CLara

Chemical Looping Gasification for Sustainable Production of Biofuels

H2020 Research and Innovation action
Grant Agreement no 817841

Deliverable D3.3:

Results of continuous testing with different fuels and oxygen carriers

Version No.:	1
Dissemination level:	Confidential
Due date of deliverable:	2020-11-31
Submission date to coordinator:	2021-03-05
Actual submission date:	2021-04-19
Start date of project:	2018-11-01
End date of project:	2022-10-31

Author(s): Amir H. Soleimanisalim, Tobias Mattisson, Juan Adánez, Francisco García Labiano, Luis F. de Diego, Oscar Condori

Affiliation: Chalmers University of Technology CTH, Consejo Superior de Investigaciones Científicas CSIC

Table of contents

1 Abstract

Six iron and manganese ores and one by-product from the steel industry was preselected as oxygen carriers for chemical looping gasification (CLG). The selected oxygen carriers have been evaluated at different scales at CTH and CSIC to develop a comprehensive understanding and establish a portfolio of suitable oxygen carriers for CLG. After pre evaluation step in Task 3.1, five oxygen carrier selected for continuous operation in Task 3.3. The selected oxygen carriers from prescreening were Ilmenite, Tierga, LD slag, Elwaleed B, and Moanda. In Task 3.3 a total of 600 hours of continuous CLG operation has been done in 10 kW_{th} reactor at CTH and 1.5 kW_{th} reactor at CSIC. After a vast experimental evaluation at CTH and CSIC, it has been confirmed that using oxygen carrier in CLG has a positive effect on gasification of biomass by reducing tar formation, increasing syngas yield, biomass conversion and H_2/CO ratio compare to conventional steam gasification using sand as a bed material. Among the tested oxygen carriers, Ilmenite and LD slag show better biomass gasification performance compared to Mn ores (Elwaleed B and Moanda) and Tierga ore. LD slag has a lower lifetime than ilmenite and needs heat pretreatment, but a slightly higher syngas yield and H_2/CO. Therefore, ilmenite has been selected for Task 3.5 and the final demonstration at TUDA (WP5), considering the operational performance, availability of the material at multi-ton scale, lifetime and pretreatments required for the material prior to CLG operation.

2   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**. 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 pyrolyzed and gasified by addition of steam/CO_2, and the oxygen carrier (Me_yO_x) can react with the intermediate gaseous species to form syngas and at the same time reduces to a metal oxide of lower oxygen content, i.e. (Me_yO_{x-1}). In the air reactor, the oxygen carrier is re-oxidized by molecular oxygen from air for regeneration.

An important issue for CLG is the selection of an appropriate oxygen carrier that must fulfil several requirements, i.e. 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. It would also be preferable if the oxygen carrier had a reversible interaction with important impurities, such as alkali. It is expected that certain Mn- and Fe-based materials could have such characteristics.

For the current project, and demonstration at 1 MW scale at TUDA it is expected that oxygen carrier material at multi-ton scale will be needed. As the project does not explicitly entail up-scaling tasks, it is expected that natural ores or waste materials will need to be used, as these have low cost and demand less processing in comparison to synthetic materials.

The main objective with WP3 is to screen different types of oxygen carrier materials with specific emphasis on characteristics important for CLG. The partners involved in the WP have vast experience with oxygen carriers for CLC. Still, particles for CLG need to have special properties with respect to selectivity towards syngas in addition to stability at lower degrees of reduction.

This deliverable will report on testing carried out at Chalmers and CSIC, specifically within Task 3.3. After the preliminary selection of materials carried out in deliverable D3.1, four materials were selected to be tested in continuous units: Ilmenite, Tierga ore, LD-slag, and Sibelco Calcined. In addition, two more materials based on Mn have been also tested.

However, Sibelco calcined was not used in Task 3.3, as the provider discontinued production of this material and it was not possible to obtain this material in sufficient scale for multi ton operation.

Early on in the project it was established, that is not feasible to manufacture synthetic materials, mainly because of the costs involved in manufacturing a few tons of particles, needed at the end of the project. Hence, it was decided to focus on natural and waste materials. A significant amount of time was actually spent on sourcing materials from various suppliers, who could with high certainty be able to deliver oxygen carrier particles in a reasonable size range at multi-ton scale.

2.1 Partners

The research group at the division of Energy Technology at Chalmers University of Technology (CTH) is world leading in chemical-looping combustion. The 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): 500W (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.

3 Material and fuels

Considerable efforts have been made in this project in order to source materials, which can retrieve in enough quantities for demonstration in TUDA. This includes sourcing for Mn- and Fe-based materials from suppliers around the world at significant quantities in order to establish viability of receiving multi-tons of materials in the future.

As it has been discussed in deliverable 3.1, CSIC and CTH had a close discussion about sourcing of materials at both institutions, and they decided to pursue testing of the ores given in

Table 1.

Evidently, these are based mainly on Mn and Fe, and are natural materials or wastes. There is no task in the project related to material manufacturing, and thus it was decided together with TUDA that the primary focus should be on cheap, readily available oxygen carriers, as it was judged to be the only accessible way to obtain the amounts needed during the final demonstration at TUDA.

