

Chemical Looping Gasification for Sustainable Production of Biofuels

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Abstract

The objective of this investigation was to demonstrate the feasibility of the Chemical Looping Gasification of wheat straw pellets under realistic conditions in small pilot plants. Hence, the effect of different operational variables such as the fuel reactor temperature, the mean residence time of solids in the fuel reactor, the oxygen-to-biomass ratio the gas velocity and fluidizing gas in the carbon stripper, on the process performance, the syngas yield and the tar generation were investigated in (a) a 100 kW CLG unit at Chalmers, and (b) a 50 kW_{th} BCLG unit at CSIC. In addition, the agglomeration behavior of ilmenite when wheat straw pellets with additives were used as feedstock as well as the interaction between straw ashes and ilmenite during the process were investigated.

The use of ilmenite as oxygen carrier for the CLG process was analyzed for 60 h using wheat straw pellets with additives as fuel in a 50 kW_{th} unit. Using ilmenite as oxygen carrier, it was possible to obtain non-diluted nitrogen syngas with high values of CO_2 capture.

No agglomerations were found; neither in the 100 kW unit after 20 h of operation, nor in the 50 kW_{th} unit after 60 h of continuous Chemical Looping Gasification of the wheat straw pellets with additives developed in WP2. Migration of Fe towards the external surface of the ilmenite was found and K present in the straw was retained in the bed particles and into the attrited fines recovered by the cyclones.

Temperature showed a major impact on the char conversion of the fuel reactor, $X_{char,FR}$, as an increase in temperature increased the reaction rates of all the reactions occurring in the gasification reactor. An increase in the mean residence time of solids also led to increased char conversion values, underlining that rection extents in the FR are kinetically limited.

Char conversion in the fuel reactor was not enhanced by the presence of the carbon stripper when pellets are used. The carbon stripper was not capable of separating the unconverted char entrained from the fuel reactor, because it still retains its initial pellet form. Increasing the gas flow rate improved the biomass conversion in the unit, X_b , while the carbon conversion efficiency in the CLG unit, η_{CC} , was reduced because the char by-pass to the air reactor was promoted.

The oxygen-to-biomass ratio, λ , was the most relevant operating variable affecting syngas production. For a better control of the process, the concepts of $\lambda_{eff,FR}$ and $\lambda_{eff,AR}$, that consider the effective oxygen transferred in the fuel and air reactors were introduced. These parameters allows the determination of the amount of oxygen reacting with the oxygen carrier in both the fuel and air reactors at each moment, and so to determine when the steady state has been reached under a given operating condition ($\Phi = \lambda_{eff,FR} / \lambda_{eff,AR} = 1$).

An increase in the oxygen-to-biomass ratio λ caused a decrease in the syngas yield and the cold gas efficiency as more syngas was consumed in combustion, as more lattice oxygen reacted in the fuel reactor. In contrast, the variation of λ had low impact on the production of CH₄ and light hydrocarbons.

As summary, to improve the syngas yield in CLG for wheat straw pellets it is necessary to use long residence times in the fuel reactor, high temperatures and use the lowest λ necessary to reach auto-thermal conditions.

1 Introduction

The CLARA project addresses the production of liquid diesel- and gasoline-like biofuels utilizing biogenic residues from the agriculture (e.g. straw) and forestry sectors through gasification followed by Fischer Tropsch (FT) synthesis. The main innovative aspect of this project is the application of chemical looping gasification (CLG) for syngas generation. CLG represents an innovative process that allows the generation of non-nitrogen diluted synthesis gas under autothermal conditions and with low tars content. In CLG, a solid oxygen carrier circulates between two reactors and provides the oxygen for partial oxidation of the feedstock to yield a concentrated syngas. In the fuel reactor, biomass is first devolatilized and the gasified by steam/CO₂. The oxygen carrier (Me_yO_x) can react with the intermediate gaseous species to form syngas and is reduced to a metal oxide of lower oxygen content, i.e. (Me_yO_{x-1}) in the process. In the air reactor, the oxygen carrier is re-oxidized by air.

For the current project, an oxygen carrier material at multi-ton scale will be needed for demonstration of the CLG technology at 1 MW scale at TUDA, using selected fuels such as pine forest residue and pre-treated wheat straw. An important issue for CLG is the selection of an appropriate oxygen carrier that fulfils several requirements, e.g. high reactivity towards hydrocarbons to yield CO and H₂, high mechanical strength, low agglomeration tendency, and low cost. In addition, these materials should be environmentally benign. Preferably, the oxygen carrier should also interact reversibly with important impurities, such as alkali. In milestone M3.1, ilmenite was selected as oxygen carrier for demonstrating CLG in the 1 MW_{th} unit at TUDA.

The main objective within WP3 was to establish the viability of the Chemical Looping Gasification of biomass using as fuels wheat straw pellets with additives and pine forest residue pellets. The partners involved in WP3, CTH and CSIC, have vast experience in Chemical Looping Gasification of biomass in small continuous units (1.5 and 10 kW_{th}). This deliverable brings together the investigation carried out in a 50 kW unit located at CSIC, regarding the behavior and performance of ilmenite when using pre-treated wheat straw pellets developed inside the project and supplied by CENER. Wheat straw pellets with additives were developed inside WP2 to avoid agglomeration inside de Chemical Looping Gasification units.

Unlike previous studies, effective oxygen-to-biomass ratios were defined to consider the proper amount of oxygen that reacts with the oxygen carrier both in the fuel and air reactors, $\lambda_{eff,FR}$ and $\lambda_{eff,AR}$, respectively.

This work aimed to investigate the effect of different operational variables such as the fuel reactor temperature, the mean residence time of solids in the fuel reactor, the oxygen-tobiomass ratio (controlled by the oxygen fed into the air reactor), as well asthe gas velocity and fluidizing gas in the carbon stripper, on the process performance, the syngas yield, and the tar generation. In addition, other aspects of the process were also investigated such as the agglomeration behavior of ilmenite when wheat straw pellets with additives were used, the interaction between straw ashes and ilmenite, the evolution of the ilmenite reactivity along the process and the lifetime of the oxygen carrier under highly reduced conditions.

1.1 Partners

The work was carried out by two world leading research groups in chemical-looping technologies, the Chalmers research group at Energy technology, and Consejo Superior de Investigaciones Científicas CSIC. The Chalmers group has worked with development of oxygen-carrier material for such processes since 1998 and was the first to successfully demonstrate the process in sustained operation, which was achieved 2003 in a 10 kW prototype unit for gaseous fuel. Chalmers was also first to demonstrate chemical-looping combustion of

solid fuels in another 10 kW prototype in 2006. Chalmers currently has four chemical-looping reactor units for gaseous/solid/liquid (G/S/L) fuels: 300 W (G/L), 10 kW (G/L), 10 kW (S) and 100 kW (S), that have totally been in operation with fuel for > 3500 h, using > 50 different oxygen carrier materials. Instituto de Carboquímica (ICB) (www.icb.csic.es) is a part of Consejo Superior de Investigaciones Científicas (CSIC), which is the largest public institution dedicated to research in Spain and the third largest in Europe. The group has a long expertise in gas-solid reaction kinetics and modelling applied to fluidized bed combustion and gasification processes as well as on Chemical Looping processes. Since 2000 the group has worked in the development, testing and characterization of oxygen carriers. ICB-CSIC currently has five Chemical-looping units for gaseous/solid/liquid fuels (G/S/L): 500 W (G), 10 kW(G), 900 W(L), 500 W(S), 50 kW (S) that have been totally in operation with fuel for > 1500h using > 15 oxygen carriers.

2 Experimental

2.1 Materials

The ilmenite used in this study was a concentrate from a Norwegian natural ore from Titania AS [Leion et al, 2008]. It was received in its reduced form, FeTiO₃, and it was crushed and sieved to obtain a sand-type material with particle size of $+100-300 \mu m$ (80% $<300 \mu m$). Figure 1 shows the particle size distribution of the fresh material used. Before its use in the continuous unit at CSIC, fresh ilmenite particles were pre-oxidized to pseudobrookite (Fe₂TiO₅) in air at 950 °C during 24 hours to improve the physical properties and initial reaction rates [Adánez et al., 2010; Cuadrat et al., 2012] and to avoid defluidization problems [Proll et al, 2009]. The composition of calcined ilmenite determined by XRD analysis was 54.7 wt% Fe₂TiO₅, 11.2 wt% Fe₂O₃, 28.6 wt% TiO₂ and 5.5 wt% of inert compounds. The oxygen transport capacity for the calcined ilmenite (R_{O,ilm}), was 4.03 wt%. The main properties of calcined ilmenite used in the pilot unit were indicated in Table 1.

