

# Experimental study of the combustion of pyrolysis gas with oxygen carriers

## XII JORNADA DE JÓVENES INVESTIGADORES DEL I3A



Instituto Universitario de Investigación en Ingeniería de Aragón  
Universidad Zaragoza

César Gracia, Javier Ábrego, Alberto Gonzalo, Jesús Arauzo, Mahnoor Nafees  
Department of Chemical and Environmental Engineering,  
University of Zaragoza. 50018-Zaragoza, Spain  
c.gracia@unizar.es



Departamento de Ingeniería Química y Tecnologías del Medio Ambiente  
Universidad Zaragoza

### RATIONALE

Pyrolysis enables obtaining valuable products (biochar and bio-oil) from residual biomass. Usually, pyrolysis gases are combusted with air to provide energy for the process.

**Low temperature** oxidation of pyrolysis gases using Cu-based oxygen carriers would allow [1]:

- Obtaining a CO<sub>2</sub> stream, available for further use.
- Providing heat for the pyrolysis process.

### OBJECTIVES & ADVANTAGES

**Objective:** To evaluate the performance of several oxygen carrier materials (OCs) for pyrolysis gas oxidation, to obtain a pure CO<sub>2</sub> stream (CO<sub>2</sub> capture) [2].

**Advantages:** CLC technology allows to capture & use CO<sub>2</sub> from the gas fraction. The process could be a NET (Negative Emission Technology) [3].

### MATERIALS

Three Cu-based OCs were used:

- CuO
- *Carulite* (mixed Cu-Mn oxide)
- CuO (13 %wt.) supported on Al<sub>2</sub>O<sub>3</sub>

CuO is exothermal when reduced with CO and CH<sub>4</sub> (other OCs have endothermal processes). OCs were tested at low temperatures, close to those of pyrolysis.

### EXPERIMENTAL RESULTS

The three OCs used in this work exhibited high pyrolysis gas oxidation efficiencies (= high CO<sub>2</sub> concentrations at the outlet)

**Figure 1** shows the behaviour of CuO as OC. A very high purity of CO<sub>2</sub> (for 625, 650 and 700 °C) in the outlet stream is achieved. For 700 °C the efficiency is almost 100 % during the whole experiment time.

Temperatures under 600 °C produce low oxidation efficiencies.

WHSV for these experiments is around 0,014 h<sup>-1</sup>.

**Figure 2:** Shows the behaviour of *Carulite* as OC. As temperature increases, CO<sub>2</sub> purity also increases. At 625 °C, the CO<sub>2</sub> purity is close to 100 % for a long reduction time (>15 minutes).

