Powder Technology 436 (2024) 119413

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.journals.elsevier.com/powder-technology

Chemical looping with oxygen uncoupling of swine manure for energy production with reduction of greenhouse gas emissions

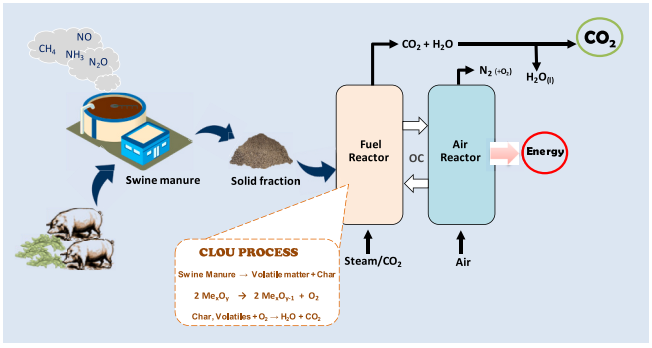
Yldeney Domingos, Alberto Abad *, Margarita de las Obras Loscertales, María T. Izquierdo, Pilar Gayán, Iñaki Adánez-Rubio

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán, 4, 50018 Zaragoza, Spain

HIGHLIGHTS

- Energy valorization of the swine manure with CLOU technology has been performed.
- Magnetic Cu based oxygen carrier was tested in a 0.5 kW_{th} CLOU plant.
- High combustion and CO_2 capture efficiencies were reached.
- N-fuel was mostly converted to N_2.
- NO concentration increased with the temperature whereas N_2O and NH_3 decreased.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
CO_2 capture
Swine manure
Combustion
Chemical looping
CLOU
Nitrogen

ABSTRACT

The thermochemical conversion of swine manure using chemical looping processes is an alternative for obtaining bioenergy with CO_2 capture and solving environmental problems related to excess nutrients and greenhouse gas emissions. In this study, the combustion of swine manure was performed in a chemical looping with oxygen uncoupling (CLOU) unit at the 0.5 kW_{th} scale with copper-based oxygen carrier particles supported on magnetic MnFe spinel. The effects of the fluidisation agent (CO_2 or steam), air excess (7%–23%), and temperature (800–950 °C) on different parameters, namely the CO_2 capture rate, combustion efficiency, and nitrogenous compound emissions, were analysed. High combustion efficiencies (95%–98%) were achieved, and tar compounds were not detected in the flue gases. Similarly, elevated CO_2 capture efficiency values (82%–99%) were also achieved, which increased by increasing the temperature. Most nitrogen (ca. 93%–96%) is converted into innocuous N_2. The NO concentration increased with temperature, whereas N_2O and NH_3 concentrations decreased.

* Corresponding author.
E-mail address: abad@icb.csic.es (A. Abad).

https://doi.org/10.1016/j.powtec.2024.119413
Received 4 September 2023; Received in revised form 4 January 2024; Accepted 11 January 2024
Available online 13 January 2024

Notation

Symbols

X_{char}	Carbon conversion in char particles (−)
f_c	Mass fraction of carbon in solid fuel (−)
M_i	atomic mass of element *i* (kg/mol)
$\dot{m}_{sf}$	Mass-based flow of solid fuel fed into the fuel reactor (kg/h)
$\dot{m}_{FR}$	Specific solid inventory (kg/MW_{th})
$\dot{m}_{OC}$	Solid circulation rate (kg/s)
R_{oc}	Oxygen transport capacity (−)

Greek letters

$\eta_{comb,FR}$	Combustion efficiency in the fuel reactor (−)
η_{CC}	CO_2 capture efficiency (−)
ϕ	Oxygen carrier to fuel ratio (−)
λ	Air excess ratio (−)
Ω_{sf}	Stoichiometric mass of O_2 to convert 1 kg of solid fuel (kg/kg)

Subscrips

AR	Air reactor
FR	Fuel reactor
Char	Carbon in char particles
OC	Oxygen carrier
Elut	Elutriated particles from fuel reactor
Fix	Fixed carbon
inAR	Inlet stream to air reactor
inFR	Inlet stream to fuel reactor
outFR	Outlet stream from fuel reactor
outAR	Outlet stream from air reactor
sf	Solid fuel

Acronyms

CLOU	Chemical Looping Combustion with Oxygen Uncoupling
CLC	Chemical Looping Combustion
LHV	Low Heating Value (kj/kg)
OC	Oxygen carrier
T	Temperature

1. Introduction

Agricultural practices contribute to the release of greenhouse gases through several, including enteric fermentation in domesticated animals, livestock manure management, agricultural soil management, the application of urea fertilisers, the use of liming materials, and the burning of agricultural residues in the field [1].

Manure management is critical for the sustainability of the livestock sector in countries where intensive farming is implemented. In particular, the pig sector is considerably important, with China, the United States, Germany, and Spain being the world's four largest pork producers [2]. The main impacts of swine manure, in solid and liquid fractions, on the environment come fundamentally from greenhouse gas emissions (GHG) and excess nutrient accumulation in the field, typically N and P compounds [3].

Swine manure is a residue composed of a mixture of solid and liquid excrement, food scraps, and cleaning water. Its composition varies depending on different factors existing in the pig farm –e.g., race, age, or food– but in general, the solid fraction of this residue is characterised by a high content of carbon (>50% daf), nitrogen (4%–5% daf), sulfur (~1% daf), and ash (~30%).

This waste is often used as an organic fertilizer in agriculture. The abuse of this solution may lead to significant environmental problems, such as aquifer pollution by N- and P-containing compounds. In addition, it may result in the accumulation of trace elements in soil (Zn and Cu) and an increase in N-containing compounds (NH_3 and NOx) and CH_4 emissions into the atmosphere, contributing to environmental acidification and an increase in the greenhouse effect. Therefore, searching for a suitable solution to this problem is crucial. Particularly, the energetic valorisation of the solid fraction of swine manure can potentially mitigate the environmental concerns associated with this residue. In addition, if technologies with reduced greenhouse gas emissions are implemented, different contamination effects may be simultaneously solved.

Several processes, including pyrolysis, gasification, and combustion [4,5], have been studied for their application to organic wastes and are versatile with different fuels. Thus, they can be applied in managing swine manure obtained from areas with intensive livestock farming. The raw swine manure has high water content (>90%), and thermochemical processes focus on the solid fraction. For this reason, solid waste can be obtained after flocculation-separation, which can eventually be treated as a semi-dry solid fuel. The use of swine manure as an input for pyrolysis has been demonstrated in waste reduction and energy production studies. Fernandez-Lopez et al. [6] determined that the thermal decomposition of swine manure mainly corresponds to that of hemicellulose. Because swine are not ruminants, hemicellulose degrades poorly in their intestines. Xiu [7] achieved a maximum oil yield of 24.2% by hydrothermal pyrolysis of swine manure at 340 °C in a high-pressure reactor (100 psi). Liquefied oil is a viable option with the potential for use as a resource for renewable fuels and chemicals.

The potential of energy valorisation of manure by combustion has also been evaluated for other types of animal waste [8–11]. Lundgren and Pettersson [9] evaluated using wood shavings and horse manure as alternative fuel sources for heat generation. The emissions of incomplete combustion products were low; however, NOx emissions of 280–350 mg/Nm^3 at 10 vol% O_2 were observed because of the elevated N fuel. The experimental results of Turzyński et al. [10] indicated that the chemical characteristics of chicken manure make it difficult to burn, and adding other materials like straw and wood facilitates the combustion process. However, a large amount of straw in the mix increases NOx emissions, causes problems owing to ash sintering, and reduces temperature and power density. Jiang et al. [11] studied the combustion properties and ignition of bovine manure. The results showed a low tendency for slag and encrustation of bovine manure ash. They concluded that this residue is an unconventional but potential raw material for heat generation.

Among the novel technologies for converting biofuels to energy, Chemical Looping Combustion (CLC) stands out because of its unique ability to convert carbonaceous materials with a high N content [5]. CLC is a combustion technology with an intrinsic capture of CO_2 and interesting characteristics for N-fuel conversion that may be highly relevant for the energy valorisation of swine manure to reduce greenhouse gas emissions and soil contamination by N compounds [12].

The fundamental principle underlying CLC technology involves the avoidance of fuel and air contact in the combustion process, which is achieved by utilising an oxygen carrier (often a metal oxide, Me_xO_y) to supply the oxygen required for the combustion of a fuel, which may be gaseous, liquid, or solid [13]. The continuous provision of oxygen for fuel oxidation is guaranteed through the following redox cycle (Fig. 1): the metal oxide undergoes reduction while oxygen is provided to the fuel, followed by subsequent reoxidation through exposure to air.