Particle size	μm	100-300
True density	kg/m ³	4100
Oxygen transport capacity, R _{O,ilm}	%	4.0
Porosity	%	1.2
Crushing strength	Ν	65.0
XRD (main species)		Fe ₂ TiO ₅ , Fe ₂ O ₃ , TiO ₂

	Table 1.	Physic-chemical	properties of	calcined ilmenite.
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Figure 1 Particle size distribution of the ilmenite.

Pellets of wheat straw biomass with additives supplied by CENER (Pamplona, Spain) (6 mm diameter and 17 mm of mean length, density of 1060 kg/m^3) were used as renewable solid fuel, see Figure 2. Table 2 shows the proximate and ultimate analysis of the biomass and Table 3 shows the chemical composition of the ashes contained in the pellets. At Chalmers, the straw pellets could not readily be fed into the 100 kW unit. To allow feeding, the straw pellets had to be crushed and mixed another fuel, in this case steam-exploded wood of similar size, which previously has been used as fuel in the unit. Table 4 shows the fuels used in the 100 kW unit.

Proximate analysis				
Moisture content	10.3	wt.%; wb		
Ash content	7.0	wt.%; db		
Volatile matter	77.7	wt.%; db		
Fixed carbon ⁽¹⁾	15.3	wt.%; db		
Ultimate analysis				
С	46.1	wt.%; db	49.6	wt.%; daf
Н	5.8	wt.%; db	6.2	wt.%; daf
Ν	0.39	wt.%; db	0.42	wt.%; daf
S	0.105	wt.%; db	0.113	wt.%; daf
Cl	0.100	wt.%; db	0.108	wt.%; daf
Net calorific value				
NCV	17.2	MJ/kg; db	18.5	MJ/kg; daf

Table 2 Proximate and ultimate analysis of Wheat Straw pellets with additives.

Al	mg/kg (w/w)	158
Ca	mg/kg (w/w)	11,500
Fe	mg/kg (w/w)	172
Κ	mg/kg (w/w)	7,330
Mg	mg/kg (w/w)	982
Na	mg/kg (w/w)	186
Р	mg/kg (w/w)	448
Si	mg/kg (w/w)	10,200
Ti	mg/kg (w/w)	10
Al	mg/kg (w/w)	158
Ca	mg/kg (w/w)	11,500
Fe	mg/kg (w/w)	172
Κ	mg/kg (w/w)	7,330
Mg	mg/kg (w/w)	982
Na	mg/kg (w/w)	186

Table 3. Major elemental ash components in Wheat Straw pellets.



Figure 2. Photograph of the Wheat Straw pellets with additives from CENER.

	Table 4. F	uels used in	Chalmers e	experiments,	as-received	basis.
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Name	Abbreviation	Previous names	LHV (MJ/kg)	Size (mm)	Volatiles (%)	C-fraction (%)
Black pellets	BP	Arbapellets	18.6	0.7-3.5	74.2	50
Straw pellets	SP		16.4	0.7-3.5	78	40
Straw 2	SP2	Granngården straw	15.5	0.5-6	75	43

2.2 100 kW CLG unit at Chalmers

The 100 kW system, shown in Figure 3, is designed as to allow operational flexibility. The system includes two interconnected circulating fluidized beds, *i.e.* air reactor (AR) and fuel reactor (FR), as well as a carbon stripper. The circulating fluidized bed in the fuel reactor adds flexibility. Variation of the fluidization regime in the fuel reactor could have consequences on gas-solid contact. Starting in the fuel reactor, the path of solids circulation is outlined below and is numbered from 1 to 28 in Figure 3. Gas and particles entrained in the fuel reactor (FR) enter the cyclone (CY2), fall down the downcomer to a loop seal (LS2) and enter the fuel reactor again. Particles not entrained may instead enter the so-called circulation riser (CR), which is placed in between the carbon stripper (CS1-4) and the loop seal (LS3) connected to the fuel reactor. The circulation riser is designed to return varying mass flows of particles to the air reactor. The carbon stripper has four chambers separated by weirs. The purpose of the carbon stripper is to gasify or separate residual char in the particle flow. The particles in the carbon stripper are passed on to a loop seal (LS4), leading to the air reactor (AR). The air reactor reoxidizes the oxygen carriers before they are transported back to the fuel reactor by passing a cyclone (CY1) and another loop seal (LS1), thus beginning a new cycle. Loop seals separate the air reactor and fuel reactor in order to avoid gas mixing. It is the fuel reactor, with an inner height of 5.0 m, that determines the overall height of the unit. The air reactor temperature is controlled by a mantle cooler, through which ambient air exchanges heat with the hot wall of the air reactor. The cooling jacket is placed around the expanded bottom part of the air reactor.



Figure 3. The Chalmers 100 kW CLC unit: a 2D sketch, drawn to scale (left), and the actual unit with oven enclosure (right).

Solids inventory		kg	140-300
Solids circulation rate		kg/min	1-35
Fuel reactor	Temperature	°Ċ	850-950
	Fluidizing gas		H_2O
	Gas velocity (bottom)	m/s	0.7 - 1
	(riser)	m/s	3 - 5.5
	Solid inventory	kg/MW _{th}	300-900
	Oxygen to fuel ratio, λ		0.1 -0.4
	Steam to biomass ratio, S/B		0.6-2
Carbon stripper	Fluidizing gas		H ₂ O or N ₂
	Gas velocity	m/s	0.2-0.4
Air reactor	Temperature	°C	900 - 1030
	Fluidizing gas		Air
	Gas velocity (bottom)	m/s	0.4 - 0.8
	(riser)	m/s	3.5-7

Table 5. Operating variables used during the experimental tests at Chalmers.

2.3 50 kW Biomass Chemical Looping Gasification unit at CSIC

Figure 4 shows a diagram of the 50 kW_{th} BCLG unit located at ICB-CSIC, consisting of two interconnected fluidized bed reactors, fuel (FR) and air (AR) reactors, with the oxygen carrier circulating between them. The carbon stripper (CS) has the purpose of separating the unconverted char in the fuel reactor from the oxygen carrier particles. Thus, char passing to the air reactor is minimized while char conversion in the fuel reactor is improved. The loop-seals avoid the gas mixing between the reactors. The biomass is fed to the fuel reactor by means of two screw feeders and a cyclone is used to separate the solids and the gas at the outlet of each reactor. More detailed information can be found in the study conducted by Abad et al. [2015].

In addition, the unit includes a system of pressure and temperature sensors distributed throughout the unit. This allows knowing the pressure difference between different locations of the unit, being mainly useful for the quantification of the amount of solids present in each reactor.

The gas composition at the air reactor outlet stream $(CO_2, CO, and O_2)$ was analyzed in an online gas analyzer. The gas composition at the fuel reactor outlet $(CO_2, CO, H_2, and CH_4)$ was also measured on-line after gas cleaning, which consisted of a tar collection system installed according to the European Tar Protocol [Simell et al., 2000]. Moreover, off-line gas analyses were carried out in a gas chromatograph to determine the amount of light hydrocarbons (C1-C3) contained in the gas outlet stream of the fuel reactor.

The solids circulation rate may be controlled by the gas velocity into the air reactor or operating on the double loop-seal (LS-D). The measurement of the circulation rate was made at the outlet of both reactors by means of two solids diverter valves. The oxygen carrier inventory in the facility was kept constant at about 75 kg. Steam was used as fluidizing gas in the fuel reactor and a mixture of nitrogen and air was used in the air reactor. The carbon-stripper and the loop-seals were fluidized with N_2 or steam.

The method of control of the oxygen used for the syngas production was based on controlling the amount of oxygen fed into the air reactor by diluting air with nitrogen. This method has been satisfactorily used in the BCLG units at lower scale, 1.5 kW_{th}, at ICB-CSIC and represents

a clear advantage over other control methods used by other authors in CLG. This control method led to the presence of highly reduced states of the oxygen carrier inside the unit.



Figure 4. Scheme of the 50 kW_{th} BCLG unit at ICB-CSIC.