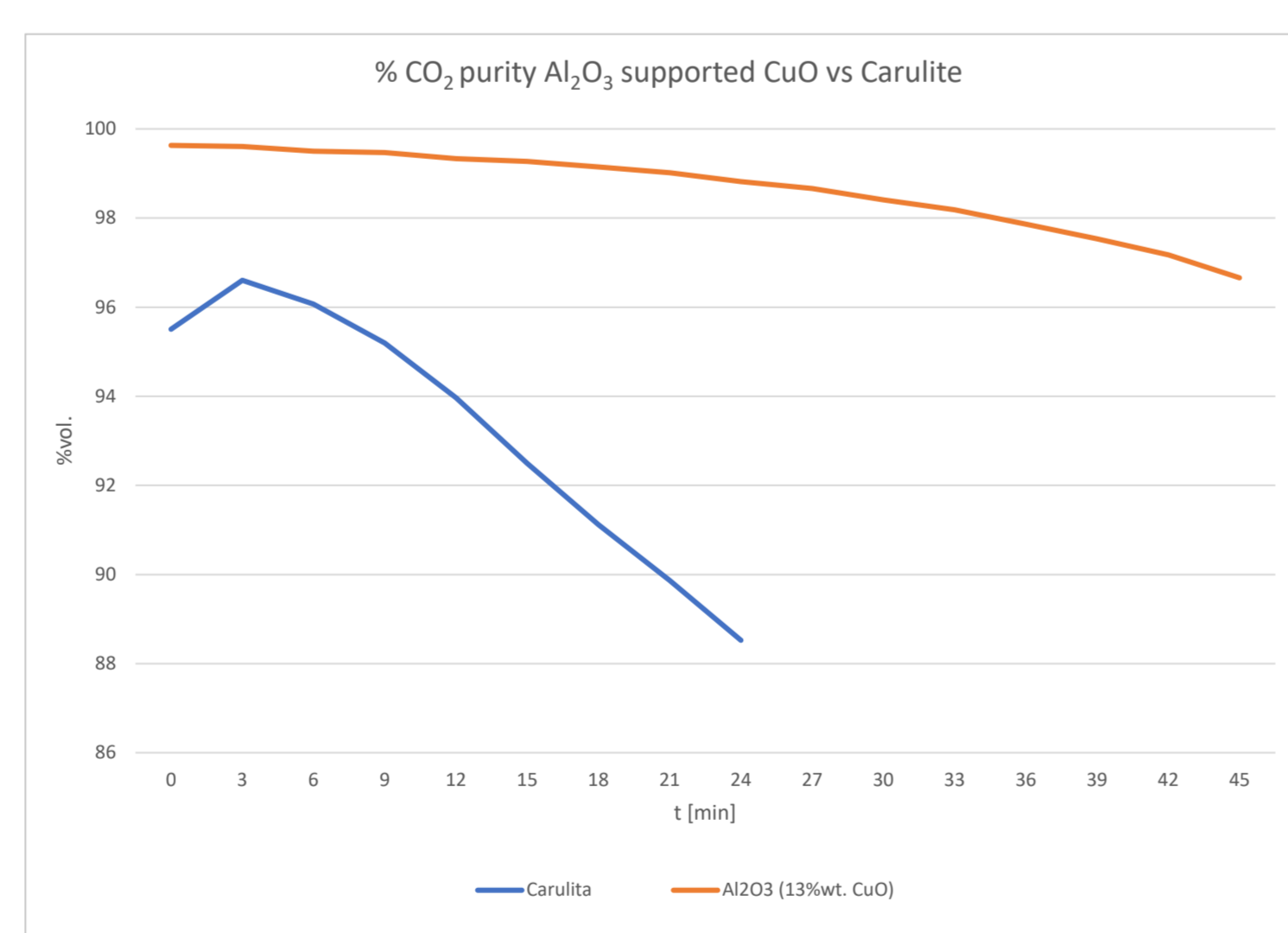
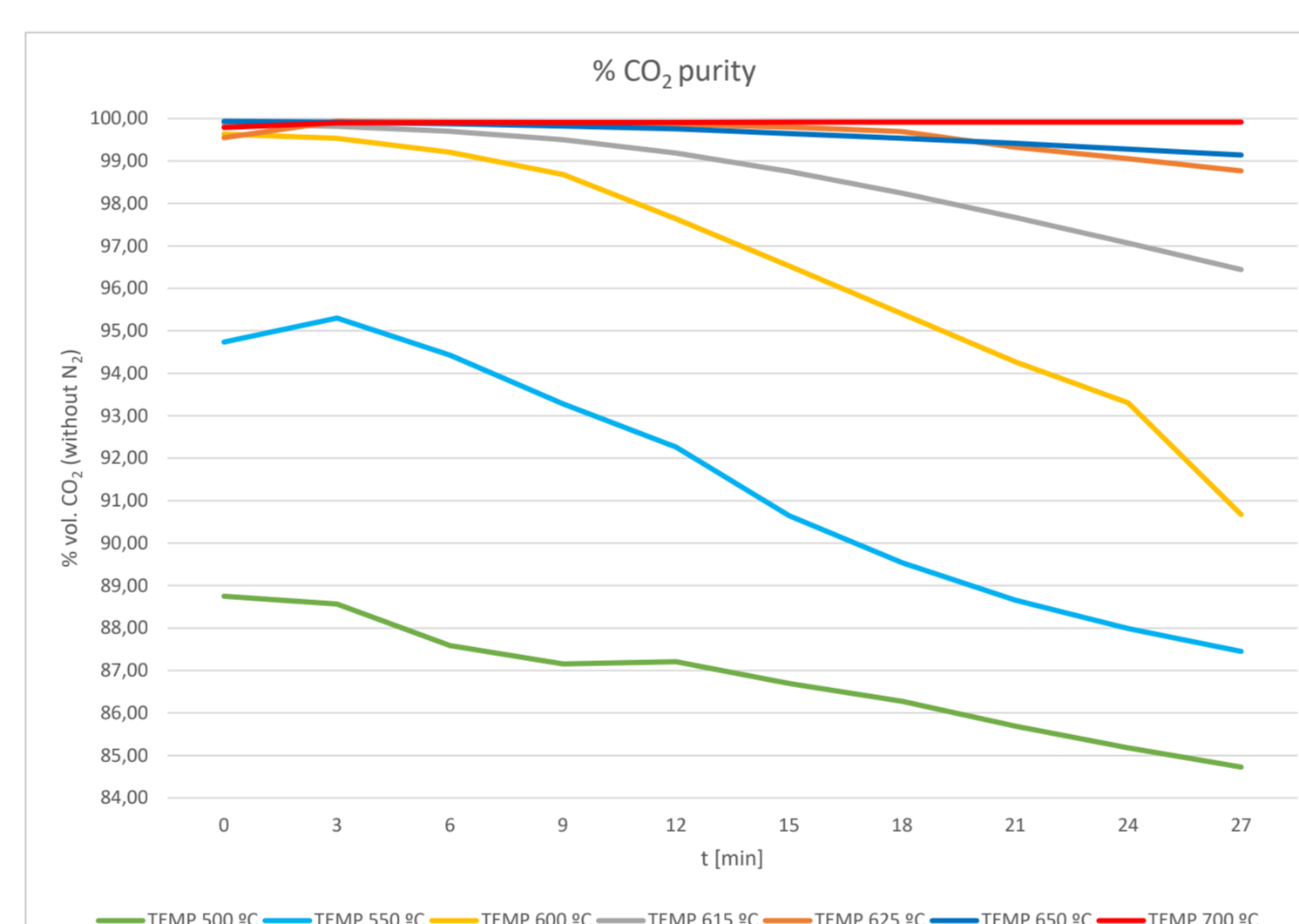
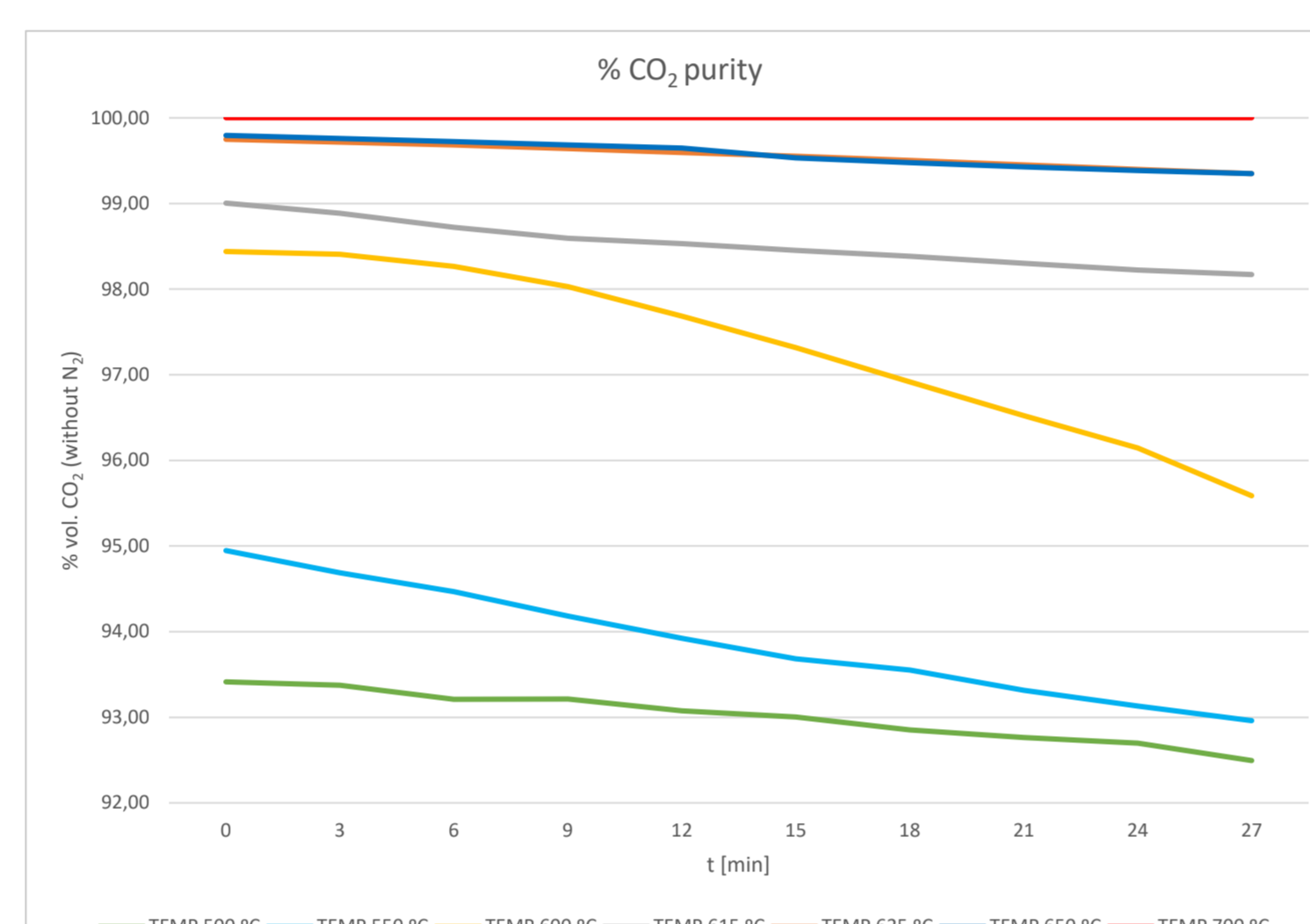
At 700 °C, CO<sub>2</sub> purity is almost 100 % for the whole experiment (30 minutes).