When using solid fuel, chemical looping with oxygen uncoupling (CLOU) improves the performance compared to common CLC using oxygen carriers capable of releasing O_2 [14]. Thus, the fuel oxidation process occurs in distinct stages: initially, it starts with its devolatilisation into the volatile matter and the char reaction (R1); then, the oxygen

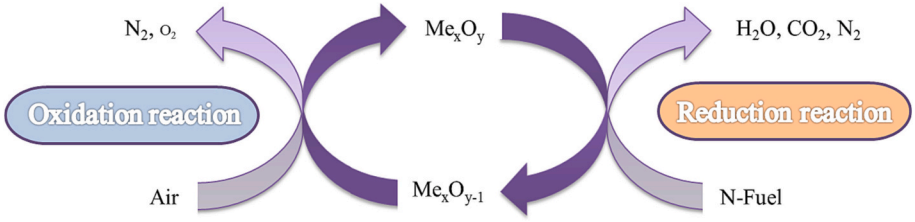


Fig. 1. Conceptual framework of biomass chemical looping combustion process.

carrier liberates the molecular oxygen reaction (R2); eventually, the volatile components and char are burned subsequently with O_2 as in the conventional combustion reaction (R3).

$$\text{Solid fuel} \rightarrow \text{Volatile matter} + \text{Char} \quad \text{(R1)}$$

$$2\,Me_xO_y \rightarrow 2\,Me_xO_{y-1} + O_2 \quad \text{(R2)}$$

$$\text{Char, Volatiles} + O_2 \rightarrow H_2O + CO_2 + \text{Ash} \quad \text{(R3)}$$

The metal oxide, M_xO_y, was regenerated in air (R4). Notably, the unconverted carbon in the char may also be burned during the regeneration step (R5), which causes a decrease in the CO_2 capture rate because some CO_2 is emitted in the air-depleted stream.

$$2\,Me_xO_{y-1} + O_2 \rightarrow 2\,Me_xO_y \quad \text{(R4)}$$

$$C + O_2 \rightarrow CO_2 \quad \text{(R5)}$$

For the CLOU process, three redox systems based on pure metal oxides, namely Mn_2O_3/Mn_3O_4, Co_3O_4/CoO, and CuO/Cu_2O [14], as well as mixed oxides or perovskite-based materials [15], have been identified with suitable thermochemical characteristics.

This technology is also versatile for use with different solid fuels. Using biomass in the CLOU technology has been demonstrated using distinct oxygen carriers based on CuO, CuMn, or MnFe mixed oxides and CaMn-based perovskites [16–18]. These studies showed the use of biomass through complete combustion of fuels with high CO_2 capture rates. In the case of biofuels, studying the fate of nitrogen is particularly relevant. During combustion, N-fuel produces NOx compounds (NO_2, NO, and N_2O). In chemical looping, molecular N_2 is detected as the main N-fuel product, with a minor presence of NO [12]. Comparing fuel-N conversion during the CLC and CLOU processes, Pérez-Astray et al. [19] used biomass almond shell, pine sawdust, and olive stone under similar experimental conditions, and they observed that the CLC mode favoured nitrogen exiting together with CO_2 because of the higher temperature used in this mode. In relation to N_2O, small amounts were detected in CLOU mode but disappeared with increasing temperature (850 °C). Neither NH_3 nor HCN was detected. NO was also detected during the regeneration step from nitrogen in the unconverted char; however, with increasing process temperature, its concentration decreased and remained within the legal limits established for power plants. Thermal NOx was not generated because of the low temperatures of the CLC and CLOU processes, and air was not mixed with the fuel.

Song et al. [20] found that the operating temperature and solid inventory may affect N-fuel conversion in the CLOU process. Thus, these parameters affected the smooth and continuous release of O_2 from the oxygen carrier and the O_2 concentration in the combustion stage. For highly volatile fuels and temperatures above 900 °C, they primarily found NO and some NO_2 and N_2O, mainly from N released in the solid fuel devolatilisation. Notably, the distribution of N and the composition of volatiles are primarily influenced by the fuel, temperature, particle size, delivery rate and pressure [21]. Although the formation of N_2O was much lower, it may have promoted heterogeneous reactions with the metal oxides in the oxygen carrier particles. Furthermore, the reduced oxygen carriers may reduce NO to N_2 [22].

Considering swine manure as a potential fuel, the high amount of nitrogen in NH_3-based compounds and high ash content is relevant. With the conversion of NH_3 using ilmenite as an oxygen carrier, Mayrhuber et al. [22] and Lyngfelt et al. [23] concluded that NH_3 can be converted entirely to NO or N_2. In addition, NO reduction may be promoted by reduced oxygen carriers. Because of their high content, the possible interactions between the metal oxides in the oxygen carrier and ash compounds should be evaluated [24]. In addition, high ash content requires continuous ash removal to prevent its accumulation in the reactor. A certain amount of the oxygen carrier is extracted from the draining stream, and it is necessary to reposition it in the system. The magnetic properties of spinel in MnFe mixed oxides can be exploited to facilitate the separation and reuse of oxygen carriers [25]. Thus, the ICB-CSIC developed [26] and patented [27] a Cu-based material with a magnetic support based on MnFe mixed oxide so that it could be separated from ash by applying a magnetic field and re-utilised in the CLOU unit [28]. Subsequently, 7.5% of kaolin was added to this material to improve the crushing strength. This material was named Cu30MnFekao7.5 [29].

The objective of this study was to evaluate swine manure combustion in a CLOU unit at the 0.5 kW_{th} scale to reduce CO_2 emissions and make nitrogen inert. Using swine manure as fuel is challenging because of the high amount of ash in its composition. A previously developed and optimised magnetic oxygen carrier, Cu30MnFekao7.5, was used. The effects of the main operation variables (temperature, fluidisation agent, and excess oxygen) on the capture of CO_2, the efficiency of combustion, and the fate of the N fuel (e.g., conversion to N_2, NH_3, and NOx) were evaluated.

2. Experimental section

2.1. Oxygen carrier

The oxygen carrier was a CuO-based material with an oxygen uncoupling capability supported on a spinel MnFe mixed oxide to provide its magnetic properties. The primary physicochemical properties of the oxygen carrier particles are listed in Table 1. The oxygen carrier, Cu30MnFekao7.5, was prepared at the ICB-CSIC by granulation of a powder mix of 30 wt% CuO (Panreac), 30.5 wt% Mn_3O_4 (Micromax - Elkem), 31.9 wt% Fe_2O_3 (Acros Organics) and 7.5 wt% kaolin (Sumitomo Seika). Produced particles (+100–300 μm) were calcined for 4 h at 1050 °C. More information on the granulator (a spouted fluidised bed from Procell LabSystem Glatt) and preparation methodology can be found elsewhere [29].

Table 1
Main physicochemical properties of the Cu30MnFekao7.5 material.

CuO (wt%)	30
Oxygen transport capacity for CLOU, R_{OC} (wt%)	3.0[1]
Particle size (μm)	100–300
Skeletal density (kg/m^3)	4719
Magnetic susceptibility (−)	3.6
Crushing strength (N)	2.6
Porosity (%)	29.5

[1] R_{OC} for reaction CuO → 0.5 Cu_2O + 0.25 O_2.

2.2. Solid fuel: Swine manure

The swine manure used as the solid combustible was supplied by a closed-herd pig farm in Northern Spain. The solid fraction of the residues was pre-dried in the atmosphere for 3 days and then dried at 75 °C for 24 h to reduce the moisture and inactivate enteric pathogenic microorganisms in swine manure. The dried material was ground and sieved to 0.5–3.35 mm, resulting in an average particle size of 2.7 mm, with an irregular shape, although proportionate in all its dimensions. The particle density was 600 kg/m^3, which resulted in a bulk density in the fuel hopper of 330 kg/m^3.

Table 2 shows the analysis of swine manure, and the lower heating value (LHV) of the dried fuel is LHV = 13,649 kJ/kg. The calculated stoichiometric oxygen required to achieve full combustion was $\Omega_{sf} = 1.1$ kg O/kg fuel.

$$\Omega_{sf} = \left(2\frac{f_C}{M_C} + 0.5\frac{f_H}{M_H} + 2\frac{f_S}{M_S} - \frac{f_O}{M_O}\right).M_O \quad (1)$$

2.3. CLOU unit

The CLOU unit consists of two interconnected fluidized bed reactors: a fuel reactor, where the fuel is fed and oxidised by the oxygen carrier, and an air reactor, where the oxygen carrier is regenerated with air (see Fig. 2). The fuel reactor (5 cm I.D., 20 cm bed height) operated in the bubbling regime and was fluidized by either steam or CO_2. Swine manure was introduced just above the distributor plate using a double-feeder system to control the fuel-feeding rate. The bottom section of the air reactor (8 cm I.D., 10 cm bed height) was connected to a riser with a diameter of 3 cm to facilitate the dragging of solids into the cyclone.