Table 1: Selected materials for initial screening at CTH and CSIC

Element (wt%)	Moanda-Gabon Mn ore	Wessels-South Africa Mn ore	Sibelco (calcined) Mn ore	Elwaleed B-Egypt Mn-Fe ore	Tierga-Spain Fe ore	LD slag Fe waste	Ilmenite Fe-Ti ore
Mn	46.7	39.8	49.9	32.3	0.05	2.2	0.2
Fe	5.1	14.6	5.2	21.6	54.9	13.7	33.1
Si	4.2	3.3	3.4	4.7	3.8	4.8	0.9
Al	3.8	0.2	4.2	1.2	2.1	0.5	0.3
Ca			1.9	1.7		27.3	0.2
XRD phases	Mn_2O_3, Fe_2O_3, Al_2O_3, SiO_2, CaO, MgO	Mn_2O_3, Mn_3O_4, Fe_2O_3	Mn_2O_3		Fe_2O_3, Al_2O_3, SiO_2, CaO, MgO		Fe_2TiO_5, Fe_2O_3, TiO_2
Active phases							
Mn_3O_4	67.5	65.6	64	44.8	--	3.0	--
Fe_2O_3	8.4	18.6	7.4	30.9	76	23.0	11.2
Fe_2TiO_5	--	--	--	--	--	--	54.7
Bulk density (kg/m^3)	2570	3150	3707	2800	3187	2764	4100
BET (m^2/g)	10.1	0.6	0.3	15.6	1.4	3.4	0.8
Porosity (%)	35.7	12.3	1.7	18.5	26.3	13.9	1.2

Different biomasses have been used for the tests in continuous units at CTH and CSIC, according to the selected in WP2. Table 2 shows the composition of the different biomasses.

Table 2: Selected materials for screening at CTH and CSIC

	Industrial wood pellets (IWP)	Straw Pellets (Straw)	Pine forest residue (PFR)	Black pellets (BP)
Proximate analysis (wt%)				
Moisture	5.6	8.8	8.0	6.9
Ashes	0.6	7.9	0.4	0.3
Volatile matter	78.5	75.0	77.8	74.2
Fixed carbon	15.3	8.3	13.8	18.7
Ultimate analysis (wt%)				
C	49.7	42.0	49.3	49.8
H	6.3	6.1	5.4	5.6
N	0.1	0.7	0.3	0.1
O	37.7	43.0	36.6	37.4
LHV (MJ/kg)	17.4	15.1	17.7	18.6

4   Methodology

The control of the oxygen used in syngas production is one of the most relevant operating conditions in the CLG process. In this process, the hot solids coming from the AR should give the heat necessary for the endothermic gasification reactions taking place in the FR. High solid circulation rates are usually used in CLC to provide both the heat and oxygen necessary to obtain full combustion of the biomass. In contrast to CLC, syngas is the desired final product in CLG. Therefore, perfect control of the lattice oxygen reacting in the FR is necessary. In this sense, three possible options could be adopted [1,2]:

- Decreasing the oxygen provided to FR by the control of the solids circulation rate of oxygen carriers. This can be archived by decreasing the airflow in AR. However, it should be considered that the heat transfer between the reactors is affected by solid circulation. Therefore, the circulation should be maintained above a certain level to be able to have good heat transfer between the reactors.
- The control of the solid circulation rate by using typical CLC oxygen carriers diluted with an inert (i.e. olivine or sand). However, the different attrition rates of the materials used in the mixture could affect the composition of the mixture along the time and so the operation. Other possibility includes the use of oxygen carriers with lower oxygen transport capacity. Under these conditions, the variation in the oxidation degree of the oxygen carriers is almost complete during each redox cycle.
- Feeding the fixed amount of oxygen, required in the FR for syngas production, into the AR. This control system fits for any solid circulation rate since uncouple the heat and mass transfer between the AR and FR, allowing an easier operation of the plant. To maintain fixed the gas velocity in the AR at different operating conditions, dilution of the air with N_2 is necessary, which could be obtained by recirculation of a part of the AR outlet stream. Under this control method, the oxygen carrier is always in a highly reduced state, which can affect the oxygen carrier behavior.

The first option has been tested in 10 kW unit at CTH and the third option was used by CSIC in 1.5 kW unit to determine the behavior of the Ilmenite and Tierga iron ore in the CLG of biomass.

In general, the main operating parameters affecting the CLG process are the temperature, the steam-to- biomass ratio (S/B), and the oxygen-to-biomass ratio, λ. This λ ratio considers the oxygen used in the FR for syngas production with respect to the stoichiometric oxygen needed to fully burn the biomass. At steady state conditions, this is the same as the oxygen transferred from the air to the oxygen carrier in the AR.

$$\lambda = \frac{2.F_{O2,ARin} - 2.F_{CO2,ARout} - 2.F_{O2,ARout}}{F_{bio}.\Omega_{bio}} \qquad (1)$$

The total oxygen demand of the biomass, Ω_{bio}, is calculated considering the elemental composition of the biomass, (obviously, the H corresponding to the moisture content is not here considered).

$$\Omega_{bio} = \frac{x_C\frac{32}{12} + x_H\frac{16}{2} + x_N\frac{32}{14} + x_S\frac{32}{32} - x_O}{16} \qquad (2)$$

The performance of the CLG unit was evaluated based on four parameters: biomass conversion, carbon conversion efficiency, syngas yield, H_2/CO ratio, cold gas efficiency and life time.