The fuel reactor is 4.0 m height with 0.1m ID and 0.08 for riser ID. The air reactor is 4.8 m height with 0.3 m ID in the bottom and 0.1 m in the riser. The carbon stripper is 0.7 m height with 0.15 m ID and has a deflector in the middle to avoid the direct shortcut of the solids to the outlet of the loop-seal.

Power		kWth	20
Solids inventory		kg	80
Solids circulation rate		kg/h	50-150
Fuel reactor	Temperature	°C	800-980
	Fluidizing gas		H_2O
	Gas velocity (bottom)	m/s	1.1 - 1.5
	(riser)	m/s	2.6 - 4.0
	Solid inventory	kg/MW _{th}	120 - 520
	Oxygen to fuel ratio, λ		0.13 -0.40
	Steam to biomass ratio, S/B		0.7
Carbon stripper	Fluidizing gas		H ₂ O or N ₂
	Gas velocity	m/s	0.07-0.34
Air reactor	Temperature	°C	820 - 990
	Fluidizing gas		Air/N ₂ mixture
	Gas velocity (bottom)	m/s	0.5 - 0.8
	(riser)	m/s	4.0 - 6.7

Table 6. Operating	variables used	during the	experimental	tests at	CSIC.

The effect of the operating variables as temperature, solid circulation flowrate, fluidizing gas velocity in the bottom and riser of the fuel and air reactors and the fluidizing gas velocity in the carbon stripper together with the solid inventory in the fuel reactor were investigated. In order to know their effect on the process performance parameters, Table 4 shows the range of the operating variables used during the experimental work in the unit.

The operating variables with the greatest impact on the BCLG process performance and syngas production are the gasification temperature and the oxygen-to-biomass ratio, λ , [Condori et al., 2021a, 2021b; Samprón et al., 2021], the latter representing the oxygen fed into the air reactor with respect to the stoichiometric oxygen needed to fully burn the biomass.

$$\lambda = \frac{\text{mol O fed to the AR}}{\text{mol O needed for full combustion of biomass}}$$
(1)

However, the oxygen transferred to the oxygen carrier in the air reactor and to the fuel in the fuel reactor may differ from the oxygen fed in air because some oxygen may react with bypassed char to the air reactor, decreasing the available oxygen to react with the oxygen carrier. Also, the oxygen transferred in the fuel and air reactors may be different during transitory periods prior to the establishment of the steady state. To know the oxygen transferred in the air and fuel reactors at any moment, the effective oxygen-to-biomass ratios in the air, $\lambda_{eff,AR}$, and fuel, $\lambda_{eff,FR}$, reactors were defined. This allows to clearly stablishing the steady state in the overall unit.

$$\lambda_{eff,AR} = \frac{\text{mol O picked up by the oxygen carrier in the AR}}{\text{mol O needed for full combustion of biomass}}$$
(2)

$$\lambda_{eff,FR} = \frac{\text{mol O released by the oxygen carrier in the FR}}{\text{mol O needed for full combustion of biomass}}$$
(3)

The mean residence time of the solid oxygen carrier in the fuel reactor, $t_{m,FR}$, was also a relevant operating variable in the process. This was defined considering the solids circulation rate between the two reactors and the solids inventory in the fuel reactor. The later was calculated from the pressure measurements that were monitored in the fuel reactor.

$$t_{m,FR} = \frac{\text{solids inventory in the FR (kg)}}{\text{solids circulation rate (kg/s)}}$$
(4)

2.4 Data evaluation

The performance of the two units was evaluated based on the following parameters:

• The biomass conversion, X_b , is defined as the amount of carbon contained in the biomass that is converted into gas, both in the fuel and air reactors.

$$X_b = \frac{\text{carbon in gases from FR and AR}}{\text{carbon in biomass}}$$
(5)

• The char conversion in the fuel reactor, $X_{char,FR}$, represents the fraction of fixed carbon converted to gas in the fuel reactor over the total fixed carbon fed.

$$X_{char,FR} = \frac{\text{fixed carbon converted in FR}}{\text{fixed carbon in biomass}}$$
(6)

• The carbon conversion efficiency, η_{CC} , indicates the fraction of the carbon converted to gas in the fuel reactor relative to the total carbon converted to gas in the fuel and air reactors.

$$\eta_{CC} = \frac{\text{fixed carbon converted in FR}}{\text{fixed carbon in biomass}}$$
(7)

• The syngas yield, Y_{syngas} , shows the amount of H₂ and CO produced over the amount of dry biomass fed into the system, expressed in Nm³/kg of dry biomass.

$$Y = \frac{\text{flow rate of } H_2 \text{ and CO } (Nm^3/h)}{\text{feeding rate of dry biomass } (kg/h)}$$
(8)

• The cold gas efficiency, η_g , is the fraction of chemical energy contained in the product gas from the fuel reactor over the total energy of the biomass fed into the system.

$$\eta_g = \frac{\text{chemical energy in gases in FR (kJ/h)}}{\text{energy in biomass (kJ/h)}}$$
(9)

• The carbon losses by the air reactor, C_{lost} , represent the fraction of carbon present in the biomass that it is released to the atmosphere by the air reactor outlet stream.

$$C_{lost} = \frac{\text{carbon present as } CO_2 \text{ in AR}}{\text{carbon present in dry biomass fed in}}$$
(10)

3 Results

3.1 Results at Chalmers in 100 kW unit

The 100 kW unit was operated at hot conditions (>800°C) for mor than 60 h, of which 3.1 h were operation with fuel, separated over 2 days. Table 7 summarizes the operation. Carbon capture efficiency was close to 100% in all tests. There are several reasons why more operation could not be achieved, the main ones being:

- Delays due to long delivery times of electronic equipment.
- The risk assessment for safe operation of the 100 kW CLG unit took more time than planned.
- The fuel feeder was incapacitated by build-ups of "caked" straw fuel on two occasions, giving significant down-time for the whole 100 kW unit.
- Leakage from fuel feeder. The feeding screw transports the fuel into the bed, where the temperature is high, and the pressure fluctuations can be substantial. When the blockage of the feeder occurred (see above), the motor shut down which led to a slight deformation of the screw, which made sealing the "back-side" of the screw all the more difficult. This was eventually fixed, but only late in April 2022.

	AR flow (Ln/min)	Duration of fuel op. (h:min)	Fuel flow (kg/h)	Fuel power (kW)	Fuel
Day 2	1060-1200	02:25	16.3	78	BP+SP
Day 5	1100	00:11	13.6	62	SP
Day 4	700-950	00:32	14.1	68	BP+SP2

Table 7. 100 kW campaign using straw pellets. For fuel abbreviations, see Table 4.

Figures 5A shows gas concentrations and the H₂/CO ratio during the tests on Day 4. Figure 5B shows biomass conversion, X_b , and syngas conversion, Y_{syngas} . Transitory periods were observed in the CLG unit when an operating condition was changed. The increase in CO₂ and biomass conversion at 0.32 h is due to a small increase in the air flow to the air reactor, which gives an increased global circulation. Increasing global circulation increases the oxygen-to-biomass ratio in the fuel reactor, λ , which is the most sensitive operating parameter in CLG. By increasing λ , biomass conversion was increased. However, CO and H₂ concentrations were decreased by increasing λ . As a result, the concentration of CO₂ is significantly increased by increase in H₂ concentration due to the reverse water gas shift reaction. Therefore, the H₂/CO ratio will decrease by increasing λ . However, CH₄ concentration is slightly decreased by increasing λ . The fuel reactor in OX₂ and the reverse water gas rather than with the hydrocarbons.

Figure 6 shows the effects of λ on CLG operation using a mixture of straw and black pellets as fuel. The syngas yield and H₂/CO ratio were decreased by increasing λ , and biomass conversion was increased. Based on the results, regardless of the operating temperature, the effect of λ on CLG operation is significant. This is in agreement with the results obtained from continuous CLG operation in 1.5 kWth, 10 kWth and 50 kWth units at CTH and CSIC.



Figure 5. CLG operation on Day 4 using a mixture of straw and black pellets as fuel. $T_{FR} = 860^{\circ}C$; $\lambda = 0.05-0.1$; $P_{fuel} = 68$ kW. Concentrations of H₂, CO, CO₂ and CH₄, and H₂/CO ratio (A). Biomass conversion, X_b, and syngas conversion, Y (B).