A U-shaped loop seal allowed the particle transfer from the fuel reactor to the air reactor, preventing gas mixing between the reactors. In the upper part, a solid valve enable the measurement and regulation of the solid flow, which should be sufficiently high to transfer the required oxygen from the air to the fuel.

The oxygen carrier from the air reactor is separated in the cyclone and returned to the fuel reactor by gravity through a solid valve (7), which controls the flow rate of solids entering the fuel reactor and, consequently, the circulation rate of solids. A diverting solid valve (6) located below the cyclone allowed for direct measurement of the solid flow rates at any time. Therefore, this design allowed us to control and measure the circulation flow rate of the solids in both reactors.

Thermocouples and pressure taps were placed in strategic points in the CLOU unit in order to measure the temperature and pressure drop in the air reactor, fuel reactor and loop seal. Due to the small size of the CLOU unit, the desired temperature in each reactor was maintained by external heating from dedicated furnaces. The information from the pressure taps were used to calculate the quantity of solids in each reactor and evaluate the good performance of specific elements, e.g. the loop seal and the riser. In addition, CO_2, CO, CH_4, H_2, and O_2 concentration in the gas from the fuel reactor and CO_2, CO, and O_2 in gas from the air reactor were continuously measured and recorded in a computer. The equipment used for the analysis of nitrogen compounds (N_2, NO, N_2O and NO_2) in the gases was an Omnistar Pfeiffer mass detection chromatograph. The identification and quantification of these nitrogen compounds was done through their mass spectra and the intensity of the signals produced by the ionization fragments of each molecule.

The sampling of NH_3 and tars was performed non-simultaneously during 1 h for each sampling. The method is based on the absorption of these compounds in impinger bottles. For NH_3, impingers with a 0.1 N H_2SO_4 solution were used to trap the ammonia as ammonium ion, in a cold bath at 0 °C. After this, the solution was analysed by Metrohm Series 800 ion chromatograph with a conductivity detector, according the recommendation of method 17 EPA. Regarding tar analysis, the sample was absorbed in an impinger with isopropanol, with temperature of cold bath −20 °C [30]. The tar compounds were quantified using a gas chromatograph coupled with a mass spectrometer.

In this study, the performed experimental campaign had >30 h of combustion operation. This unit was operated at 1.5 kW_{th} during previous CLOU tests with coal [12]. However, the maximum power used in this study was 0.5 kW_{th} because of the high ash content of swine manure. The CLOU unit operated with 3.2 kg of the Cu30MnFekao7.5 material and a circulation rate of solids of ca. 20 kg/h, which is well above the required flow for the complete fuel combustion. Table 3 lists the primary experimental conditions used in the tests. Thus, the effects of the temperature in the fuel reactor (800–950 °C) and the type of fluidising gas–steam or CO_2, which also acts as gasification agents– on the combustion degree and CO_2 capture efficiency were investigated. In addition, the air ratio in the CLOU may influence the combustion performance, especially when materials based on mixed oxides are used, for example, MnFe [31], CuMn [32], or CuMnFe [28]. Therefore, it was decided to investigate also the effect of the air excess, which was varied between 7% and 23%.

The gas flow into the fuel reactor was 200 L_N/h of water steam, or carbon dioxide. Argon was used in the loop seal (90 L_N/h) and screw feeder (12 L_N/h) to avoid any possible reverse gas flow towards the fuel hopper. Gaseous N_2 was not introduced into the fuel reactor to prevent interference in the equilibrium and reaction mechanism of nitrogen compounds. Thus, no additional nitrogen was introduced into the fuel reactor compared with that from the fuel. The airflow to the air reactor varied according to the desired air excess. However, a constant gas flow rate (2100 L_N/h) was used to maintain an adequate gas velocity in the riser. For this purpose, the airflow was completed using inert N_2.

Table 2
Proximate and ultimate analysis (as received) and elements in ash of the swine manure used in this study (wt%).

Proximate analysis (wt%)		Ultimate analysis (wt%)		Elements in ash (wt%)	
Moisture	2.2	C	36.2	Ca	17
Ash	29.0	H	4.5	P	13
Volatile matter	57.8	N	2.9	Mg	6.6
Fixed carbon	11.0	S	0.8	Si	6.0
		O[1]	24.4	K	2.2
				Fe	1.0
				Na	0.86
				Al	0.59
				Mn	0.28
				Ti	0.05

[1] To balance.

2.4. Data evaluation

The oxygen availability in the fuel reactor is evaluated through the oxygen carrier-to-fuel ratio parameter, ϕ, which evaluates the flow of oxygen available in the oxygen carrier compared to the oxygen required for the fuel combustion. This parameter was calculated by including only the oxygen involved in the oxygen uncoupling reaction (i.e., the R_{OC} value for the CuO/Cu_2O redox pair) and assuming the complete oxidation of the oxygen carrier in the air reactor. When ϕ is equal to 1, oxygen transferred in the CuO reduction to Cu_2O is equal to the stoichiometric oxygen for the complete combustion of the fuel. The following equations were used for the calculation:

$$\phi = \frac{R_{oc}\dot{m}_{OC}}{\Omega_{sf}\dot{m}_{sf}} \quad (2)$$

The excess of air was evaluated by using the air ratio parameter, λ, being the ratio between the oxygen in the air and the stoichiometric oxygen for the fuel combustion.

$$\lambda = \frac{Oxygen\ flow\ in\ air}{Oxygen\ demanded\ by\ fuel} = \frac{0.21F_{air}M_{O_2}}{\Omega_{sf}\dot{m}_{sf}} \quad (3)$$

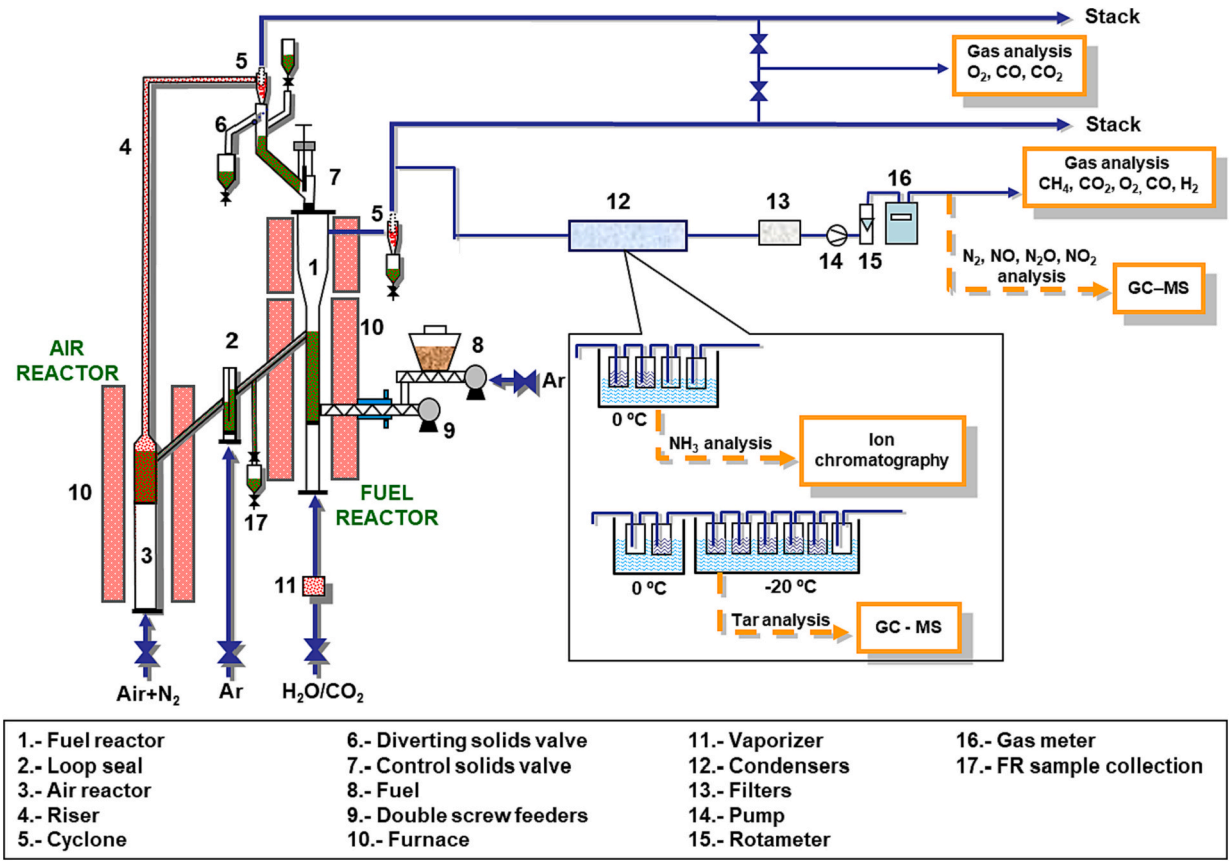


Fig. 2. Diagram of the CLOU unit at ICB-CSIC for solid fuels [12], operated at 0.5 kW_{th} in this work.

