Chemical Looping Combustion with liquid fuels in a 1 kWth unit using a Fe-based oxygen carrier

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1. Introduction
Our society is at a turning moment to develop an effective strategy to address climate change.

400 ppm CO$_2$

IPCC warned that it is imperative to take urgent and effective actions to reduce global emissions.
CCS technologies play an important role as they are capable of achieving 14% of the reductions needed to keep the rise in global temperature below 2 °C [1].

CLC is based on the transfer of oxygen from air to fuel by means of an OC which is continuously reduced and oxidized. Doing so, direct contact between air and fuel is avoided and a pure stream of CO$_2$ is produced.
Introduction

Renewable fuels

They have the advantage of achieving **negative CO₂ emissions**

**EtOH**

Its production and use have increased dramatically since early 2000. In 2014, ≈93.7 billion litres of ethanol were produced and this trend is expected to continue [2]

Fossil fuels

In the transition to a low-carbon economy, the implementation of CLC technology with liquid fuels from refineries could reduce 1 billion metric tons CO₂/year [3]

**Diesel – Engine oil**

They were selected as representatives fuels obtained in refineries, but the ultimate goal in future works will involve the use of heavy residual oils

This work intended to analyze the employability of **ethanol, diesel and engine oil** as fuels in a continuous **CLC** unit with a Fe-based **OC**.
2. Experimental
Given the relevance of the impurities in the performance of CLC, these compounds were determined.

### Elementary analysis

<table>
<thead>
<tr>
<th></th>
<th>EtOH C₂H₅OH</th>
<th>Diesel C₁₅H₂₅</th>
<th>Engine oil C₁₈H₃₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, % mass</td>
<td>52,1</td>
<td>86,5</td>
<td>85,1</td>
</tr>
<tr>
<td>H</td>
<td>13,1</td>
<td>13,7</td>
<td>13,6</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>0</td>
<td>0,5</td>
</tr>
<tr>
<td>S</td>
<td>0</td>
<td>0</td>
<td>0,7</td>
</tr>
<tr>
<td>O</td>
<td>34,8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>--</td>
<td>--*</td>
<td>0,0003</td>
</tr>
<tr>
<td>Ca</td>
<td>--</td>
<td>--</td>
<td>0,4759</td>
</tr>
<tr>
<td>Zn</td>
<td>--</td>
<td>--</td>
<td>0,3075</td>
</tr>
<tr>
<td>Ba</td>
<td>--</td>
<td>--</td>
<td>0,0016</td>
</tr>
<tr>
<td>Pb</td>
<td>--</td>
<td>--</td>
<td>0,0071</td>
</tr>
<tr>
<td>P</td>
<td>--</td>
<td>--</td>
<td>0,1655</td>
</tr>
<tr>
<td>S</td>
<td>--</td>
<td>--</td>
<td>0,1508</td>
</tr>
</tbody>
</table>

* Ash content <0,01 %m/m

### Distillation curves

Three different behaviours were observed according to their different molecular structure:

- EtOH
- Diesel
- Engine oil
**OXYGEN CARRIER**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fresh particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size, μm</td>
<td>100-300</td>
</tr>
<tr>
<td>Fe$_2$O$_3$, %</td>
<td>20,0</td>
</tr>
<tr>
<td>Oxygen transport capacity, R$_{OC}$, %</td>
<td>2,0</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>50,5</td>
</tr>
<tr>
<td>Apparent density, kg/m$^3$</td>
<td>3950</td>
</tr>
<tr>
<td>BET specific surface area, m$^2$/g</td>
<td>39,1</td>
</tr>
<tr>
<td>Crystalline phases</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

OC developed by ICB-CSIC [4]

Prepared by *incipient wetness impregnation*

To ensure that OC maintained its properties after operation, the fresh OC was characterized

1 kW\textsubscript{th} CLC FACILITY

Components
2 interconnected fluidized bed reactors, a riser, a cyclone, a valve to manage solid circulation flow and a loop seal to prevent gas mixing between reactors.

Dimensions
FR 0.026-0.085 m. i. d.
AR 0.052 m. i. d.

Fuel supply
It was controlled by peristaltic pumps.
The fuel flow was completely evaporated in a furnace before it reached the FR.