Figure 6. CLG operation using a mixture of straw and black pellets as fuel. Each dot represents stable operation during at least 20 minutes. $T_{FR} = 870-920^{\circ}C$.

Agglomeration

No agglomeration observed during the tests, except at first heat up. Ilmenite goes through a phase change from ilmenite (FeTiO3) to pseudo-brookite (FeTi2O5) during the first exposure to heat in an oxidative environment. As a consequence, there is a risk of agglomeration during this period if heat up is not done very slowly and carefully. Agglomeration during first heat-up has happened a number of times in different pilots. At the start of these experiments and despite the best efforts of the operators, agglomeration could not be avoided. After the first experience of agglomeration, it was decided that only heat-treated ilmenite was to be used, even though the time required to heat-treat the ilmenite in a separate oven is significantly longer that the time it takes to use the pilots for heat-treatment.

3.2 Results in 50 kW BCLG unit at CSIC

The effect of different operating conditions on the process performance and on the syngas yield was analyzed in Task 3.4. The first experimental campaign covers about 40 hours of continuous operation in a 50 kW_{th} BCLG unit using ilmenite as oxygen carrier and wheat straw pellets with additives as fuel. Steam was fed as gasifying agent into the fuel reactor with a steam-to-biomass ratio of 0.7 kg/kg dry biomass. The most relevant variables affecting to the CLG process were the gasification temperature and the solids residence time in the fuel reactor, the oxygen-to-biomass ratio (controlled by the oxygen fed to the air reactor), and the gas velocity in the carbon stripper. All of them have a significant effect on the process performance although having different effect depending on the parameter.

After this campaign the CLG unit was modified in order to improve its operating capabilities, i.e.:

- to reduce the time needed to reach the steady state for the solids in the unit
- to use H_2O as fluidizing gas in the CS; to reduce the amount of N_2 used in the AR
- to improve the accuracy of the measurements taken in the unit.

To reach these objectives, the following adaptions were carried out:

- the volume of the AR was reduced which produce a variation in the solids inventory from 50 to 22 kg;
- the riser diameter of the AR was reduced from 102 mm to 80.9 mm;
- two quantometers were installed at the fuel and air reactor outlets to know at each moment the gas flow going out.
- Moreover, to increase the unit stability the height of the loop-seal connecting the carbon stripper and the air reactor (LS-CS) was modified increasing the pressure drop from 6 to 10 kPa.

The second experimental campaign covers about 20 hours of operation after implementation of the unit modifications. Some initial tests were carried out at the same conditions to experimental campaign 1, to assure that the results do not depended on the unit configuration. After that and additionally to the analysis of the effect of the operating variables, H_2O or N_2 were used as fluidizing gas in CS to analyze its effect on the process performance.

Table 5 shows the experimental conditions used in the experiments carried out in campaigns 1 and 2 to know the process performance.

Tables A1 and A2 in Annex 1 shows the operating variables, gas compositions and performance parameters found during the tests carried out in the 50 kW_{th} unit using ilmenite and wheat straw pellets, including campaigns 1 and 2. It is remarkable that CH₄ and C₂-C₃ hydrocarbons were not fully converted in any of the experimental conditions. CH₄ concentrations around 9-10 % and 1-2 % of C₂-C₃ were usually found at the fuel reactor outlet.

Figure 7 shows an example of the effect on the biomass conversion, X_b and on the carbon capture efficiency, η_{CC} , as well as in the gas composition for test 2.

Test	Power	T _{FR}	S/B	λ	m _{FR}	CS		
	kW	°C	kg/kg d.b	mol/mol	kg/MW	LN/h		
1.1	18.3	830	0.70	0.40	224	2000		
1.2	18.3	880	0.70	0.40	196	2000		
1.3	18.3	890	0.70	0.20	234	2000		
2.1	18.3	910	0.99	0.40	308	1000		
2.2	18.3	910	0.70	0.40	352	1000		
2.3	18.3	915	0.70	0.30	411	1000		
2.4	18.3	915	0.70	0.25	375	1000		
2.5	18.3	915	0.70	0.36	379	1000		
2.6	18.3	915	0.70	0.36	362	1000		
2.7	18.3	800	0.70	0.36	435	1000		
3.1	18.3	805	0.70	0.30	456	1000		
3.2	18.3	810	0.70	0.30	525	1000		
3.3	18.3	985	0.70	0.30	354	1000		
3.4	18.3	900	0.70	0.30	268	3000		
3.5	18.3	910	0.70	0.30	406	3000		
4.1	18.3	800	0.70	0.30	560	3000		
4.2	18.3	800	0.70	0.30	419	3000		
4.3	18.3	800	0.70	0.30	602	3000		
4.4	18.3	945	0.70	0.30	429	2000		
5.1	19.0	890	0.68	0.29	282	2000		
5.2	19.0	985	0.68	0.29	265	2000		
5.3	19.0	980	0.68	0.29	273	3500		
5.4	19.0	980	0.68	0.29	270	5000		
5.5	19.0	810	0.68	0.29	328	2000		
5.6	19.0	815	0.68	0.29	664	5000		
6.1a	19.0	930	0.68	0.39	353	5000		
6.1b	19.0	955	0.68	0.39	339	5000		
6.1c	19.0	980	0.68	0.39	348	5000		
6.2	19.0	980	0.68	0.36	339	5000		
6.3a	19.0	880	0.68	0.13	208	5000		
6.3b	19.0	925	0.68	0.29	413	5000		
10.1	18.5	900	0.69	0.43	269	5000		
10.2	18.5	920	0.69	0.43	272	5000		
10.3	18.5	950	0.69	0.43	264	5000		
10.4a	18.5	940	0.69	0.43	325	5000		
10.4b	18.5	910	0.69	0.00	252	5000		
10.4c	18.5	935	0.69	0.43	314	5000		
10.5a	18.5	945	0.69	0.43	479	2000		
10.5b	18.5	935	0.69	0.43	398	2000		
10.5c	18.5	885	0.69	0.43	225	2000		
10.5d	18.5	935	0.69	0.43	403	2000		
10.6	18.5	935	0.83	0.43	402	2000		
10.7	18.5	895	0.83	0.43	469	2000		
10.8a	18.5	855	0.83	0.43	517	2000		
10.8b	18.5	860	0.83	0.43	504	2000		
10.8c	18.5	860	0.83	0.43	490	2000		
10.9a	18.5	950	0.83	0.43	456	2000		
10.9b	18.5	935	0.83	0.43	357	2000		
10.10	18.5	930	0.69	0.43	336	5000		

 Table 8. Operating conditions used in the experimental campaign 1 and 2.



Figure 7. Effect of operating conditions on gas composition and process performance in test 2.

3.2.1 Effect of temperature and mean residence time in the fuel reactor

It is well known that temperature affects to the reaction rates present in any process. To carry out this evaluation, the gasification temperature was varied in the usual range of gasification processes (800 - 980 °C). A previous work carried out by our research group inside Task T3.3 with ilmenite in the BCLG process at 1.5 kW_{th} scale showed that temperature had little effect on syngas composition; see Deliverable D3.3 and Condori et al., [2021a]. Similar results were also observed using other type of materials based on Fe and Mn as oxygen carrier in continuous operation [Condori et al., 2021b]. However, both the char gasification rate and syngas yield were affected by the reacting temperature.

Figure 8 shows the effect of temperature and mean residence time of the oxygen carrier in the fuel reactor on char conversion. Conversion of char in the fuel reactor increased with the mean residence time of the oxygen carrier, $t_{mr,FR}$. This fact suggests that the residence time of char particles in the fuel reactor was affected by the solids circulation rate of the oxygen carrier. The size of the biomass pellets used in this work was quite large, and entrainment of the char to the cyclone would not be expected considering the gas velocity in the fuel reactor. However, entrainment of pellets was evident after an examination of the solids exiting the fuel reactor cyclone; see Figure 9. A more detailed evaluation of solids leaving the fuel reactor did not show

the presence of a significant amount of char in the form of powder; in contrast, pelletized biomass retained the initial cylindrical shape of the biomass pellets after its partial gasification in the fuel reactor. Therefore, it was concluded that the entrainment of oxygen carrier particles promotes the entrainment of large char particles.