Table 3
Experimental conditions used in the CLOU tests for the combustion of swine manure with Cu30MnFekao7.5 oxygen carrier.

Test	Fluidizing agent in FR	T_{FR} (°C)	$\dot{m}_{SF}$ (kg/h)	Power (W)	λ (−)	m_{FR} (kg/MW)	$\dot{m}_{OC}$ (kg/h)	ϕ (−)	η_{comb} (%)	η_{CC} (%)
T01	H_2O	800	0.132	500	1.23	1570	21.8	4.60	97.1	81.5
T02	H_2O	850	0.132	500	1.23	1570	21.8	4.58	98.2	93.1
T03	H_2O	900	0.132	500	1.23	1570	24.6	5.18	98.8	96.6
T04	H_2O	950	0.132	500	1.23	1570	14.7	3.09	98.0	97.7
T05	CO_2	800	0.132	500	1.23	1570	28.6	6.00	95.8	82.6
T06	CO_2	850	0.132	500	1.23	1570	28.6	6.00	95.9	90.3
T07	CO_2	900	0.132	500	1.23	1570	20.5	4.30	96.6	95.9
T08	CO_2	950	0.132	500	1.23	1570	15.7	3.31	97.2	99.3
T09	CO_2	900	0.132	500	1.23	1570	20.5	4.30	96.6	95.9
T10	CO_2	900	0.125	474	1.17	1657	19.6	4.35	96.7	95.2
T11	CO_2	900	0.125	474	1.12	1657	19.6	4.35	96.8	93.9
T12	CO_2	900	0.125	474	1.07	1657	17.3	3.85	96.7	92.7

The air excess compared to the stoichiometric amount required to burn the fuel can be calculated as.

$$\text{Air excess}\ (\%) = 100\cdot(\lambda - 1) \tag{4}$$

The mass balance to carbon and oxygen in the whole unit was performed as:

$$\frac{f_C}{M_C}.\dot{m}_{sf} = \left(F_{CO_2,OutFR} + F_{CO,outFR} + F_{CH_4,outFR}\right) + F_{CO_2,outAR} + F_{C,elut} - F_{CO_2,inFR} \tag{5}$$

$$M_{O_2}\left(F_{CO_2} + F_{O_2} + 0.5F_{CO} + 0.5F_{H_2O} + F_{SO_2}\right)_{outFR} - \left(\frac{f_{H_2O}}{M_{H_2O}} + \frac{f_O}{M_O}\right)\dot{m}_{sf} - F_{CO_2,inFR} - F_{H_2O,inFR} = M_{O_2}\left[F_{O_2,inAR} - \left(F_{O_2,outAR} + F_{CO_2,outAR}\right)\right] \tag{6}$$

In this case, sulfur was assumed to have been burned into SO_2 in the fuel reactor. To account for the oxygen carried away by the water produced in the combustion process, it was presumed that the source of water was the fluidising gas, including the moisture in the fuel and its hydrogen content:

$$F_{H_2O,outFR} = F_{H_2O,inFR} + \left(0.5\,\frac{f_H}{f_{M_H}} + \frac{f_{H_2O}}{fM_{H_2O}}\right)\dot{m}_{sf} - \left(F_{H_2,outFR} + 2F_{CH_4,outFR}\right). \tag{7}$$

The swine manure conversion performance in the CLOU unit was assessed by evaluating the combustion efficiency and CO_2 capture rate under each operating condition, as shown in Table 3. The combustion efficiency was defined for fuel oxidation in the fuel reactor, $\eta_{comb,FR}$, and it considered the degree of combustion of the fuel converted in the reactor.

$$\eta_{comb,FR} = 1 - \frac{F_{CO,FR} + 4\cdot F_{CH_4,FR} + F_{H_2,FR}}{\frac{1000}{16}.\dot{m}_{sf}\Omega_{sf} - 2\cdot F_{C,elut} - 2\cdot F_{CO_2,AR}} \tag{8}$$

The CO_2 capture rate, η_{CC}, accounts for the carbon in gases exiting the fuel reactor compared to the total carbon in gases from the CLOU unit, i.e. the sum of the fuel and air reactors. Thus, the uncaptured CO_2 was present in the exhaust gas from the air reactor.

$$\eta_{CC} = \frac{F_{CO,FR} + F_{CO_2,FR} + F_{CH_4,FR}}{F_{CO,FR} + F_{CO_2,FR} + F_{CH_4,FR} + F_{CO_2,AR}} \quad (9)$$

CO_2 capture is directly affected by the carbon in the char converted into fuel in the reactor. This parameter was calculated to provide a value for the char conversion that may be useful for extrapolation calculations or the scale-up process, considering uniquely the char fraction that has had the chance to be converted, i.e., the elutriated char should be subtracted, as described by Eq. (10) [12].

$$X_{char} = \frac{C_{Fi\,x} - C_{out\,AR} - C_{elut}}{C_{Fix} - C_{elut}} \quad (10)$$

Further information regarding the appropriate use of these parameters can be found elsewhere [12].

3. Results and discussion

The experiments were conducted for 30 h of combustion in a continuous CLOU pilot plant (Fig. 2). The combustion of swine manure was performed using a Cu-based material (Cu30MnFekao7.5) as the oxygen carrier. CO_2 and steam were used as the gasification agents. The composition of the exhaust gases from both reactors was studied. Fig. 3 shows the gas concentrations (on a dry basis) measured as a function of the operating time (Experimental tests T01–T04), with temperatures in the fuel reactor ranging from 800 to 950 °C.

The same temperature was maintained in both fuel and air reactors. This condition is feasible in a real system because the global processes occurring in each reactor are exothermic with Cu-based materials [33]. Thus, the oxidation reactions (R4) and (R5) in the air reactor were exothermic. Also, the reactions in the fuel reactor, considering the complete path of solid fuel combustion, i.e. the release of O_2 by the oxygen carrier and burn of the fuel, are globally exothermic.

As shown in Fig. 3, as the temperature of the fuel reactor increases, there is a corresponding increase in the concentration of CO_2 in the gas stream exiting the reactor. When the fuel reactor temperature exceeded 900 °C, an observable presence of O_2 occurred, owing to the CLOU effect. In addition, tar was not detected in any experiment. The accuracy of the oxygen and carbon mass balances was confirmed by comparing the measurements obtained from the analysers in the air and fuel reactors. Thus, carbon balance was close to 96% − 99%, which suggests carbon accounted as elutriated char was of low relevance.

A steady state was quickly achieved, showing good agreement between the oxygen that reacted in the fuel and air reactors (see Eq. (6). During tests T01 − T04, the air ratio was constant at $\lambda = 1.23$. Under these conditions, the oxygen concentration in the air reactor was lower than expected, owing to the dilution of nitrogen in the total airflow entering the reactor. In addition, some CO_2 was detected in the air reactor due to the combustion of the bypassed char with the OC stream.

3.1. Combustion efficiency

In all cases, high combustion efficiencies were achieved. This observation emphasises the significance of the oxygen uncoupling capability of the Cu30MnFekao7.5 oxygen carrier in the combustion performance of swine manure, characterised by a high volatile matter content (Table 2). Otherwise, incomplete combustion is expected with regular oxygen carrier materials without oxygen-uncoupling capabilities [12,13].