- Biomass conversion, X_b

The biomass conversion, X_b, is a measurement of the amount of solid fuel converted to gas in the CLG unit, i.e. both in the fuel and air reactor.

$$X_b = \frac{F_{C,FR,out}+F_{C,AR,out}}{F_{C,b}} = \frac{\left[F_{CO_2}+F_{CO}+F_{CH_4}+xF_{C_xH_y}\right]_{FR,out}+\left[F_{CO_2}\right]_{AR,out}}{\frac{1000}{12}F_b x_C} = \frac{F_{C,b}-F_{C,elut}}{F_{C,b}} \qquad (3)$$

- Carbon conversion efficiency, η_{cc}

This parameter represents the fraction of C contained in the biomass that it is converted to gas in the FR

$$\eta_{CC} = \frac{F_{C,FR,out}}{F_{C,b}} \qquad (4)$$

- Syngas yield, Y, (Nm³/kg dry biomass)

The syngas yield, Y, indicated the amount of H_2 and CO produced over the biomass fed into the system,

$$Y = Y_{H2} + Y_{CO} = \frac{G_{H_2}}{F_b} + \frac{G_{CO}}{F_b} \qquad (5)$$

- H₂/CO ratio

This ratio considers the ratio between the production of H_2 and CO in the process. It depends on the gasifying agent used and it is useful to consider the final use of the syngas.

$$H2/CO = \frac{Y_{H_2}}{Y_{CO}} \qquad (6)$$

- Cold gas efficiency, η_g

This parameter represents the fraction of energy contained in the syngas over the total energy of the biomass

$$\eta_g = \frac{F_{g,FR,out} \cdot LHV_g}{F_b \cdot LHV_b} \cdot 100 \qquad (7)$$

- Life time

Another relevant aspect to consider in the CLG process is the lifetime of the oxygen carrier particles considering its special feature. The lifetime (t_{life}) of the oxygen carrier particles is calculated after knowing the L_f, as shown in the following equation.

$$t_{life} = \frac{100}{L_f} \qquad (8)$$

L_f is the loss rate of fines that have a size smaller than 63 μm. These fines were collected from air-reactor filters, FR chimney and water sea. L_f is calculated as shown in the following equation:

$$L_f = \frac{\Delta m_{fines}}{\Delta t} \times \frac{1}{m_I} \qquad (9)$$

where the Δm_{fines} (kg) is the mass of fines collected at a time period of Δt (h), and m_I (kg) represents the corresponding oxygen carrier inventory in that period.

4.1 Experimental setup and methodology at CTH

4.1.1 10 kW unit experiments

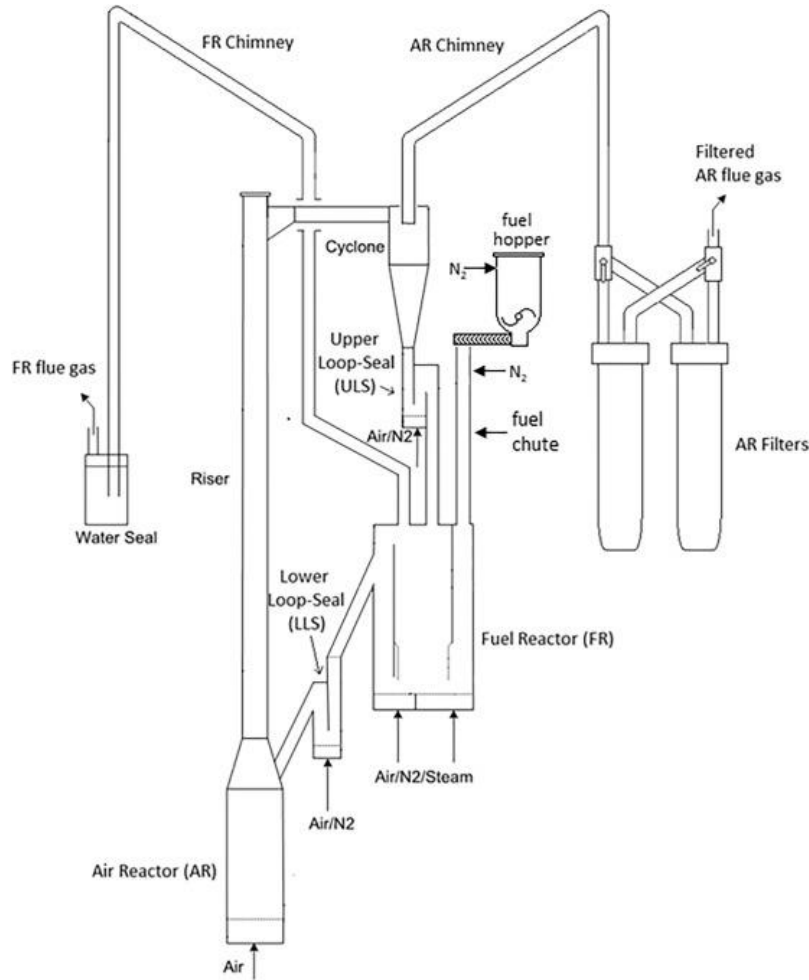Figure 1 shows a diagram of the 10 kW$_{th}$ CLG unit located at CTH.