In addition, an increase in temperature led to an increase in char conversion for a given solids residence time due to the increase in the char gasification rates. For example, in order to have char conversion values as high as 70-80% in the fuel reactor, the mean residence time of solids in the fuel reactor should be 300-400 s at 910 °C, when N₂ was used as fluidization agent in CS.

Figure 8 also shows the effect of the use of H₂O as fluidizing gas in CS indicating that its use increases the char conversion, $X_{char, FR}$.



Figure 8. Effect of temperature and mean residence time on char conversion in the fuel reactor in campaigns 1 and 2.



Figure 9. Unconverted char on the fuel reactor, carbon stripper and air reactor

The fate of unconverted carbon in the fuel reactor is uncertain. CO_2 was observed in the exhaust gases from the air reactor in some tests. This means that some unconverted char particles

reached the air reactor and were burned in contact with the gaseous oxygen, reducing the carbon conversion efficiency, η_{CC} , of the process. The sample taken from the carbon stripper showed that some of the non-gasified pelletized char was being accumulated there; see Figure 9 (CS). Note that in these experiments N₂ was used as fluidizing gas in the carbon stripper. This gas was selected instead of H₂O or CO₂ –which would be used in an industrial process– to prevent the gasification of the char in the carbon stripper and to facilitate the interpretation of the results obtained in the CLG facility. Neither char nor oxygen carrier particles were entrained from the carbon stripper did not have a relevant function when pelletized biomass was used as fuel. However, no char pellets were found in the sample taken from the air reactor. Only a small amount of powdered char was observed, suggesting that the char reaching the air reactor was quickly consumed by combustion.

The biomass conversion in the CLG unit varied between 60 and 100% in all the tests of the experimental campaign. The total carbon conversion in the unit was affected by temperature, since it directly depends on the char conversion in the fuel reactor. At lower temperatures, the lower reaction rates in the fuel reactor caused char accumulation in the fuel reactor, which reduced $X_{char,FR}$ and consequently lower values of X_b were obtained. Therefore, it is believed that carbon was being accumulated in the carbon stripper. The following tests were carried out to confirm this assumption.

3.2.2 Effect of the gas flow fed to the carbon stripper (CS)

Another variable studied in this work was the gas flowrate fed to the carbon stripper. The carbon stripper was designed for powdered fuels, which may be easily separated from the oxygen carrier particles due to their differences on size and density; thus, unconverted char particles may be entrained to the fuel reactor by controlling the gas velocity in the carbon stripper [Abad et al., 2015]. However, the behaviour with pelletized biomass may be different than with powdered fuels.

It was observed that an increase in the CS gas velocity increased the amount of unconverted char from the fuel reactor reaching the air reactor. When being exposed to the oxygen present in the air reactor, the combustion of the char occurred, causing an increase in the CO₂ concentration at the gas outlet and decreasing the carbon conversion efficiency, η_{cc} . This was observed in tests 5.2, 5.4 and 6.2 showed in Table 8 and in Table A1, where an increase in u_{CS} from 14 (Test 5.2) to 35 cm/s (Test 5.4 and 6.2) produced a decrease in η_{cc} from 90% to 80.6% and 75.8%, respectively. Eventually, the biomass conversion in the CLG unit reached values close to 100% with the highest gas velocity tested in the carbon stripper (Tests 5.4 and 6.2).

This indicated that there was no char build-up on the unit, as well as no significant char elutriation. In addition, no increase in char conversion was observed in the fuel reactor (Tests 5.2 and 5.4 in Table 8 and Table A1), indicating that the unconverted char leaving the fuel reactor was not separated from the oxygen carrier in the carbon stripper and was not recirculated to the fuel reactor. In conclusion, although the biomass conversion increased considerably, the carbon capture efficiency, η_{CC} , was reduced.

3.2.3 Effect of the oxygen-to-biomass ratio

It is known that the oxygen-to-fuel ratio, λ , is the most relevant operating variable affecting the syngas yield, since it represents the amount of oxygen used for gasification/combustion and,

therefore, the degree of partial combustion of the gasification products. In addition to its impact on the quality of the synthesis gas, this variable is crucial for the objective of achieving autothermal operating conditions in the system. In this work, this parameter was varied by controlling the air flow to the air reactor, diluting the air with N₂, which demonstrated to be an easy and accurate control method in operating BCLG units. A previous work carried out by our research group in Task T3.3 showed that the optimal value of λ to achieve the auto-thermal BCLG process with the higher syngas quality varied between 0.33 and 0.38, (Deliverable D3.3 and [Samprón et al, 2021]). An increase in λ values led to an increase in CO₂ content and lower syngas yields.

Two new parameters were introduced to consider the correct amount of oxygen that reacts with the oxygen carrier in the fuel and air reactors, $\lambda_{eff,AR}$ and $\lambda_{eff,FR}$, respectively. These effective oxygen-to- biomass ratios should be equal when steady state is reached ($\Phi = \lambda_{eff,FR} / \lambda_{eff,AR} = 1$). Moreover, its value under steady state conditions should be less than λ , since part of the oxygen fed to the air reactor could react with the char coming from the fuel reactor instead of being used for ilmenite oxidation.

Transitory periods were observed in the CLG unit when some operating condition was varied. Figure 10 shows points where the steady state for solids has not been reached as the effective transfer of oxygen in the fuel reactor was lower (Φ <1) or higher (Φ >1) than the oxygen transferred in the air reactor to the oxygen carrier. For example, Φ <1 values were observed when the air flow, and therefore λ , was suddenly increased in the air reactor. In this case, the highly reduced ilmenite reacted with the excess of oxygen but it took some time to transfer it to the fuel reactor. In contrast, Φ >1 values were often evidenced when the solids circulation rate decreased due to a transitory lack of oxygen in the fuel reactor while solids in the air reactor reached a higher oxidation degree. Temperature changes may also affect to the Φ value at the beginning of the operation. For example, an increase in the gasification rate or to an excess of char caused by previous accumulation. Therefore, there is a higher oxygen demand in the fuel reactor due to the increased fuel conversion that was initially taken from the accumulated lattice oxygen and consumed in the fuel reactor.

During the 2^{nd} experimental campaign after the unit modification, the dispersion of the experimental results was reduced as a consequence of the decrease in the oxygen carrier inventory and in the residence time in AR, as it can be seen in Figure 10.

Among the three oxygen-to-biomass ratio defined by equations (1-3), the effective oxygen- tobiomass ratio in the fuel reactor, $\lambda_{eff,FR}$, had a direct influence on the syngas yield. Figure 11 shows the effect of $\lambda_{eff,FR}$ on the syngas yield for different values of char conversion obtained in the fuel reactor. For a given char conversion value in the fuel reactor, an increase in the ratio $\lambda_{eff,FR}$ caused a decrease in the syngas yield since a part of the syngas produced was burnt to CO₂ and H₂O. As a consequence, ilmenite released a larger amount of lattice oxygen in the fuel reactor. Thus, the concentration of CO₂ increased while the concentration of H₂ and CO decreased.



Figure 10. Relationship between effective oxygen-to-biomass ratios in fuel and air reactors, $\lambda_{eff,AR}$ and $\lambda_{eff,FR}$, respectively. Solids points represent steady state conditions. Empty points represent transitory states.



Figure 11. Effect of the effective oxygen-to-biomass ratio in the FR, $\lambda_{eff,FR}$, on the syngas yield, Y_{syngas} , and yield to HCs, Y_{HCs} , for different char conversions in the FR, $X_{char,FR}$.

In addition, it was observed that neither the temperature nor the mean residence time of solids in the fuel reactor are variables with a direct effect on the syngas yield, but rather on the conversion of char in the fuel reactor, $X_{char,FR}$. Obviously, temperature and solids residence time have a direct effect on char conversion, as shown in Figure 8. For example, considering the results showed in Figure 8, a decrease in t_{mr,FR} from 124 s (Test 5.4, Table 8) to 53 (Tests 6.2) produced a decrease in $X_{char,FR}$ from 41 to 16, respectively, while the syngas yield was maintained at values about 0.65 Nm³/kg.

The oxygen to fuel ratio $\lambda_{eff,FR}$ controls the syngas yield, that decreases when this ratio increases, and it is highly dependent on the char conversion. In auto-thermal conditions syngas yields

higher than 0.6 Nm³/kg of dry biomass can be obtained. With high char conversion ≈ 90 %, syngas yields higher than 0.8 Nm³/kg of dry biomass can be obtained in the CLG unit. It can be concluded that to increase the syngas, it is necessary to operate the FR at high temperatures with high char conversion and λ values near to the auto-thermal value.