The increase in temperature in the fuel reactor slightly improved the combustion efficiency (see Fig. 4). Analogous behaviour with

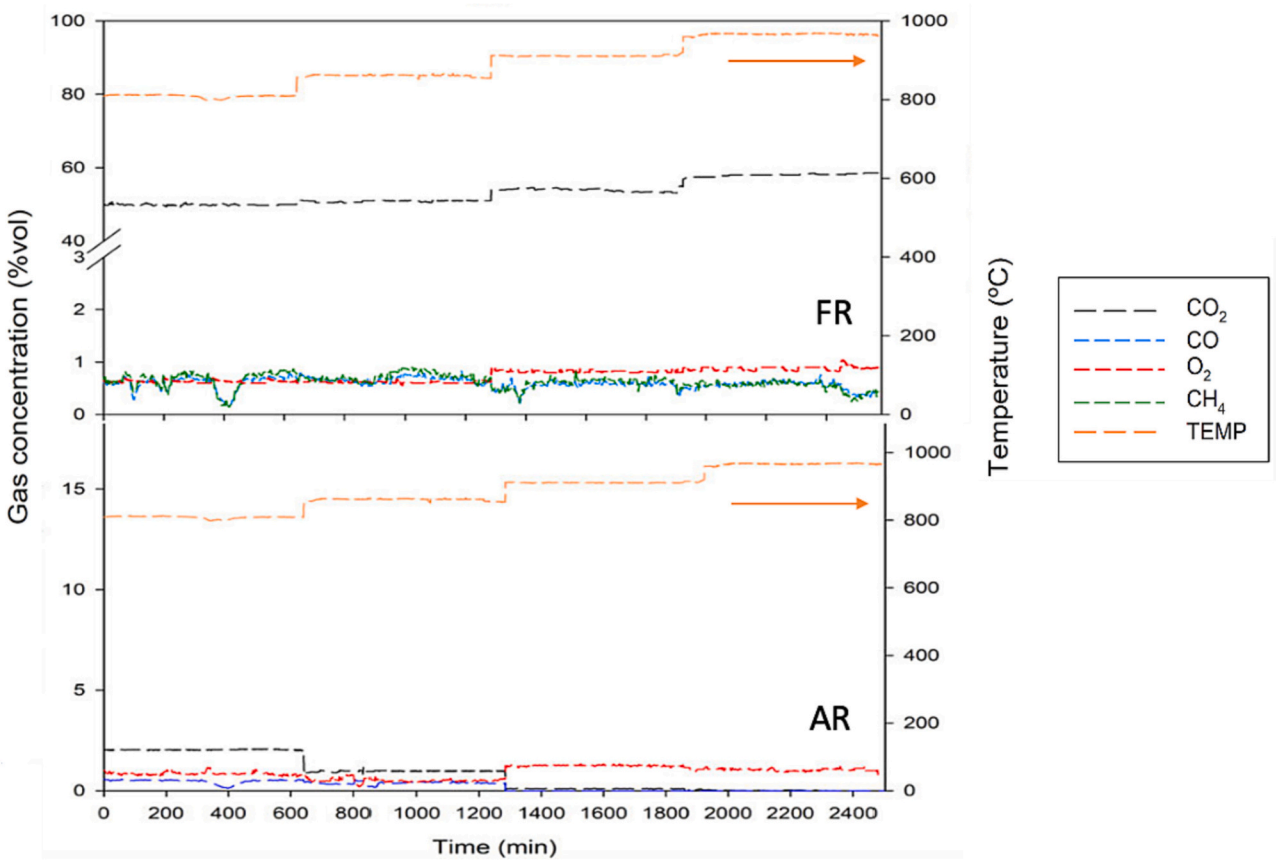


Fig. 3. Gas composition profile in the fuel and air reactors as temperature in the CLOU unit was increased. Experimental tests T01–T04.

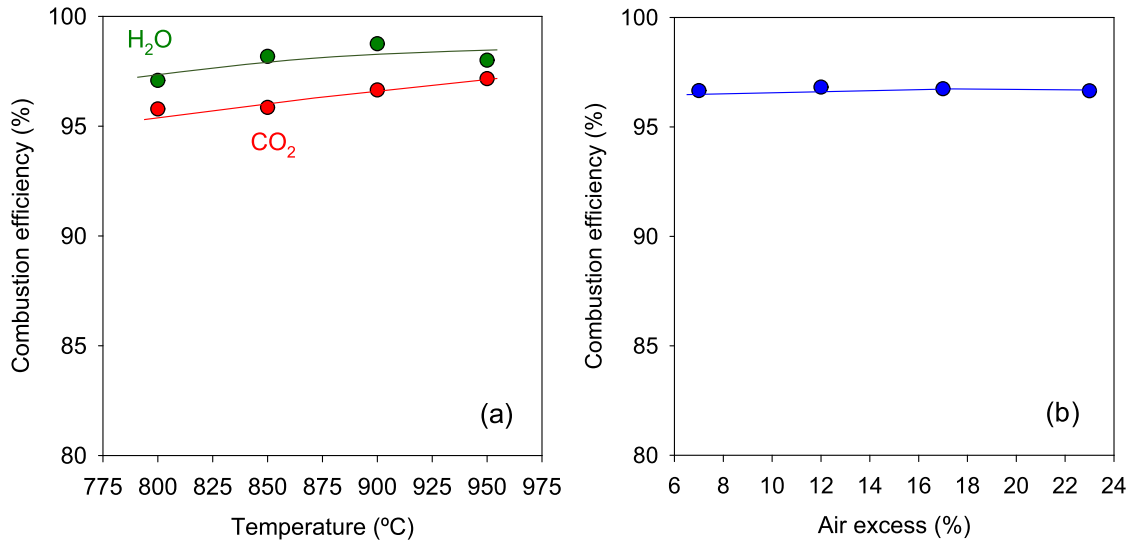


Fig. 4. Combustion efficiency as a function of (a) fuel reactor temperature with CO_2 or steam as fluidizing agents and (b) excess of air in the air reactor at 900 °C and CO_2 as the fluidizing agent.

temperature was observed when H_2O or CO_2 was used as the fluidising agent. Notably, both the oxygen uncoupling kinetics and oxygen concentration at equilibrium increase with temperature [34], which increases the availability of molecular O_2 in the fuel reactor for swine manure combustion. In these tests in CLOU mode, it was impossible to determine the relevance of gas combustion with O_2 from oxygen uncoupling compared to the conventional gas-solid reaction with lattice oxygen in the oxygen carrier. However, oxygen uncoupling may play a relevant role because combustion with gaseous oxygen becomes more relevant as the oxygen uncoupling capability of the metal oxide increases [35]. For example, the oxygen uncoupling capability may increase in the order $(Mn_xFe_{1-x})_2O_3 < CuMn_2O_4 < CuO$ or the fuel reactor temperature may increase [12].

Generally, the combustion efficiency was slightly higher when H_2O was used as the fluidising gas instead of CO_2. The char gasification —reactions (R6) and (R7)— promotes the formation of H_2 or CO in the case of using H_2O or CO_2, respectively. This process may improve the combustion efficiency with H_2O because H_2 is more reactive than CO. This result is explained by evaluating the exhaust gases of the fuel reactor, where CO was the primary unconverted product at lower combustion efficiency values along with carbon dioxide. This result also suggests that CO reacts more slowly than H_2, which also appears as a product of steam gasification but in lower amounts. Furthermore, the CO formed with H_2O can be transformed into H_2 in the presence of steam through the water-gas shift equilibrium (WGS) reaction (R8); thus, the utilisation of steam in the experiments exhibited a higher combustion efficiency compared to experiments employing CO_2 [36].

$$C + H_2O \rightarrow H_2 + CO \quad \text{(R6)}$$

$$C + CO_2 \rightarrow 2\,CO \quad \text{(R7)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(R8)}$$

In addition, the effect of excess air on the combustion efficiency was evaluated. These tests were performed to investigate the influence of the regeneration capability of the oxygen carrier on oxygen transfer in the fuel reactor. The results shown in Fig. 4(b) suggest that the

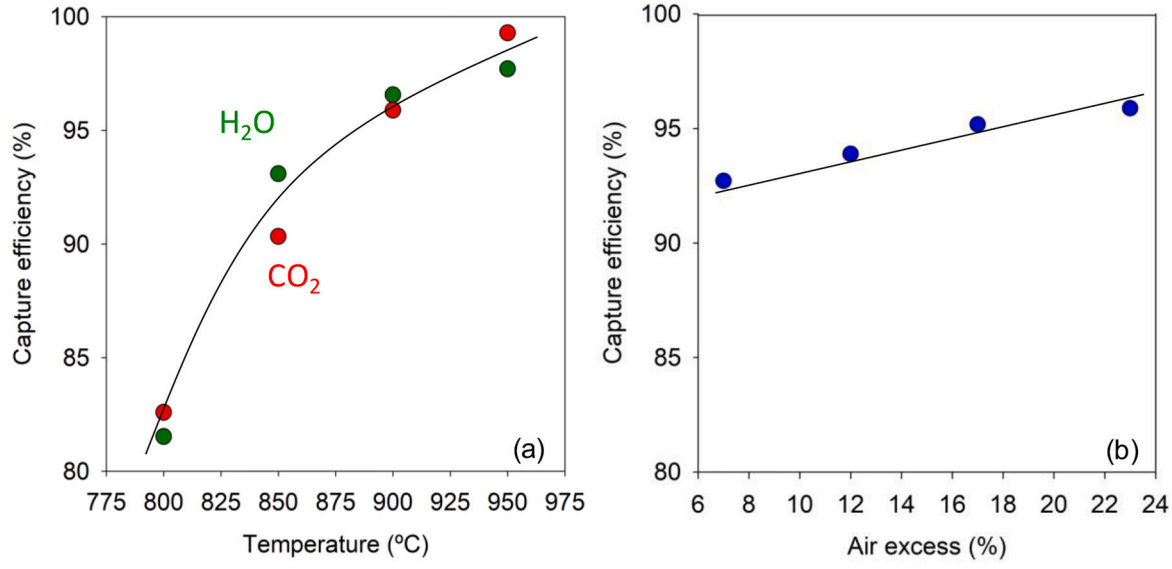


Fig. 5. CO_2 capture efficiency as a function of (a) fuel reactor temperature with CO_2 or steam as fluidizing agent; and (b) excess of air in the air reactor at 900 °C with CO_2 being the fluidizing agent.