Figure 1. 10 kW$_{th}$ CLG unit used at CTH [3]**.**

The 10 kW$_{th}$ unit at CTH has been used for CLC test before and modified to be able to accommodate CLG tests. A detailed overview of the unit can be found in our previous work published by Gogolev et al. [3]. The 10 kW$_{th}$ unit is based on the concept of interconnected circulating fluidized beds with a fuel reactor (FR) and air reactor (AR), where the gas velocity in the air reactor provides the driving force for particle circulation. Separation of the OC particles from air after AR is achieved by a cyclone. The bed height in FR is controlled by an overflow, which means the bed inventory in FR is fixed for each tested OC. Two loop seals have been used to avoid the gas leakage between FR and AR. The AR works at atmospheric pressure and the FR pressure is slightly higher than atmospheric; it can be adjusted by the level

of water in the water seal at the end of the chimney. The unit is enclosed in an oven. The main modification in 10 kW$_{th}$ unit was adding a volatile distributor in FR to be able to use the high volatile biomass residues for CLG. Figure 2 shows a section view of the volatile distributor.
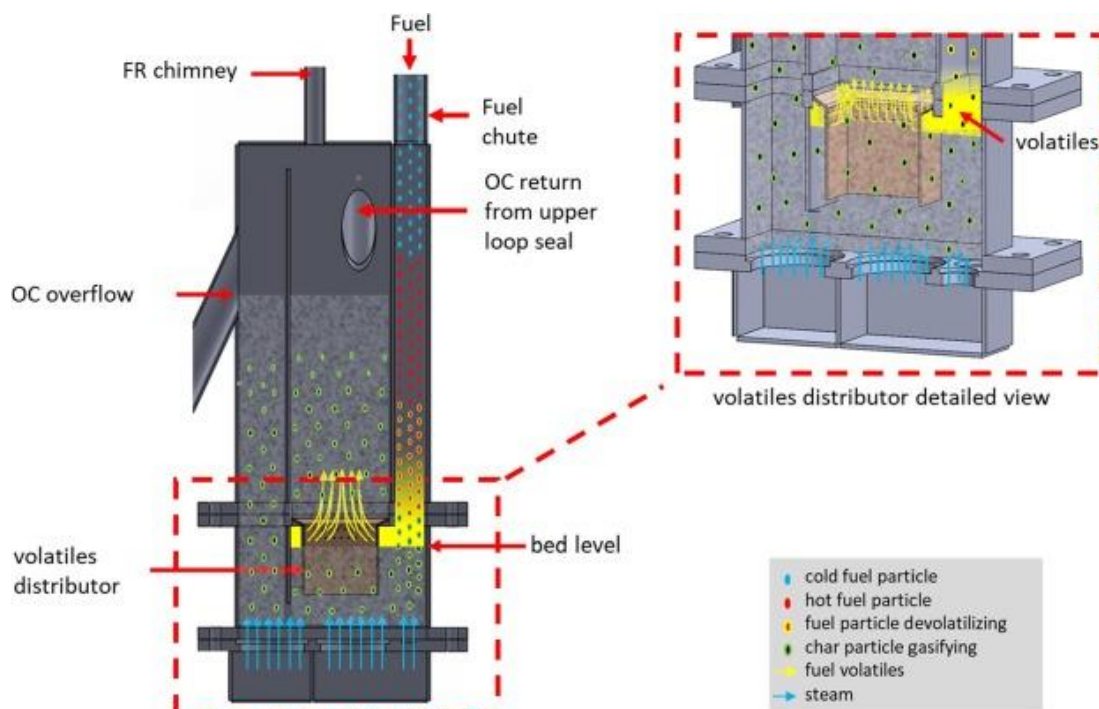

Figure 2. Section view of volatile distributor [3]**.**

The gas sampling system has been modified to be able to measure the product gases along with tar. The gas composition at the AR and FR outlet stream was analysed with several on-line gas analysers. The Solid-Phase Adsorption (SPA) method for measuring tar has been used and the method has been described by Israelsson et al. [4]. For tar sampling, flue gases was extracted from the FR chimney just above the furnace. Flue gases was sucked out into a heated line from the reactor using a venturi pump system. The line was heated to 350-375°C. From this line a 100 ml sample of flue gas 100 ml was extracted through a heated metallic filter with a mesh size of 7 µm to remove solid particles from the flue gas. This extraction was done using a pneumatic pump system connected with to the syringe that was pressed through a septum next to the heated metallic filter, see Figure 3. The 100 ml sample gas was sucked through a SPA (Solid Phase Adsorption) column that should absorb the tars in the sample gas. The SPA column was Superclean^{TM} Envi-Carb^{TM}/LC-NH$_2$ 3 ml tubes delivered by Supelco. The SPA columns were then by the end of the day transported to a freezer at -20°C and stored until elution was performed 1-2 days later. The elute from the SPA columns was analysed using a Bruker GC430 connected to an FID detector using hydrogen as carrier gas. A 30 m mid-polar column was used with a temperature program up to 340°C. Every sample was analysed three times and compared to an external standard containing: Benzene, Toluene, p-Xylene, o-Xylene, Styrene, Methylstyrene40, Methylstyrene60, Phenol, 2,3-benzo(b)furan, Indene, o-Cresol, p-Cresol, 1,2-dihydroNaphtalene, Naphthalene, 2-MethylNaphthalene, Intern standard, 1-MethylNaphthalene, Biphenyl, Acenaphthylene, Acenaphthene, Dibenzofuran, 1-naphtol, 2-naphtol, Fluorene, Xantene, Phenantrene, Anthracene, Fluoranthene, Pyrene, Crysene/Triphenylene.
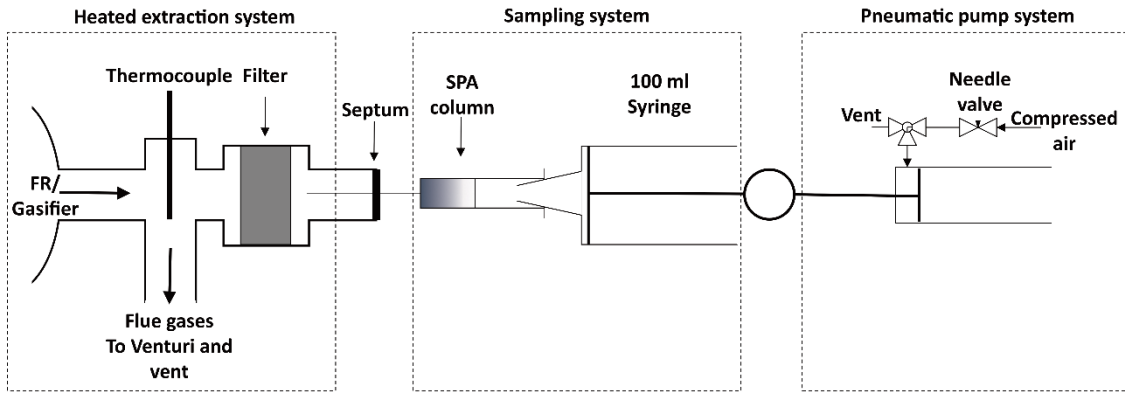
Figure 3. The entire tar sampling system. Left: Heated system where flue gas is extracted from the Fuel Reactor (FR). Middle: The sampling system where a needle pierces a septum to extract 100 ml filtered hot flue gas and tars are absorbed in the SPA column. Right: The Pneumatic pump system used to control the syringe to extract with same suction rate for every sample.

