies. It should be noted that the theoretical efficiency was calculated based on an average specific heat ratio.

Table 6. Comparison between real and ideal thermodynamic efficiencies

<table>
<thead>
<tr>
<th>Oxidizers</th>
<th>$\gamma$</th>
<th>$R_C$</th>
<th>$\eta_{otto}$</th>
<th>$\eta_{real}$</th>
<th>$\eta_{real}/\eta_{otto}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.32</td>
<td>7.5</td>
<td>47.5%</td>
<td>37.2%</td>
<td>78.3%</td>
</tr>
<tr>
<td>N$_2$ + O$_2$</td>
<td>1.32</td>
<td>7.5</td>
<td>47.5%</td>
<td>36.9%</td>
<td>77.7%</td>
</tr>
<tr>
<td>CO$_2$ + O$_2$</td>
<td>1.21</td>
<td>16.5</td>
<td>44.5%</td>
<td>25.9%</td>
<td>58.2%</td>
</tr>
</tbody>
</table>

Gas exchange efficiency $\eta_{ge}$

Some of the energy released is used to pull a fresh charge into the cylinder and push out the exhaust. The efficiency of this process is known as the gas exchange efficiency. CO$_2$ is a heavier molecule, requiring more work to push and pull. Thus, it is expected to have a lower gas exchange efficiency, as shown in figure 18.

Figure 18. Gas exchange efficiency for three mixtures

Figure 19 summarizes the previous results, showing the indicated thermal efficiency for the three cases. As previously mentioned, the CO$_2$ mixture decreased engine efficiency for three main reasons: (1) decreased in-cylinder temperature, leading to lower combustion efficiency (2) lower specific heat ratio $\gamma$ leading to reduced thermodynamic efficiency, and finally (3) CO$_2$ is a heavier molecule, and this results in lower gas exchange efficiency.

Figure 19. Indicated thermal efficiency for three mixtures

Conclusion

This study investigated the effect of CO$_2$ replacing N$_2$ in an HCCI engine. Experiments were conducted in a single cylinder variable compression CFR engine. Comparison was made among three different oxidizers: air, synthetic air (O$_2$+N$_2$), and O$_2$+CO$_2$. n-heptane was selected as the fuel since the O$_2$+CO$_2$ mixture reduced the in-cylinder temperature significantly and auto-ignition temperature of higher octane fuels could not be achieved. The compression ratio $R_c$ was adjusted to maintain combustion phasing at TDC. In-cylinder pressure was measured and used for the generation of other engine outputs. Emissions were also measured using an FTIR analyzer to estimate combustion efficiency and
compare the emissions per se. The following list summarizes the conclusions of this study:

1. It is possible to operate an HCCI engine with only CO₂ and fuel added. The CO₂ can be captured from exhaust as the exhaust is only CO₂ and water. The low specific heat ratio of the CO₂ mixture required higher compression ratio to achieve the same combustion phasing.

2. To get combustion with a reasonable compression ratio, pure n-heptane was selected as fuel. This required 7.5:1 for air and 16.5:1 for CO₂+4O₂. The low specific heat ratio of the CO₂ mixture required higher compression ratio than air to have the same combustion phasing, CA50 at TDC.

3. The low gamma of CO₂+O₂ gave much higher pressures for the same temperature at TDC.

4. Using n-heptane as fuel resulted in prominent low temperature heat release (LTHR). Low temperature heat release takes longer time than the main heat release especially for air and synthetic air mixtures.

5. It takes longer time for the CO₂ mixture to achieve the auto ignition temperature as CO₂ has lower specific heat ratio.

6. CO₂ mixture (almost) eliminated NOx emissions but at the same time increased CO and UHC emissions.

7. CO₂ mixture resulted in deteriorated thermodynamic efficiency.

8. Decreased in-cylinder temperature also lead to lower combustion thermodynamic efficiency.

9. As CO₂ is a heavier molecule also a lower gas exchange efficiency resulted.

10. Overall, it is not a very good idea to use a CO₂-cycle if high efficiency is desired.

11. Argon is a much better alternative bulk gas as shown in a previous paper.

References


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**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CA50</td>
<td>Crank angle degree at which 50% of heat is already released</td>
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<tr>
<td>CAD</td>
<td>Crank angle degree</td>
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<tr>
<td>CCS</td>
<td>Carbon capture and storage</td>
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<tr>
<td>CFR engine</td>
<td>Cooperative fuel research engine</td>
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<td>EGR</td>
<td>Exhaust gas recirculation</td>
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<tr>
<td>FID</td>
<td>Flame ionization detector</td>
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<td>FTIR</td>
<td>Fourier transform infra-red radiation</td>
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<td>GHG</td>
<td>Greenhouse gas</td>
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<td>HR</td>
<td>Heat release</td>
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<td>HRR</td>
<td>Heat release rate</td>
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<td>ICE</td>
<td>Internal combustion engine</td>
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<td>IMEP</td>
<td>Indicated mean effective pressure</td>
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<tr>
<td>IR</td>
<td>Infra-red</td>
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<td>LHV</td>
<td>Lower heating value</td>
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<td>LTHR</td>
<td>Low temperature heat release</td>
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<td>MON</td>
<td>Motor octane number</td>
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<tr>
<td>PID controller</td>
<td>Proportional–integral–derivative controller</td>
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<tr>
<td>PRF</td>
<td>Primary reference fuel</td>
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<td>RON</td>
<td>Research octane number</td>
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<tr>
<td>SI</td>
<td>Spark ignition</td>
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<tr>
<td>TDC</td>
<td>Top dead center</td>
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<tr>
<td>THC</td>
<td>Total hydrocarbons</td>
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<tr>
<td>UHC</td>
<td>Unburned hydrocarbons</td>
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