Cu30MnFekao7.5 oxygen carrier can be easily regenerated, even when a small amount of excess air is used.

3.2. CO_2 capture efficiency

Fig. 5 shows the effects of temperature, gasification agent, and excess oxygen on the CO_2 capture efficiency. The CO_2 capture efficiencies were similar when using water vapour or CO_2. This result suggests that char combustion with the evolved O_2 (reaction (R3)) is more relevant than the char gasification process. Thus, although steam is usually a more reactive gas than CO_2 in the gasification reaction, it is hardly relevant to the CLOU. For example, Zheng et al. [36] found that <3% and 18% of the char conversion in CLOU originated from CO_2- and H_2O-char gasification, respectively. Hence, CO_2 capture was barely affected by H_2O or CO_2 as fluidising agents in the fuel reactor.

The CO_2 capture efficiency improved with increasing of the fuel reactor temperature, which reached values as high as 99% at 950 °C. Because the oxygen uncoupling capability of the oxygen carrier is favoured at high temperatures, as is the gasification of char, an increase in temperature enhances the CO_2 capture efficiency. Thus, as the temperature in the fuel reactor increased, there was a corresponding increase in the char conversion rate, eventually increasing the CO_2 capture efficiency.

The effect of the increase in excess air was not significant, but the CO_2 capture efficiency also improved with this parameter (Fig. 5 (b)). In this case, it can be deduced that the regeneration of the oxygen carrier improves with excess air. This result implies that the oxygen uncoupling capability of the recirculated oxygen carrier increases as excess air increases. The higher oxygen uncoupling capability affected the char combustion with the released O_2 as the CO_2 capture improved; however, it did not affect the combustion efficiency (Fig. 4 (b)). Therefore, the higher O_2 release as the excess air increased led to a higher combustion of char instead of a higher conversion of volatile matter.

3.3. Fate of N-fuel

With respect to the emission of nitrogenous compounds, a major conversion of the N present in the swine manure to innocuous N_2 was observed in the fuel reactor. Minor amounts of NO, NO_2, N_2O, and NH_3 were detected (Figs. 6 and 7). No NOx was detected in the gas stream of the air reactor. This result implies that the N-fuel in the swine manure was emitted fully in the fuel reactor, which is considerably different from the N in other fuels, such as coal or biomass [12]. Notably, the N in the compounds from the fuel reactor only came from the fuel because argon was used in the loop seal and screw feeder, and the reactor was fluidised either by H_2O or CO_2. Thus, any other sources of N_2 in the gases fed into the system were avoided to evaluate the nitrogen chemistry in the fuel reactor properly.

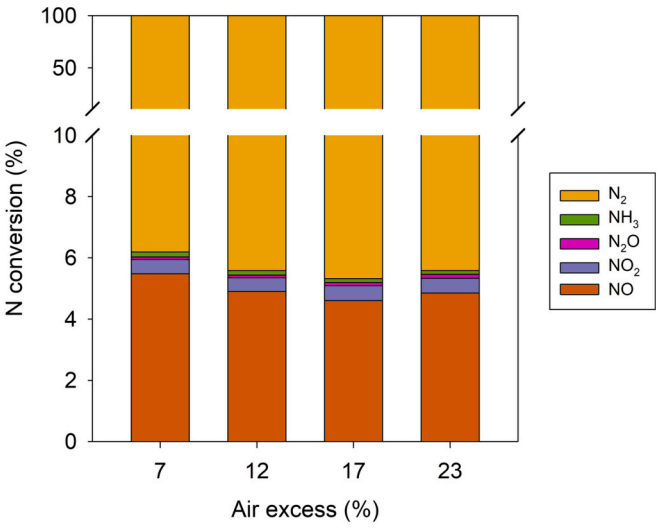


Fig. 7. Distribution of nitrogenous compounds at fuel reactor outlet as a function of the air excess with CO_2 being the fluidizing agent at 900 °C.

During the devolatilisation process, the nitrogen in swine manure can be liberated as ammonia (NH_3) or hydrogen cyanide (HCN). These nitrogenized species can evolve into N_2, NO, NO_2, or N_2O based on the specific combustion conditions. The formation mechanism of fuel-NO arises from the reaction of the nitrogen present in the fuel, either through volatile-N or char-N. Liberated N, along with the volatiles, undergoes decomposition into cyanide and amine species that might react to produce N_2 or NO. The overall distribution of NO and N_2 is influenced by various factors, such as the nitrogen content of the fuel, volatility of the compounds involved, and stoichiometry [37–39]. Usually, the selectivity for N_2 or NO mainly depends on the temperature and gas composition [39,40].

However, the N chemistry in CLOU may differ from that in combustion with air, as nitrogen is not present in the combustion gases, and

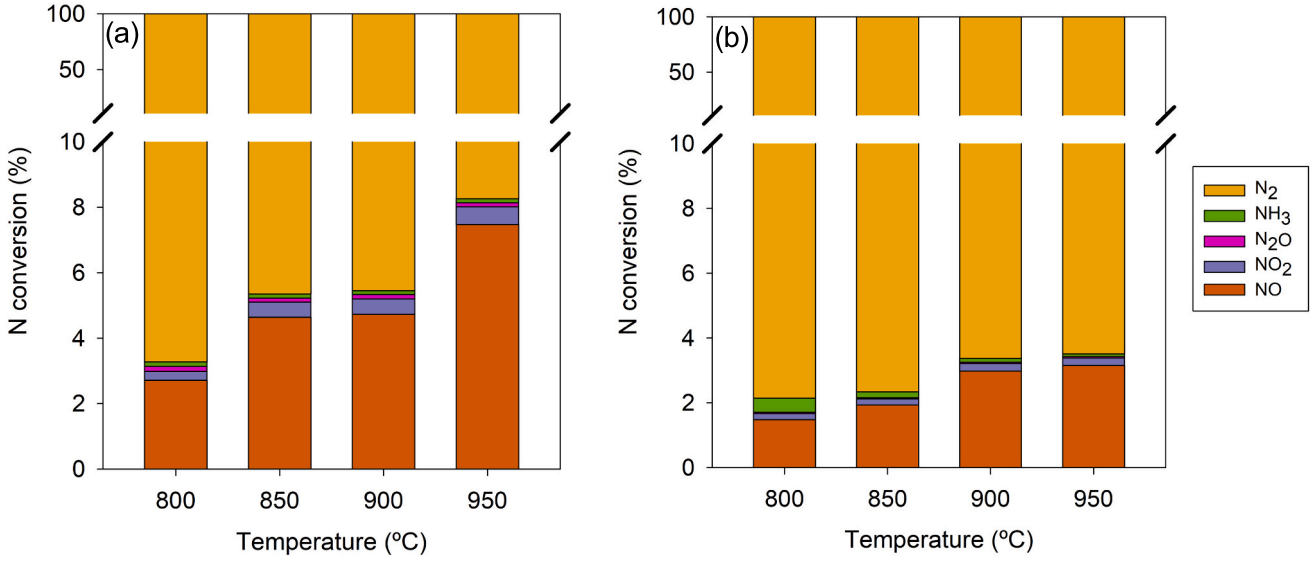


Fig. 6. Distribution of nitrogenous compounds of fuel reactor outlet with (a) CO_2 as a fluidizing agent and (b) H_2O as a fluidizing agent.

the formation of N_2 may be thermodynamically favoured. Thus, the typical stages of the de-NOx process begin with the decomposition of NH_3 through reactions with radicals, resulting in the formation of NH_2, which can undergo NO generation via oxidation or react with NO to form N_2. The oxygen level can restrict the oxidation of NH_2 and limit NO formation, and the NO produced in the initial stages of pyrolysis can react with NH_2 to form N_2 and H_2O [40].

For all different experimental conditions used in this study under CLOU conditions, the priority conversion to nitrogenous specimens was $N_2 > > NO > NO_2 > NH_3 > N_2O$. Fig. 6 shows that ~97% of the nitrogen in the swine manure was converted to N_2 at 800 °C, but it decreased to 93% at 950 °C. By contrast, an increase in temperature improved the NO conversion regardless of the fluidizing agent.