4.1.2 Operating parameters at CTH

The experimental procedure for all the oxygen carriers tested at CTH has been summarized in Table 3. In summary, more than 200 h of operational CLG tests under steady state have been carried out in the 10 kW$_{th}$ unit at CTH using four bed materials (Ilmenite, LD slag, Elwaleed B and silica sand) and three biomass fuels (Pine wood, Black Pellets and Straw pellets) to analyse the effect of the main operating variables.

Table 3: Operating conditions tested at CTH

Operation parameter	Unit	Oxygen carrier		
		Ilmenite		
Biomass		Pine wood	Straw pellets	Black pellets
Temperature	°C	820 - 970	820 - 970	820 - 970
Steam-to-fuel ratio	kg/kg$_{drybiomass}$	0.9 - 1.6	1.5 - 1.9	0.85
Oxygen-to-fuel ratio (λ)	mol/mol	0.1 - 0.6	0.3	0.2 - 0.65
		LD slag		
Biomass		Pine wood		Black pellets
Temperature	°C	820 - 970		820 - 970
Steam-to-fuel ratio	kg/kg$_{drybiomass}$	0.9 - 1.6		0.85 - 1.8
Oxygen-to-fuel ratio (λ)	mol/mol	0.1 - 0.7		0.1 - 0.7
		Elwaleed B		
Biomass		Pine wood		Black pellets
Temperature	°C	820 - 970		820 - 970
Steam-to-fuel ratio	kg/kg$_{drybiomass}$	0.9 - 1.6		0.85 - 1.8
Oxygen-to-fuel ratio (λ)	mol/mol	0.2 - 0.6		0.2 - 0.6
		Silica Sand		
Biomass		Pine wood	Straw pellets	Black pellets
Temperature	°C	820 - 970	820 - 970	820 - 970
Steam-to-fuel ratio	kg/kg$_{drybiomass}$	0.9 - 1.6	1.0 - 1.9	0.85 - 1.8

4.2 Experimental setup and methodology at CSIC

4.2.1 1.5 kW unit experiments

Figure 4 shows a diagram of the 1.5 kW_{th} CLG unit located at ICB-CSIC. The unit consists of two bubbling interconnected fluidized beds, fuel (FR) and air (AR) reactors, with solids circulating between them. The fuel and air reactors are connected by means of two loop seals. The biomass is fed by means of two screw feeders: the first controls the biomass feeding rate and the second one introduces the biomass as quick as possible into the reactor to avoid the pyrolysis in the feeding pipe. The reduced solids from the FR go to the AR through a fluidized bed (FB) loop seal to avoid gas mixing between reactors. In the AR, the oxygen carrier is oxidized and sent to the riser to be recovered by a cyclone and sent to a deposit acting as an upper loop seal. A solids valve provides control of the solids flow sent from this reservoir back to the FR. The solids circulation rate can be also measured by a solids diverter valve.

The oxygen carrier inventory into the facility was kept steady at about 2-3 kg, depending on the density of the oxygen carrier used. H_2O was used as fluidizing gas in the FR; meanwhile a mixture of N_2 and air was fed in the AR. This method allows us the perfect control of the oxygen used in the FR for syngas production.

The gas stream obtained at the FR can be used in a double way:
- It can be burnt with oxygen in an external reactor. The analysis of the O_2 consumed is used to calculate the oxygen demand by the syngas and help us to better close the mass balances. CO, CO_2 and O_2 are measured at the outlet.
- It can be sent to a tar recovery system at the desired flowrate. CO, CO_2, H_2, CH_4 concentrations were measured on-line after gas cleaning. Moreover, an off-line gas analysis was carried out in a gas chromatograph to analyse the presence of C1-C5 hydrocarbons in the gas outlet stream of the FR. The tar recovery system was installed according to the tar protocol [5].

In addition, CO, CO_2 and O_2 were analysed at the AR outlet stream. Several on-line gas analysers were used in the unit: a non-dispersive infrared (NDIR) analyser (Siemens Ultramat 23) was used for CH_4, CO and CO_2; a paramagnetic analyser (Siemens Ultramat 23 and Oxymat 6) was used for O_2 concentration measurement; and a thermal conductivity detector (Siemens Calomat 6) was used for H_2. A gas chromatograph (Perkin Elmer CLARUS 580) was used for the C1-C5 determination.