WHSV for these experiments is around 0,041 h<sup>-1</sup>.

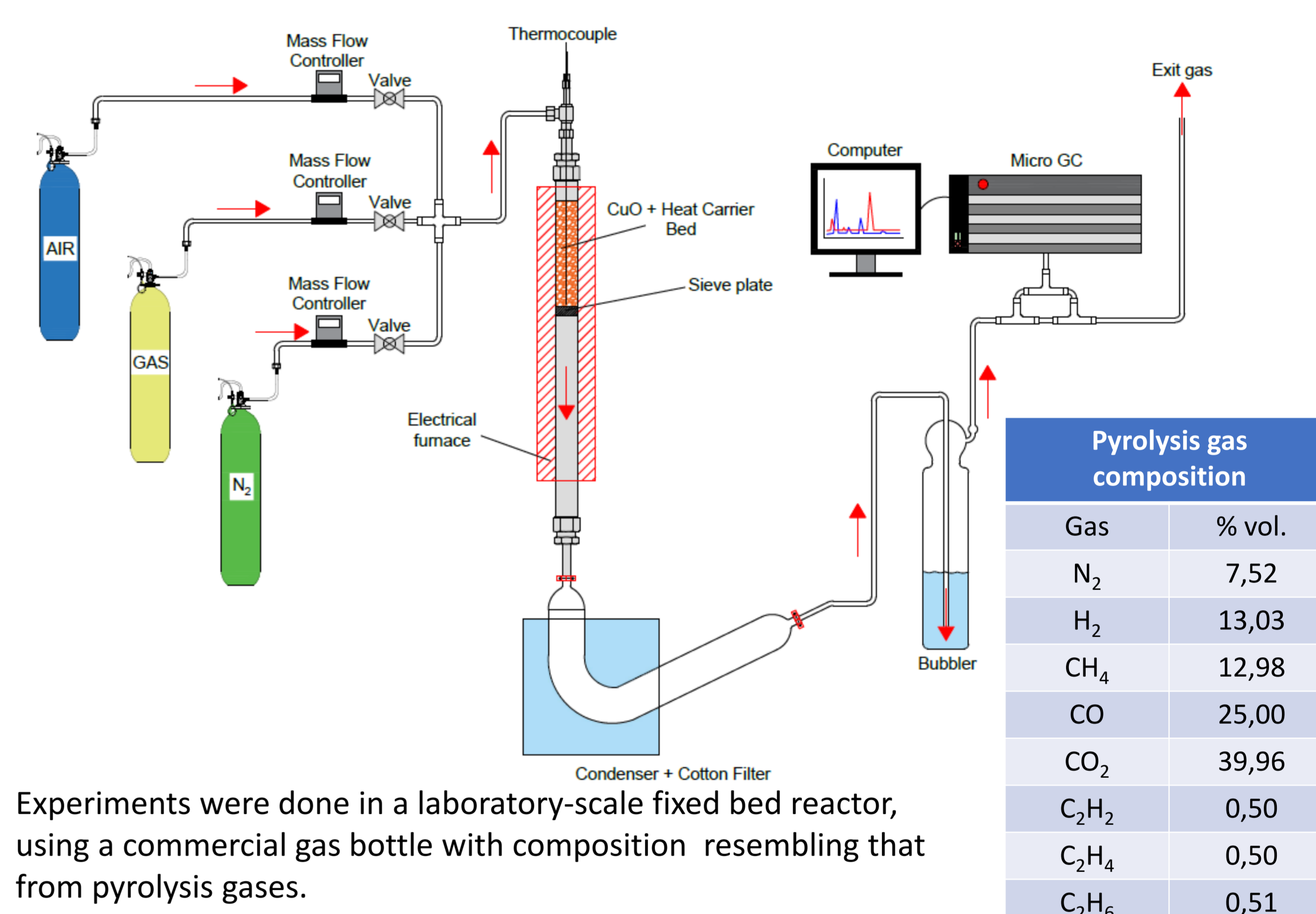
**Figure 3:** Al<sub>2</sub>O<sub>3</sub>-supported CuO showed the most promising CLC performance, taking into account that the total amount of CuO was much lower. In Figure 3, a comparison with *Carulite* is shown.