A small fraction (between 0.1% and 0.5%) of the total nitrogen in the swine manure remained as unburnt NH_3 at the outlet of the fuel reactor, which decreased with increasing the operating temperature. Interestingly, the smallest fraction of remaining NH_3 was obtained when the gasifying agent was CO_2, which also showed an increasing tendency for NO_2 formation with increasing temperature. Minor amounts of N_2O were detected, and the effect of the experimental conditions on the yields of these compounds was low.

Furthermore, increasing the percentage of excess air to 23% did not significantly affect the yield of NO over N_2 or to the other N compounds (see Fig. 7). This result agrees with the low relevance of the greater oxidising environment in the fuel reactor on the combustion efficiency, as the excess air in the air reactor was increased (see Fig. 4 (b)).

Nevertheless, contrary to expectation, a higher fraction of NO and NH_3 was observed at the lowest air excess of 7%. This effect may be related to the existence of an onset temperature for the joint reduction of NO and NH_3, which is ~900 °C [41]. The onset temperature increases as the oxygen concentration decreases. Thus, the onset temperature may be higher than the reaction temperature (900 °C) for the lower air excess of 7%, which would slightly increase both in NO and NH_3. In any case, this effect is minimally significant and is less relevant than the oxygen concentration, which is highly affected by the reaction temperature (see Fig. 6).

All N-compounds are emitted to the atmosphere during the CLOU process because they are found in the captured CO_2 current. However, the presence of the N component in the CO_2 stream is significant in terms of the quality of CO_2 to be transported and stored in sources such as geological storage, ocean storage, and mineral carbonation. Commercial guidelines establish specific CO_2 values for each case of transport by pipe, whereas for the N_2, the recommendation is <4% vol. [42].

The concentration of NO_x ($NO + NO_2$) at the output of the fuel reactor showed values of 1045–5030 ppm, above those established by commercial guidelines, which recommend that NO_x levels in CO_2 should be limited to 100 ppm from a health and safety perspective [42]. This CO_2 stream can be applied for other purposes, such as direct use or technological, biological, and chemical uses; however, a complementary treatment process must be employed.

4. Conclusions

This study used a Cu30MnFekao7.5 oxygen carrier in a CLOU pilot plant at the 0.5 kW_{th} scale using swine manure as fuel. Experiments were conducted by changing the fuel reactor temperature, type of gasification agent (CO_2 or steam), and excess air in the air reactor to evaluate the combustion efficiency, CO_2 capture, and distribution of nitrogen compounds. Consequently, after over 30 h of continuous operation, high CO_2 capture and combustion efficiencies were obtained. CO_2 capture was as high as 99% at 950 °C, whereas the combustion efficiency was ~97%. Excess air in the air reactor improved the CO_2 capture, but no relevant effect was observed on the combustion efficiency.

The nitrogen contained in the fuel is primarily converted to innocuous N_2. NO and NO_2 were also found in relevant amounts, with the same trend observed with respect to the temperature. At the highest temperature with H_2O as a gasifying agent, the NO yield was ~3%, but a minor amount of NH_3 was found (0.1%).

In general, based on the results obtained in this work, it can be concluded that the CLOU technology can be a good alternative for the energy valorization of the swine manure, obtaining high combustion and CO_2 capture efficiencies with a major conversion of N to inert N_2. For this reason, CLOU technology can contribute to the reduction of greenhouse emissions and polluting gases in the atmosphere from swine manure.

CRediT authorship contribution statement

Yldeney Domingos: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Alberto Abad:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Margarita de las Obras Loscertales:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization. **María T. Izquierdo:** Resources, Methodology, Investigation, Conceptualization. **Pilar Gayán:** Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Iñaki Adánez-Rubio:** Validation, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was supported by project SWINELOOP, grant PID2019-106441RB-I00 founded by MCIN/AEI/10.13039/501100011033 and the grant 2023AEP041 founded by CSIC. Authors thanks Sumitomo Seika Europe for providing agglomerant for oxygen carrier granulation. Y. Domingos thanks for the grant PRE-092769 Pre-Doctoral fellowship, founded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in your future". Adánez-Rubio acknowledges the "Juan de la Cierva" programme (Grant IJC2019-038987-I funded by MCIN/AEI/10.13039/501100011033).

References

[1] United States of Environmental of Protection Agency – EPA 430-R-22-003, Inventory of U.S. Greenhouse Gas Emission and Sink 1990–2020. https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2020, 2023.
[2] Ministry of Agriculture, Fisheries and Food, Main Economic Indicators: The Pork Sector in Figures 2020. https://cpage.mpr.gob.es/producto/el-sector-de-la-carne-de-cerdo-en-cifras-principales-indicadores-economicos-4/, 2023.
[3] Ministry of the Environment and Rural and Marine Environment, Characterization of manure management systems: Intensive Swine Sector; 2010. https://www.mapa.gob.es/es/ganaderia/publicaciones/, 2023.
[4] R.K. Srivastava, N.P. Shetti, K.R. Reddy, M.N. Nadagouda, M. Badawi, A. Bonilla-Petriciolet, T.M. Aminabhavi, Valorization of biowastes for clean energy production, environmental depollution and soil fertility, J. Environ. Manag. 332 (2023) 117410.
[5] N. Banerjee, Biomass to energy — an analysis of current technologies, prospects, and challenges, Bioenergy Res. 16 (2023) 683–716.