To better know the behaviour of the oxygen carriers during the process, solid samples were extracted both from the fuel and air reactors at different operating times. These samples were physically and chemically characterized and were used to obtain information about the oxidation degree of the oxygen carrier in the two reactors, as well as the evolution of the oxygen transport capacity and reactivity with time.

Finally, an off-line method for the sampling and analysis of tars based on the European Tar Protocol [5] was used. Figure 5 shows the scheme of the installation used. The liquid products sampled in isopropanol were used to quantify both the water and tar contents in the gas stream. Water content was determined in a Mitsubishi Karl-Fischer titrator KF-31. Tar determination was carried out with a gas chromatograph GC-2010 Plus coupled to a mass detector QP2020 from Shimadzu. Three standards were used for external calibration: Benzene 99.8% purity, Naphthalene 99%+ purity and EPA 525 PAH MIX-A certified reference material that contains a total of 13 analytes. Furthermore, standard solutions of four different concentration levels,

obtained by suitable dilutions of the standard reference, were prepared to implement the calibration.
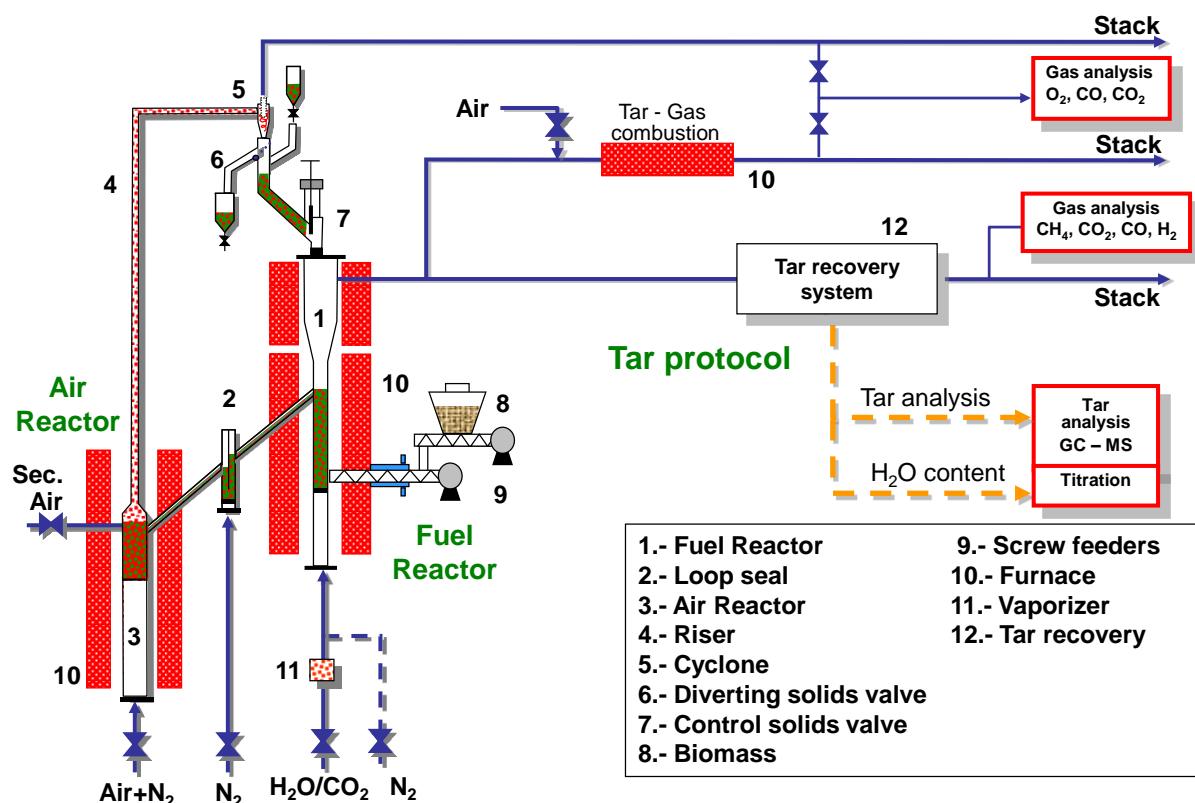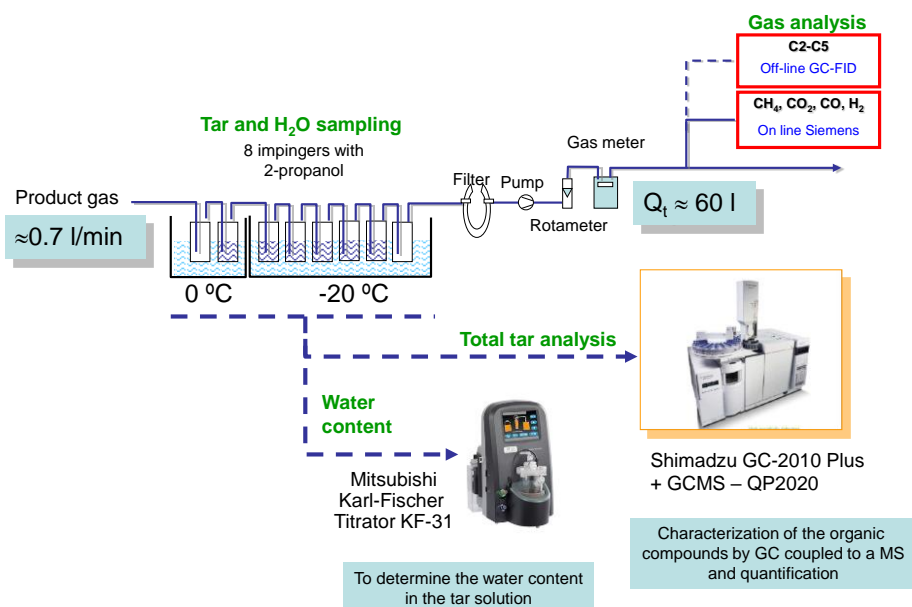

Figure 4. 1.5 kW CLG unit used at CSIC.