The cold gas efficiency, η_g , was another parameter affected by the oxygen-to-biomass ratio, since it also depends directly on the syngas composition. By decreasing the syngas quality, its calorific value is also reduced. This trend was also observed in previous studies at the 1.5 kW_{th} scale based on the same oxygen control method as the one used in this work [Condori et al., 2021a; 2021b], as well as in other research based on the biomass-feeding variation for controlling oxygen [Ge et al, 2016; Wei et al., 2015].

On the other hand, it can be seen in Figure 11 that the yield to light hydrocarbons (CH₄ and C₂-C₃ coming from biomass devolatilization), Y_{HCs} , was hardly affected by the variation in the ratio $\lambda_{eff,FR}$. In fact, Abad et al. [Abad et al., 2011] found a low reactivity of ilmenite with CH₄. In CLG, the conditions of the fuel reactor are deficient in oxygen and it was likely to react mainly with H₂ and CO in the syngas rather than with light hydrocarbons. There was also no clear effect of the char conversion in the fuel reactor on the production of light hydrocarbons. Thus, the results obtained in previous works during continuous operation in a 1.5 kW_{th} BCLG unit, where the amount of HCs were hardly affected by the amount of lattice oxygen transported to the fuel reactor [Condori et al., 2021a, 2021b], were corroborated in this work at higher scale.

Carbon losses by the air reactor are a consequence of the unconverted char transferred from the fuel to the air reactor. There, the char is burnt and at the same time the oxygen carrier is oxidized. Thus, two parallel reactions are competing for the gaseous oxygen. Figure 12 shows that carbon losses by the air reactor increased with λ value. Carbon losses in the 2nd experimental campaign were very low because the contact time in AR was lower than in the first one by the decrease in the AR solids bed inventory and thus, in the residence time of char particles in this reactor.



Figure 12. Carbon losses by the air reactor as a function of $\lambda_{eff,AR}$.

3.2.4 Tar emissions

The European tar protocol was used to determine the amount of tar present at the fuel reactor outlet in some experiments.

Figure 13 shows the total amount of tar present in the syngas as a function of temperature. Typical values of around 2.5 g/kg of dried biomass were found, corresponding to 3.1 g/Nm³ dry syngas. Although these values correspond to tests carried out at different conditions regarding oxygen-to-fuel ratios and solids residence time, it is concluded that an increase in temperature reduce the tar content on the syngas. In addition, speciation of recovered tars was made gas chromatography coupled to mass spectroscopy. The main component found when using wheat straw pellets as fuel was benzene with lower amounts of toluene and naphthalene (see Figure 14) in contrast to the results obtained when using pine in which the main component was naphthalene.



Figure 13. Tar content as a function of temperature.



Figure 14. Distribution of tar compounds for different tests carried with wheat straw pellets.

3.2.5 Interaction of fuel ashes with the oxygen carrier.

One important concern regarding the use of wheat straw pellets for gasification is the possible bed agglomeration originated by the low melting point of straw ashes, especially at the highly reducing conditions as those present in gasifiers. In case of Chemical Looping Gasification the presence of an oxygen carrier, ilmenite, has to be considered, as it entails the possibility of bed agglomeration or the formation of small agglomerates in the reactors by the interaction between the oxygen carrier and the components of the fuel ashes, leading to a deficient fluidization of the bed. Thus, the 50 kW_{th} unit was fully emptied after the first experimental campaign (after 40 h of gasification) to analyze the oxygen carrier. Ilmenite was sieved in order to determine if agglomerates can be retrieved. The study concluded that no agglomerates were detected, demonstrating the efficiency to avoid agglomeration of the additives used in the preparation of the wheat straw pellets by CENER in WP2. In addition, samples of ilmenite were taken regularly from the unit for further analysis of their chemical and structural characterization and to investigate possible interaction between fuel ashes and the oxygen carrier.

A characterization of ilmenite taken from the reactor after 40 h of Chemical Looping Gasification was finally made. The crushing strength of the used particles was found to decrease slightly after the reaction from 2.2 N to 1.6. In contrast, the Attrition Jet Index (AJI) decreased from 0.6 to 0.3, indicating that the attrition resistance of the used particles had increased. Particle size distribution (PSD) of calcined ilmenite and after reaction was compared showing a slight decrease of the PSD, as shown in Figure 15.



Figure 15. Particle size distributions of calcined ilmenite and after use in BCLG.

The evolution of different metals present in the wheat straw pellets with additives used as fuel and in the ilmenite was made using samples taken from the reactors at different reaction times. Metal content evolution was determined by ICP analysis of samples using a Jobi-Xpectroblue equipment. Figure 16 shows the evolution with time of Fe, Ti, Mg, Na, Ca, K and Si during the BCLG reaction. Results in dotted lines corresponds to the components present in calcined ilmenite, while the discontinuous line corresponds to that corresponding to one uniform distribution of elements present in the ilmenite together those present in the straw pellets fed in up to that time. The distribution of metals is indicated as rounded dots in the bed ilmenite sample while square dots indicate metals present in the fines recovered in the air reactor.



Figure 16. Evolution with time of metals present in the oxygen carrier after BCLG operation. Dotted lines-elements present in calcined ilmenite; discontinuous line-uniform distribution of elements from ilmenite and straw fed in; rounded points-metals in ilmenite bed; squared points-elements presents in recovered fiend.

Results found were not fully conclusive for this experimental work because it was directed to determine biomass Chemical Looping Gasification performance and to know possible agglomeration phenomena in the reactors, and because more operating time would be necessary to obtain conclusive results. However, partial conclusions were achieved. Only a relevant content of Ca, K and Si was found in the attrited fine particles recovered in the air reactor cyclone. Some K was also retained by the ilmenite. For the rest of metals, Fe, Mg and Na, no relevant changes were detected in the distribution between bed and fine particles.

Figure 17 shows SEM images of entire and cut particles taken from the bed at different reaction times. One external layer in the ilmenite particles was observed and also particles with some cracks after 40 h of BCLG operation, although this last behavior was not consistent in all the particles. Moreover, SEM-EDX of cut particles fresh and recovered at different reaction times was made determining the line profiles corresponding to Fe, Ti, O, K, Ca and Si in the particles (Figure 18). Elements were uniformly distributed in the fresh calcined particles. Black particles present in the samples were mainly composed by alumino-silicates, likely coming from the ilmenite impurities present in the raw material. However, after 18 h of operation, Fe migration toward the surface was found, see Figure 18. Fe was present as one Fe₂O₃ shell in similar way to that found in Chemical Looping Combustion of coal [Cuadrat, 2012] or biomass.



Figure 17. SEM images of internal section of the particles along time.



Figure 18. SEM-EDX and line profiles of a cut particle of calcined ilmenite and after BCLG operation.

In order to find the fate of Fe, Ti, K, Ca, Si and O in the ilmenite particles, mapping of these elements was made in several cut particle samples recovered from the unit along time. As an example, Figures 19 and 20 show the results obtained for a particle taken from the bed. The migration of Fe towards the external surface of the particles but without Ti was observed. Si and Ca were preferably deposited in the external layer of the particles. K was enriched in zones were Si is present (darker grey zones), and even can be penetrate inside the particles when cracks are present.



Figure 19. Mapping of the cut particles for detection of Fe, Ti, K, Ca, Si and O in samples taken after 23 h of operation.



Figure 20. Mapping of some elements inside ilmenite particles after 40 hours operation in 50 kW_{th} unit.

3.2.6 Reactivity of the ilmenite after used

Reactivity of ilmenite particles after different BCLG reaction times was measured by TGA, is shown in Figure 21. Not significant differences in reactivity were observed with samples taken at different reaction times, although the oxygen transport capacity suffer from one small reduction originated by the Fe migration to external part of the particles as Fe_3O_4 with lower oxygen transport capacity.



Figure 21. Comparison of the reactivity of the ilmenite calcined and after 40 h of operation. TGA conditions: 15 vol% CO + 20 vol% CO₂.

4 Conclusions

The use of ilmenite as oxygen carrier for the CLG process was investigated in two pilots; one at Chalmers, Sweden, and the other at CSIC, Spain. The results demonstrate the possibility to obtain non-diluted syngas with high CO_2 capture. Wheat straw pellets with additives was used as fuel. At Chalmers, the straw pellets had to be crushed and mixed with wood ("BP") for feeding purposes.