[6] M. Fernandez-Lopez, M. Puig-Gamero, D. Lopez-Gonzalez, A. Avalos-Ramirez, J. Valverde, L. Sanchez-Silva, Life cycle assessment of swine and dairy manure: pyrolysis and combustion processes, Bioresour. Technol. 182 (2015) 184–192.
[7] S. Xiu, A. Shahbazi, V. Shirley, D. Cheng, Hydrothermal pyrolysis of swine manure to bio-oil: effects of operating parameters on products yield and characterization of bio-oil, J. Anal. Appl. Pyrolysis 88 (2010) 73–79.
[8] L. Da Lio, P. Castello, G. Gianfelice, R. Cavalli, P. Canu, Effective energy exploitation from horse manure combustion, Waste Manag. 128 (2021) 243–250.
[9] J. Lundgren, E. Pettersson, Combustion of horse manure for heat production, Bioresour. Technol. 100 (2009) 3121–3126.
[10] T. Turzyński, J. Kluska, D. Kardaś, Study on chicken manure combustion and heat production in terms of thermal self-sufficiency of a poultry farm, Renew. Energy 191 (2022) 84–91.
[11] C. Jiang, Q. Lin, C. Wang, X. Jiang, H. Bi, L. Bao, Experimental study of the ignition and combustion characteristics of cattle manure under different environmental conditions, Energy. 197 (2020) 117143.
[12] J. Adánez, A. Abad, T. Mendiara, P. Gayán, L.F. de Diego, F. García-Labiano, Chemical looping combustion of solid fuels, Prog. Energy Combust. Sci. 65 (2018) 6–66.
[13] T. Mendiara, F. García-Labiano, A. Abad, P. Gayán, L.F. de Diego, M.T. Izquierdo, J. Adánez, Negative CO_2 emissions through the use of biofuels in chemical looping technology: a review, Appl. Energy 232 (2018) 657–684.
[14] T. Mattisson, A. Lyngfelt, H. Leion, Chemical-looping with oxygen uncoupling for combustion of solid fuels, Int. J. Greenhouse Gas Control 3 (2009) 11–19.
[15] M. Rydén, H. Leion, T. Mattisson, A. Lyngfelt, Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling, Appl. Energy 113 (2014) 1924–1932.
[16] I. Adánez-Rubio, A. Pérez-Astray, A. Abad, P. Gayán, L.F. De Diego, J. Adánez, Chemical looping with oxygen uncoupling: an advanced biomass combustion technology to avoid CO_2 emissions, Mitig. Adapt. Strateg. Glob. Chang. 24 (2019) 1293–1306.
[17] A. Pérez-Astray, T. Mendiara, L.F. de Diego, A. Abad, F. García-Labiano, M. T. Izquierdo, J. Adánez, Behavior of a manganese-iron mixed oxide doped with titanium in reducing the oxygen demand for CLC of biomass, Fuel 292 (2021) 120381.
[18] M. Rydén, A. Lyngfelt, T. Mattisson, $CaMn_{0.875}Ti_{0.125}O_3$ as oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU)—experiments in a continuously operating fluidized-bed reactor system, Int. J. Greenhouse Gas Control 5 (2011) 356–366.
[19] A. Pérez-Astray, I. Adánez-Rubio, T. Mendiara, M.T. Izquierdo, A. Abad, P. Gayán, F. García-Labiano, L.F. de Diego, J. Adánez, Comparative study of fuel-N and tar evolution in chemical looping combustion of biomass under both iG-CLC and CLOU modes, Fuel 236 (2019) 598–607.
[20] T. Song, W. Guo, L. Shen, Fuel nitrogen conversion in chemical looping with oxygen uncoupling of coal with a CuO-based oxygen carrier, Energy Fuel 29 (6) (2015) 3820–3832.
[21] P. Glarborg, A.D. Jensen, J.E. Johnsson, Fuel nitrogen conversion in solid fuel fired systems, Prog. Energy Combust. Sci. 29 (2003) 89–113.
[22] S. Mayrhuber, F. Normann, D. Yilmaz, H. Leion, Effect of the oxygen carrier ilmenite on NO_X formation in chemical-looping combustion, Fuel Process. Technol. 222 (2021) 106962.
[23] A. Lyngfelt, A. Hedayati, E. Augustsson, Fate of NO and Ammonia in chemical looping combustion—investigation in a 300W chemical looping combustion reactor system, Energy Fuel 36 (2022) 9628–9647.
[24] J. Ma, X. Tian, H. Zhao, J. Ma, C. Zheng, Effect of coal ash on the performance of $CuO@TiO_2$-Al_2O_3 in chemical looping with oxygen uncoupling, Fuel Process. Technol. 221 (2021) 106935.
[25] A. Abad, R. Pérez-Vega, M.T. Izquierdo, P. Gayán, F. García-Labiano, L.F. de Diego, J. Adánez, Novel magnetic manganese-iron materials for separation of solids used in high-temperature processes: application to oxygen carriers for chemical looping combustion, Fuel 320 (2022) 123901.
[26] I. Adánez-Rubio, H. Bautista, M.T. Izquierdo, P. Gayán, A. Abad, J. Adánez, Development of a magnetic cu-based oxygen carrier for the chemical looping with oxygen uncoupling (CLOU) process, Fuel Process. Technol. 218 (2021) 106836.
[27] J. Adánez, L. Diego, F. García-Labiano, P. Gayán, A. Abad, M. Abian, M. T. Izquierdo, R. Pérez-Vega, Magnetic system and support as O_2 and CO_2 transporters, Spain Patente (2019). PCT/ES19/070122.
[28] I. Adánez-Rubio, I. Samprón, M.T. Izquierdo, A. Abad, P. Gayán, J. Adánez, Coal and biomass combustion with CO_2 capture by CLOU process using a magnetic Fe-Mn-supported CuO oxygen carrier, Fuel 314 (2022) 122742.
[29] A. Filsouf, I. Adánez-Rubio, T. Mendiara, A. Abad, J. Adánez, Developing magnetic, durable, agglomeration resistant and reactive copper-based oxygen carrier particles by promoting a kaolin-reinforced, manganese-iron mixed oxide support, Fuel Process. Technol. 241 (2023) 107616.
[30] P. Simell, P. Ståhlberg, E. Kurkela, J. Albrecht, S. Deutsch, K. Sjöström, Provisional protocol for the sampling and analysis of tar and particulates in the gas from large-scale biomass gasifiers. Version 1998, Biomass Bioenergy 18 (2000) 19–38.
[31] R. Pérez-Vega, A. Abad, P. Gayán, F. García-Labiano, M.T. Izquierdo, L.F. de Diego, J. Adánez, Coal combustion via chemical looping assisted by oxygen uncoupling with a manganese-iron mixed oxide doped with titanium, Fuel Process. Technol. 197 (2020) 106184.
[32] I. Adánez-Rubio, A. Pérez-Astray, T. Mendiara, M.T. Izquierdo, A. Abad, P. Gayán, et al., Chemical looping combustion of biomass: CLOU experiments with a Cu-Mn mixed oxide, Fuel Process. Technol. 172 (2018) 179–186.
[33] A. Abad, J. Adánez, F. García-Labiano, L.F. de Diego, P. Gayán, J. Celaya, Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion, Chem. Eng. Sci. 62 (2007) 533–549.
[34] I. Adánez-Rubio, P. Gayán, A. Abad, F. García-Labiano, L.F. de Diego, J. Adánez, Kinetic analysis of a Cu-based oxygen carrier: relevance of temperature and oxygen partial pressure on reduction and oxidation reactions rates in chemical looping with oxygen uncoupling (CLOU), Chem. Eng. J. 256 (2014) 69–84.
[35] A. Abad, P. Gayán, L.F. de Diego, F. García-Labiano, J. Adánez, Modelling chemical-looping assisted by oxygen uncoupling (CLaOU): assessment of natural gas combustion with calcium manganite as oxygen carrier, Proc. Combust. Inst. 37 (2019) 4361–4369.
[36] C. Zheng, M. Su, H. Zhao, Identifying the contribution of rich-CO_2/H_2O gasification on the char conversion in typical atmospheres of chemical looping with oxygen uncoupling via single particle simulation, Combust. Flame 229 (2021) 111397.
[37] K. Svoboda, D. Baxter, J. Martinec, Nitrous oxide emissions from waste incineration, ChemInform 60 (2006) 78–90.
[38] M.B. Toftegaard, J. Brix, P.A. Jensen, P. Glarborg, A.D. Jensen, Oxy-fuel combustion of solid fuels, Prog. Energy Combust. Sci. 36 (5) (2010) 581–625.
[39] R.F. Pachler, S. Penthor, K. Mayer, H. Hofbauer, Investigation of the fate of nitrogen in chemical looping combustion of gaseous fuels using two different oxygen carriers, Energy. 195 (2020) 116926.
[40] J. Zhou, S.M. Masutani, D.M. Ishimura, S.Q. Turn, C.M. Kinoshita, Release of fuel-bound nitrogen during biomass gasification, Ind. Eng. Chem. Res. 39 (3) (2000) 626–634.
[41] F. Kasuya, P. Glarborg, J.E. Johnsson, K. Dam-Johansen, The thermal De NOx process: influence of partial pressures and temperaturas, Chem. Eng. Sci. 50 (1995) 1455–1466.
[42] E. de Visser, C. Hendriks, M. Barrio, M.J. Mølnvik, G. de Koeijer, S. Liljemark, Y. Le Gallo, Dynamis CO_2 quality recommendations, Int. J. Greenhouse Gas Control. 2 (4) (2008) 478–484.

Yldeney Domingos is a research fellow at the Instituto de Carboquímica (ICB) at the Spanish National Research Council (CSIC) in the Combustion and Gasification research group, and Ph.D. student in Chemical Engineering and Environment at the Universidad de Zaragoza. She has 10 years of experience in the characterization of materials and solid waste, analysis and environmental bioremediation, and monitoring atmospheric emissions and air quality. Currently, she works with advanced and clean combustion, and gasification processes in fluidized bed reactors for energy or hydrogen production with CO_2 capture, focusing on chemical looping technologies with solid waste from livestock.

Alberto Abad is a Senior Researcher at Spanish National Research Council (CSIC). He belongs to the Combustion and Gasification group at Instituto de Carboquimica, where he has developed advanced and clean combustion and gasification processes in fluidized bed reactors to produce energy or hydrogen with CO_2 capture. In the last years, he has had an intense activity in the development of chemical looping technologies, mainly focused on the advance of oxygen carriers, the design and operation of pilot plants, as well as the process modelling and techno-economic assessment. He has published >200 publications in peer review journals.

Margarita de las Obras Loscertales is a postdoctoral researcher in the Combustion and Gasification group belonging to The Spanish National Research Council (CSIC). She has a comprehensive experience in the development of CO_2 capture technologies based on fluidized bed reactors for energy and hydrogen production. In the last few years, she has focused on developing chemical looping combustion technologies with negative CO_2 emissions by performing the characterization of different oxygen carriers and conducting experimental campaigns in pilot plants using biomass as fuel. So far, she is coauthor of 28 publications in scientific research journals.

María T. Izquierdo is senior researcher at Instituto de Carboquímica Spanish National Research Council, CSIC). Her research lines focused on the development of materials linked to environmental challenges in energy production, with long experience in the development tail-end technologies and currently with CO_2 capture technologies based on Chemical Looping processes, mainly focused on the development of oxygen carriers.

Pilar Gayán is a chemical engineering researcher working in the Institute of Carboquimica (CSIC) in Zaragoza, Spain. Her research lines focused on the development of advanced energy generation processes, both combustion and gasification processes in fluidized beds, as well as in the area of CO_2 capture, by the Chemical Looping Combustion (CLC) processes, both from the point of view of development of suitable materials to the process and the technology demonstration at pilot plant scale. She is author of >170 JCR publications.

Iñaki Adánez-Rubio is a Post-doctoral Researcher at Spanish National Research Council (CSIC). He belongs to the Combustion and Gasification group at Instituto de Carboquimica, where he has developed chemical looping technologies, an advanced and clean combustion and reforming processes in fluidized bed reactors to produce energy or hydrogen with CO_2 capture. In the last years, he has focused on Chemical Looping with Oxygen Uncoupling process in the developing of oxygen carriers and in the operation of pilot plants. He has published 36 publications in peer review journals.