Figure 5. Scheme of the tar sampling and analysis system used at CSIC.

4.2.2 Operating parameters at CSIC

The experimental procedure was similar for all the oxygen carriers tested: ilmenite, Tierga iron ore, LD slag, and Gabon Mn ore. In summary, more than 200 h of operational CLG tests under steady state have been carried out in the 1.5 kW$_{th}$ unit at CSIC to analyze the effect of the main operating variables. In addition, the effect of use CO_2 as gasifying agent instead of the usual H_2O was tested with the LD slag oxygen carrier. Table 4 gives the range of operating variables used for each bed material.

Table 4: Operating conditions tested at CSIC.

Operation parameter	Unit	Oxygen carrier			
		Ilmenite	Tierga iron ore	LD slag	Gabón Mn ore
Biomass		IWP	IWP	IWP	IWP
Temperature	°C	820 - 940	820 - 940	820 - 940	820 - 940
Steam-to-fuel ratio (S/B)	kg/kg$_{drybiomass}$	0 - 0.9	0 – 0.6	0 – 0.6	0 – 0.6
Oxygen-to-fuel ratio (λ)	mol/mol	0.15 - 0.35	0.15 – 0.50	0.15 – 0.50	0.15 – 0.50
Hot circulation	h	75	52	70	55
Gasification time	h	55	40	60	50

5 Results from the experimental evaluations (CTH, CSIC)

The experimental work was conducted in close collaboration with CSIC and CTH in order to achieve as much information about the materials as possible. As discussed above the units are highly complementary, and it was decided to investigate that the most promising materials in both plants using two different strategies for CLG.

5.1 Work performed at CTH

Based on the work in Tasks 3.1 and 3.2, selected oxygen carriers were evaluated in continuous 10 kW$_{th}$ unit CTH using solid biomass fuel. In CTH, normal silica sand, as a reference case, has been tested in 10 kW$_{th}$ unit in addition to three selected oxygen carriers to better understand the effect of CLG compare to conventional steam gasification.

The aim of this task is to select a promising oxygen carrier for CLG test in Task 3.4 in small pilot plants (50 kW$_{th}$ at CSIC and 100 kW$_{th}$ units at CTH).

5.1.1 Results obtained in the 10 kW$_{th}$ CLG unit

-Effects of different biomass fuels

Using ilmenite as an oxygen carrier in the 10 kW unit at CTH, several biomass fuels were studied. The operating conditions are summarized in Table 3. Figure 6 shows the results of experiments with biomass fuels and Ilmenite at 970 ºC and steam to biomass ratio of 1.7.

The results show that H$_2$ to CO ratio for the straw pellets is 1.6 and higher than the ratio obtained by using pine forest residue or black pellets. This can be due to the high ash content in straw which acts as a catalyst for the water gas shift reaction and increase the yield of H$_2$. However, values between 58 and 66 % were obtained for syngas yield which shows the different composition of fuels has negligible effects on syngas yield. The carbon capture efficiency for all the fuels is higher than 98% and confirms that fuel has been converted to gases in FR with minimum char transferred to AR.
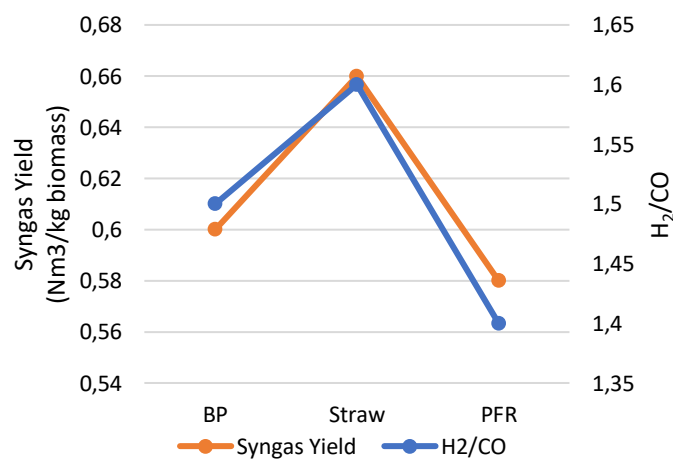

Figure 6. Effect of biomass fuels on the CLG process using Ilmenite as an oxygen carrier. T=870 ºC, λ= 0.2, S/B=0.95.
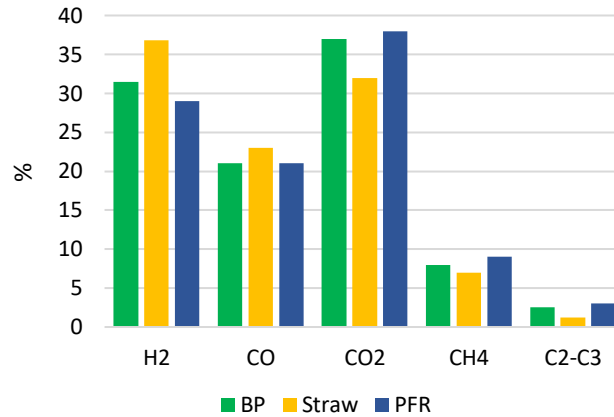
Figure 6 (continued). Effect of biomass fuels on the CLG process using Ilmenite as an oxygen carrier. T=870 ºC, λ= 0.2, S/B=0.95.