Ilmenite showed good behavior and no agglomeration during operation, except at first heat up at Chalmers. Some migration of Fe toward the external surface of the ilmenite was found and K present in the wheat straw was retained in the bed particles and in the fines recovered by the cyclones.

The main operating variables of the process were the oxygen to fuel ratio (λ), the fuel reactor temperature and the mean residence time of solids in the fuel reactor. Temperature showed a major impact on the char conversion of the fuel reactor, $X_{char,FR}$, as an increase in temperature increased the reaction rates of all the reactions occurring in the gasification reactor. An increase in the mean residence time of solids also led to increased char conversion values.

Char conversion in the fuel reactor was not enhanced by the presence of the carbon stripper when pellets are used. The carbon stripper was not capable of separating the unconverted char entrained from the fuel reactor, because it still retains its initial pellet form. Increasing the gas velocity, improved the biomass conversion in the unit, X_b , while the carbon conversion efficiency in the CLG unit, η_{CC} , was reduced because the char by-pass to the air reactor was promoted. When carbon stripper was fluidized with steam it acts as a secondary gasifier increasing the char conversion and the syngas yields.

The oxygen-to-biomass ratio, λ , was the most relevant operating variable affecting syngas production. However, depending on the operating conditions, this variable did not consider the exact amount of oxygen that reacted with the oxygen carrier in both fuel and air reactors. Therefore, the effective oxygen-to-biomass ratios were used, $\lambda_{eff,FR}$ and $\lambda_{eff,AR}$, respectively. These parameters helped us to know when the steady state had been reached ($\Phi = \lambda_{eff,FR} / \lambda_{eff,AR} = 1$) under certain operating conditions. An increase in the ratio $\lambda_{eff,FR}$ caused a decrease in the syngas yield and the cold gas efficiency as more syngas was consumed in combustion because more lattice oxygen reacted in the fuel reactor. In addition, it was observed that the variation of λ had low impact on the production of CH₄ and light hydrocarbons.

To improve the syngas yield in the CLG with wheat straw pellets it is necessary to use high residence times in the fuel reactor, high temperatures and use the lower λ necessary to maintain auto-thermal conditions.

5 Disclaimer

The content of this deliverable reflects only the author's view, and the European Commission is not responsible for any use that may be made of the information it contains.

6 References

- Abad A, Adánez J, Cuadrat A, García-Labiano F, Gayán P, de Diego LF, Kinetics of redox reactions of ilmenite for chemical-looping combustion, Chem Eng Sci 66, 4 (2011) 689-702
- Abad A, Pérez-Vega R, de Diego LF, García-Labiano F, Gayán P, Adánez J, Design and operation of a 50 kW_{th} Chemical Looping Combustion (CLC) unit for solid fuels, App Energy 157 (2015) 295-303.
- Adánez J, Cuadrat A, Abad A, Gayán P, de Diego LF, García-Labiano F, Ilmenite activation during consecutive redox cycles in chemical-looping combustion, Energy Fuel 24 (2010) 1402–13.
- Condori O, García-Labiano F, de Diego LF, Izquierdo MT, Abad A, Adánez J, Biomass chemical looping gasification for syngas production using ilmenite as oxygen carrier in a 1.5 kWth unit, Chem Eng J 405 (2021a) 126679.
- Condori O, de Diego LF, García-Labiano F, Izquierdo MT, Abad A, Adánez J, Syngas Production in a 1.5 kWth Biomass Chemical Looping Gasification Unit Using Fe and Mn Ores as the Oxygen Carrier, Energy Fuels 35 (2021b) 17182-17196.
- CLARA Deliverable D3.1. Report on oxygen carrier screening and selection. 2019. Hedayati A, Mattisson T, Adánez J, García-Labiano F
- CLARA Deliverable D3.3. Results on continuous testing with different fuels and oxygen carriers. 2020. Soleimanisalim A, Mattisson T, Adánez J, García-Labiano F, de Diego LF, Condori O
- Cuadrat A, Chemical-looping combustion of coal using ilmenite as oxygen carrier. Doctoral Thesis at the University of Zaragoza. Instituto de Carboquímica (ICB-CSIC), 2012.
- Ge H, Guo W, Shen L, Song T, Xiao J, Biomass gasification using chemical looping in a 25 kW th reactor with natural hematite as oxygen carrier, Chem Eng J 286 (2016) 174–183.
- Leion H, Lyngfelt A, Johansson M, Jerndal E, Mattisson T, The use of ilmenite as an oxygen carrier in chemical-looping combustion, Chem Eng Res Des 86 (2008) 1017–26.
- Pröll T, Mayer K, Bolhàr-Nordenkampf J, Kolbitsch P, Mattisson T, Lyngfelt A, Hofbauer H, Natural minerals as oxygen carrier for chemical looping combustion in a dual circulating fluidized bed system. GHGT-9. Energy Procedia 1 (2009) 27–34.
- Samprón I, de Diego LF, García-Labiano F, Izquierdo MT, Optimization of synthesis gas production in the biomass chemical looping gasification process operating under auto-thermal conditions, Energy 226 (2021) 120317.
- Simell P, Ståhlberg P, Kurkela E, Albrecht J, Deutsch S, Sjöström K, 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.
- Wei G, He F, Zhao Z, Huang Z, Zheng A, Zhao K, Li H, Performance of Fe-Ni bimetallic oxygen carriers for chemical looping gasification of biomass in a 10 kW_{th} interconnected circulating fluidised bed reactor, Int J Hydrogen Energy 40 (2015) 16021–16032.