Unfortunately, only a little amount of this commercial material was available for the experiments. Thus further research is needed in order to evaluate its adequacy.

WHSV for these experiments is around 1,466 h<sup>-1</sup>.



### EXPERIMENTAL SYSTEM



Experiments were done in a laboratory-scale fixed bed reactor, using a commercial gas bottle with composition resembling that from pyrolysis gases.

Experimental conditions were the following:

- T = 500 -700 °C
- P = Patm = 1,01 bar
- Q = 30 mL/min of pyrolysis gas
- Outlet gas composition was determined using a gas microchromatograph

Pyrolysis gas composition	
Gas	% vol.
N <sub>2</sub>	7,52
H <sub>2</sub>	13,03
CH <sub>4</sub>	12,98
CO	25,00
CO <sub>2</sub>	39,96
C <sub>2</sub> H <sub>2</sub>	0,50
C <sub>2</sub> H <sub>4</sub>	0,50
C <sub>2</sub> H <sub>6</sub>	0,51

### CONCLUSIONS

- Complete oxidation of pyrolysis gases to CO<sub>2</sub> (and H<sub>2</sub>O) at relatively low temperatures using CuO-based OCs has been proven.
- Both the OC type and temperature affect the pyrolysis gases oxidation process. Temperatures around 650 °C have been determined as adequate for the process.
- OC reoxidations (not shown in this work) are relatively fast at these temperatures.
- CH<sub>4</sub> is the less reactive gas of the pyrolysis gases. Its content increases in the outlet gas as the CO<sub>2</sub> purity decreases due to progressive OC reduction.
- CuO appears to work better as OC when is supported in other material such as Al<sub>2</sub>O<sub>3</sub>; however, further experiments are required.
- Future works should focus on testing tailor-made, supported copper oxide OCs.
- The reoxidation stage and the cycle repeatability should also be investigated.
- Equivalent WHSV should be also investigated.

### References

- [1]. ÁBREGO, J., ATIENZA-MARTÍNEZ, M., PLOU, F. and ARAUZO, J. Heat requirement for fixed bed pyrolysis of beechwood chips. *Energy*. 2019, no.178, pp.145-157. Available from: doi.org/10.1016/j.energy.2019.04.078.
- [2]. SAN PIO, M.A., ROGHAI, I., GALLUCCI, F., VAN SINT ANNALAND, M. Investigation on the decrease in the reduction rate of oxygen carriers for chemical looping combustion. *Powder Technology*. 2016, no.301, pp.429-439. Available from: dx.doi.org/10.1016/j.powtec.2016.06.031
- [3]. YINGYING, S., BEIBEI, D., LIANG, W., HAILONG, L. and THORIN, E. Technology selection for capturing CO<sub>2</sub> from wood pyrolysis. *Energy Conversion and Management*. 2022, no. 266. Available from: doi.org/10.1016/j.enconman.2022.115835