Gas Chromatograph quantified HCs.
DATA ANALYSIS

**Oxygen carrier reduction**
- **Ethanol**
  \[ \text{C}_2\text{H}_5\text{OH} + 6 \text{Fe}_2\text{O}_3 + 12 \text{Al}_2\text{O}_3 \leftrightarrow 12 \text{FeAl}_2\text{O}_4 + 2 \text{CO}_2 + 3 \text{H}_2\text{O} \]
- **Diesel**
  \[ \text{C}_{15}\text{H}_{29} + 44.5 \text{Fe}_2\text{O}_3 + 89 \text{Al}_2\text{O}_3 \leftrightarrow 89 \text{FeAl}_2\text{O}_4 + 15 \text{CO}_2 + 14.5 \text{H}_2\text{O} \]
- **Engine oil**
  \[ \text{C}_{18}\text{H}_{34} + 53 \text{Fe}_2\text{O}_3 + 106 \text{Al}_2\text{O}_3 \leftrightarrow 106 \text{FeAl}_2\text{O}_4 + 18 \text{CO}_2 + 17 \text{H}_2\text{O} \]

**Oxygen carrier oxidation**
- \[ 4\text{FeAl}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4 \text{Al}_2\text{O}_3 \]

**Combustion efficiency**
\[ \eta_c = \frac{(2x_{\text{CO}_2} + x_{\text{CO}} + z\cdot x_{\text{C}_x\text{H}_y\text{O}_z})_{\text{out}} \cdot F_{\text{out}} - z\cdot(x_{\text{C}_x\text{H}_y\text{O}_z})_{\text{in}} \cdot F_{\text{in}}}{b\cdot(x_{\text{C}_x\text{H}_y\text{O}_z})_{\text{in}} \cdot F_{\text{in}}} \]

**CO₂ capture efficiency**
\[ \eta_{cc} = \frac{(x_{\text{CO}_2} + x_{\text{CO}} + x\cdot x_{\text{C}_x\text{H}_y\text{O}_z})_{\text{out}} \cdot F_{\text{out}}}{(x_{\text{C}_x\text{H}_y\text{O}_z})_{\text{in}} \cdot F_{\text{in}}} \]

**Oxygen carrier to fuel ratio**
\[ \Phi = \frac{F_{\text{Fe}_2\text{O}_3}}{b\cdot F_{\text{fuel}}} \]
3. Results
In the range 800-900°C, an increase in T produced an increase in $\eta_c$ as OC reactivity is improved with T.

Regarding gas product distribution, light hydrocarbons were never measured. CO$_2$ was the major compound together with a mixture of CO+H$_2$+CH$_4$ to a lesser extent.
Results

**DIESEL**

- In the range 800-900°C, temperature had a slight effect on $\eta_c$.

- Regarding gas product distribution, again mixture CO+H$_2$+CH$_4$ were the only compounds decreasing $\eta_c$.

- As in the previous case, CH$_4$ was measured which suggests that CH$_4$ could be an intermediate on HCs conversion to CO$_2$. 
Results

ENGINE OIL

- In the range 800-900°C, temperature played an important role for $\Phi<1.8$

- Only the mixture CO+H$_2$+CH$_4$ decreased $\eta_c$ and CH$_4$ remained constant suggesting again that it could be a stable intermediate.
In accordance with the results obtained, engine oil performed better despite its greater difficulties to be handled. Thus, long term tests and a comprehensive OC characterization were done to analyze deeper the influence of impurities.
Results

LONG TERM TESTS - ENGINE OIL

- 50 h burning fuel
  Carefull assessment of the combustion process

- Combustion efficiency was unaffected by operation hours/impurities
  For a given $\phi$ value, almost same $\eta_c$ was achieved at different operation hours

- Effect of $S$
  The OC did not show any sign of deactivation or poisoning

![Graph showing combustion efficiency over time and operation hours for engine oil and long term tests.](image-url)
Results

LONG TERM TESTS - ENGINE OIL

- Reactivity tests in TGA
  Fresh and used OC particles were subjected to successive redox cycles to study its evolution during operation

- Conversion VS time curves
  As shown, OC reactivity was hardly affected by operation hours or the presence of impurities
• SEM-EDX analyses

Particles were rounded due to operation hours in ICB-CSIC-liq1.

Fe distribution was homogeneous along the cross section, both on fresh and used.

Regarding possible deposition of impurities on the particles, no significant amount of none of them were detected.
Results

SUMMARY

- **200 h successful operation**
  
  During the experimental campaign 200 h were achieved with the same batch of particles

- **Results summary**
  
  $\eta_c$ obtained values provide a quick overview of the main findings. EtOH and diesel followed the same trend but engine oil behaved contrary to expectations better than the others at low $\phi$ values likely due to the different thermal decomposition mechanism.
4. Conclusions
Conclusions

• Three different liquid fuels, ethanol, diesel and engine oil, were evaluated in a 1 kw\textsubscript{th} CLC continuous unit using a Fe- based oxygen carrier prepared by impregnation method.

• A total of 200 hours of operation were successfully accomplished with the same batch of Fe20-γAl\textsubscript{2}O\textsubscript{3} particles

• The three liquid fuels behaved properly under CLC conditions working with Fe20-γAl\textsubscript{2}O\textsubscript{3} oxygen carrier

• The behavior of engine oil was especially noteworthy as it was able to achieve even better combustion efficiencies at low \( \phi \) values despite its greater molecular complexity
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Thanks for attending this presentation

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