7 Annex 1

Table A1 Operating	variables, performance	parameters and gas	composition for	the first experimental (campaign.
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	Operating variables									Process performance							Gas composition (vol%)					
Test	Power	T_{FR}	S/B	λ	Θ	m _{FR}	CS	t _{mr,FR}	X _b	Char, _{El}	$X_{\text{char},\text{FR}}$	η _{сс}	C _{lost}	Y_{Syngas}	Y _{HCs}	CO ₂	СО	H_2	CH_4	C_xH_y		
	kW	٥C	-	_		Kg/MW	LN/h	S	%	%	%	%	%	Nm³/kg	Nm³/kg							
1.1	18.3	827	0.70	0.40	0.98	224	2000	296	87.9	36.6	43.7	92.6	6.5	0.37	0.11	47.3	15.5	25.5	8.8	3.0		
1.2	18.3	882	0.70	0.40	0.90	196	2000	185	86.8	39.9	39.2	92.0	6.9	0.46	0.10	41.6	18.5	29.6	8.4	2.0		
1.3	18.3	891	0.70	0.20	1.44	234	2000	221	83.8	48.8	41.1	96.0	3.3	0.55	0.10	35.5	20.7	33.7	8.3	1.8		
2.1	18.3	911	0.99	0.40	0.81	308	1000	135	74.6	76.9	16.2	97.0	2.3	0.38	0.09	45.9	15.2	28.8	8.5	1.6		
2.2	18.3	909	0.70	0.40	0.92	352	1000	154	83.0	51.5	41.7	97.3	2.3	0.48	0.08	42.6	19.1	30.3	6.7	1.3		
2.3	18.3	915	0.70	0.30	1.02	411	1000	151	80.1	60.1	31.8	96.7	2.7	0.50	0.09	38.8	19.9	32.1	7.4	1.8		
2.4	18.3	912	0.70	0.25	1.14	375	1000	165	85.7	43.3	49.8	97.3	2.3	0.57	0.10	35.9	20.5	33.7	8.2	1.7		
2.5	18.3	914	0.70	0.36	0.70	379	1000	116	79.5	62.1	30.8	97.0	2.4	0.59	0.09	34.0	21.1	36.4	7.2	1.4		
2.6	18.3	915	0.70	0.36	0.76	362	1000	111	74.8	76.2	13.4	95.4	3.5	0.47	0.09	38.3	19.2	32.8	8.2	1.5		
2.7	18.3	803	0.70	0.36	0.59	435	1000	430	68.2	96.2	-6.3	95.1	3.3	0.38	0.09	38.7	17.3	31.8	8.7	3.5		
3.1	18.3	807	0.70	0.30	0.27	456	1000	1074	65.5	104.4	-9.8	97.3	1.8	0.49	0.11	28.5	19.2	39.0	9.6	3.7		
3.2	18.3	810	0.70	0.30	1.24	525	1000	936	99.6	1.3	80.1	93.8	6.2	0.52	0.13	41.1	17.0	30.2	8.8	3.0		
3.3	18.3	984	0.70	0.30	0.92	354	1000	542	110.8	-32.6	127.1	98.4	1.8	0.93	0.13	28.3	25.7	37.3	7.8	0.9		
3.4	18.3	897	0.70	0.30	1.00	268	3000	413	92.5	22.6	73.8	98.7	1.2	0.62	0.11	36.4	20.6	33.3	8.1	1.7		
3.5	18.3	910	0.70	0.30	1.17	406	3000	337	93.3	20.1	70.8	96.8	3.0	0.54	0.11	40.0	18.9	30.6	8.7	1.7		
4.1	18.3	801	0.70	0.30	0.52	560	3000	516	71.2	86.9	3.0	95.3	3.3	0.47	0.11	33.6	17.5	36.4	9.1	3.4		
4.2	18.3	797	0.70	0.30	0.48	419	3000	349	68.0	96.6	2.4	99.5	0.3	0.47	0.11	33.1	18.4	36.2	8.9	3.4		
4.3	18.3	801	0.70	0.30	0.53	602	3000	198	75.6	73.8	20.1	97.3	2.0	0.51	0.12	33.9	17.2	36.7	8.7	3.5		
4.4	18.3	945	0.70	0.30	1.40	429	2000	358	107.2	-21.8	89.0	89.9	10.8	0.90	0.08	27.5	28.0	38.9	4.9	0.8		
5.1	19.0	891	0.68	0.29	1.11	282	2000	170	90.5	28.6	45.3	90.5	8.6	0.52	0.12	36.1	20.4	31.6	9.1	2.7		
5.2	19.0	986	0.68	0.29	0.99	265	2000	121	91.1	26.8	45.7	90.0	9.1	0.64	0.11	30.0	24.4	35.1	9.5	1.1		
5.3	19.0	981	0.68	0.29	1.72	273	3500	125	102.0	-6.1	49.4	81.6	18.8	0.65	0.12	29.7	23.9	35.5	9.7	1.2		
5.4	19.0	983	0.68	0.29	1.33	270	5000	124	99.8	0.7	40.8	80.6	19.4	0.69	0.12	26.6	24.3	38.2	9.8	1.2		
5.5	19.0	809	0.68	0.29	0.69	328	2000	140	71.7	85.6	-18.0	85.0	10.7	0.47	0.10	29.3	22.7	35.9	10.6	1.5		
5.6	19.0	813	0.68	0.29	-0.56	664	5000	700	122.3	-67.3	19.7	60.1	48.8	0.45	0.15	30.9	20.1	31.5	12.7	4.7		
6.1a	19.0	930	0.68	0.39	0.44	353	5000	210	57.2	129.3	-48.6	88.8	6.4	0.35	0.08	33.1	21.1	33.7	10.3	1.8		
6.1b	19.0	956	0.68	0.39	1.35	339	5000	148	81.7	55.2	-32.7	68.6	25.6	0.34	0.08	37.6	20.6	29.9	10.4	1.5		
6.1c	19.0	980	0.68	0.39	1.10	348	5000	152	81.3	56.5	-29.5	70.3	24.1	0.38	0.08	34.6	21.4	32.2	10.6	1.3		
6.2	19.0	978	0.68	0.36	0.98	339	5000	53	95.1	14.7	15.6	75.8	23.1	0.61	0.11	27.4	23.3	38.3	9.8	1.2		
6.3a	19.0	879	0.68	0.13	0.76	208	5000	142	79.1	63.2	20.5	93.2	5.4	0.73	0.11	22.0	24.5	43.0	8.5	2.0		
6.3b	19.0	927	0.68	0.29	2.89	413	5000	188	206.6	-322.1	389.7	94.8	10.7	1.36	0.25	35.3	21.2	33.6	8.5	1.5		

	Operating variables								Process performance							Gas composition (vol%)					
Test	Power	T_{FR}	S/B	CS	λ	Θ	m _{FR}	CS	t _{mr,FR}	X _b	Char, _{El}	$X_{char,FR}$	η _{cc}	C _{lost}	Y _{Synga} s	Y _{HCs}	CO ₂	СО	H ₂	CH₄	C_xH_y
	kW	٥C	-	gas	_		Kg/M W	LN/h	S	%	%	%	%	%	Nm ³ /kg	Nm³/kg					
10.1	18.5	900	0.69	N_2	0.43	1.04	269	5000	257	87.6	37.4	59.8	99.0	0.9	0.36	0.10	50.7	17.1	21.5	8.9	1.8
10.2	18.5	920	0.69	N_2	0.43	1.03	272	5000	259	94.3	17.3	78.7	98.6	1.3	0.45	0.11	46.3	18.9	24.4	8.7	1.6
10.3	18.5	947	0.69	N_2	0.43	0.95	264	5000	179	94.2	17.4	79.7	99.0	1.0	0.53	0.10	41.8	21.0	27.5	8.4	1.3
10.4a	18.5	939	0.69	N_2	0.43	1.07	325	5000	145	89.6	31.4	67.3	99.5	0.4	0.37	0.10	50.5	17.3	21.6	9.2	1.5
10.4b	18.5	911	0.69	N_2	0.00	-	252	5000	-	71.3	86.6	13.4	100.0	0.0	0.73	0.11	21.4	23.7	44.3	8.9	1.7
10.4c	18.5	934	0.69	N_2	0.43	1.01	314	5000	207	92.4	22.9	75.4	99.4	0.6	0.44	0.11	46.5	18.8	24.4	8.8	1.5
10.5a	18.5	944	0.69	H_2O	0.43	0.92	479	2000	213	98.5	4.6	92.1	98.9	1.1	0.59	0.11	42.2	16.5	32.1	8.0	1.2
10.5b	18.5	933	0.69	H_2O	0.43	0.82	398	2000	177	95.3	14.1	74.3	96.0	3.8	0.59	0.11	39.8	16.9	33.6	8.4	1.4
10.5c	18.5	884	0.69	H_2O	0.43	0.36	225	2000	150	89.6	31.5	55.7	95.3	4.2	0.81	0.12	26.9	19.3	44.2	7.8	1.8
10.5d	18.5	935	0.69	H_2O	0.43	0.99	403	2000	224	104.5	13.7	110.7	99.1	1.0	0.64	0.11	42.0	17.5	32.0	7.1	1.4
10.6	18.5	936	0.83	H_2O	0.43	0.90	402	2000	321	98.1	5.6	92.5	99.4	0.6	0.59	0.11	42.4	15.5	32.8	7.9	1.3
10.7	18.5	894	0.83	H_2O	0.43	0.77	469	2000	374	95.6	13.2	83.7	98.9	1.0	0.56	0.12	41.8	14.7	33.0	8.3	2.3
10.8a	18.5	854	0.83	H_2O	0.43	0.70	517	2000	230	88.9	33.5	62.0	98.3	1.5	0.51	0.12	41.7	14.3	32.7	8.8	2.5
10.8b	18.5	857	0.83	H_2O	0.43	0.73	504	2000	258	92.0	24.2	70.6	98.1	1.7	0.50	0.13	42.2	14.6	31.5	8.8	2.9
10.8c	18.5	858	0.83	H_2O	0.43	0.74	490	2000	218	90.2	29.7	63.8	97.6	2.2	0.50	0.12	41.9	15.1	31.9	8.8	2.4
10.9a	18.5	948	0.83	N_2	0.43	0.94	456	2000	277	99.7	1.1	92.3	97.8	2.2	0.59	0.11	40.5	19.9	30.1	8.1	1.3
10.9b	18.5	936	0.83	N_2	0.43	0.91	357	2000	149	87.5	37.8	57.6	98.3	1.5	0.53	0.10	41.5	18.7	30.3	9.2	0.2
10.10	18.5	928	0.69	N_2	0.43	0.82	336	5000	140	102.3	-6.9	100.7	98.0	2.0	0.63	0.13	37.6	20.8	30.7	9.3	1.6

Table 1.2 Operating variables, performance parameters and gas composition for the second experimental cam	nair	m
Table A2 Operating variables, performance parameters and gas composition for the second experimental cam	րուչ	<u>511</u> .