-Effects of temperature

The effect of increasing the operating temperature of CLG, from 870 ºC to 970 ºC, on gas biomass conversion, syngas yield and H_2/CO ratio is shown in Figure 7 (continued). The biomass conversion has been increased with increasing temperature using all three selected oxygen carriers. Also, the biomass conversion in CLG is generally higher than the conventional steam gasification using silica sand. In case of the H_2/CO ratio, increasing temperature resulted in higher H_2/CO in CLG. However, Elwaleed B has the lower H_2/CO than ilmenite and LD slag at all the temperatures, due to its higher oxygen transport capacity.

The H_2/CO ratio for conventional steam gasification, using sand as a bed material, is slightly higher than CLG using ilmenite or LD slag at higher temperatures. However, the syngas yield for conventional steam gasification is about 30% less than the syngas yield in case of CLG.
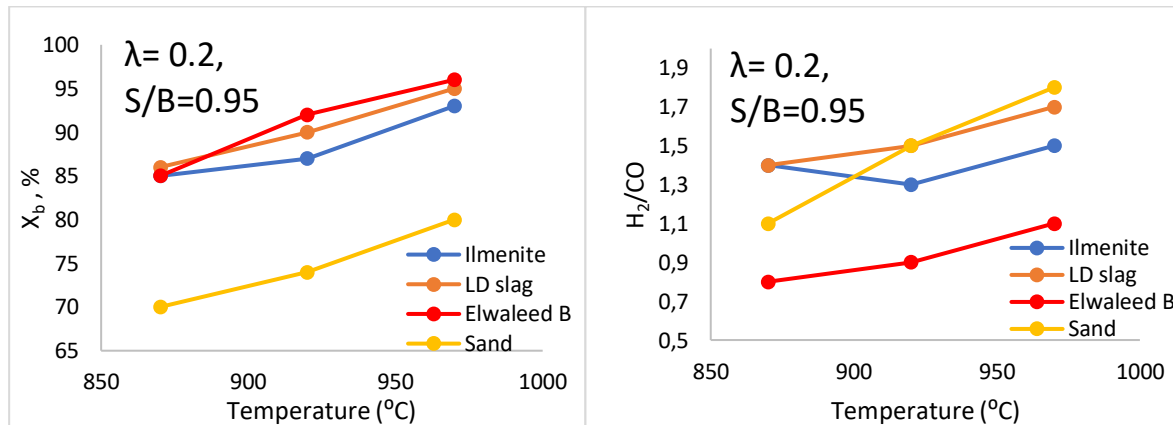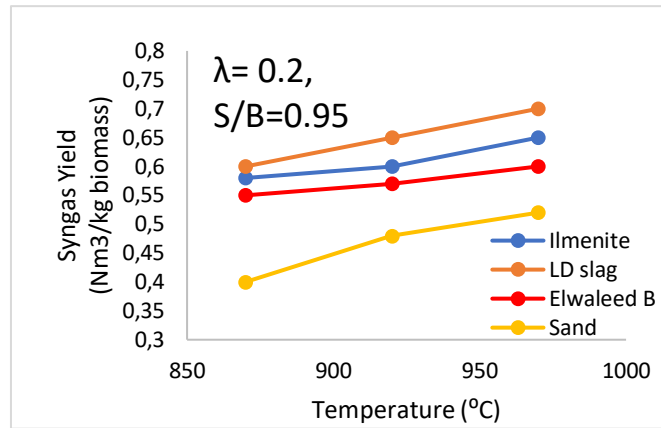

Figure 7: Effects of temperature on CLG.

17

Figure 7 (continued): Effects of temperature on CLG.

-Effects of steam to biomass ratio, S/B

Steam has been used in CTH as the gasifying agent. It is well known that increasing the ratio of steam to biomass will increase the gasification rate and also will increase the production of hydrogen via water gas shift reaction. The effects of steam to biomass ration have been investigated in the 10 kW$_{th}$ unit using the three selected OCs and the silica sand, and the results are presented in Figure 8. Increasing the S/B ratio from 0.95 to 1.7, will increase the biomass conversion during conventional gasification from 80% to 85%, respectively. Increasing steam to biomass ratio, S/B, has no significant effect on biomass conversion in case of CLG. In CLG, the biomass conversion is above 90% for all tested oxygen carriers at 970 ºC. However, Increasing S/B ratio from 0.95 to 1.7, will increase the biomass conversion during conventional gasification from 80% to 85%, respectively. The syngas yield and H$_2$/CO ratio will increase by increasing the S/B ratio due to the water gas shift reaction. In general, the H$_2$/CO ratio and syngas yield for LD slag are slightly higher than the values for ilmenite and much higher than for Elwaleed B. LD slag has the lower oxygen transport capacity than ilmenite and Elwaleed B, which is more favorable for gasification. Also, LD slag has high amount of calcium, 27.3 wt%, which catalyzes the water gas shift reaction and leads to higher syngas yield and H$_2$/CO ratio compared to ilmenite and LD slag.
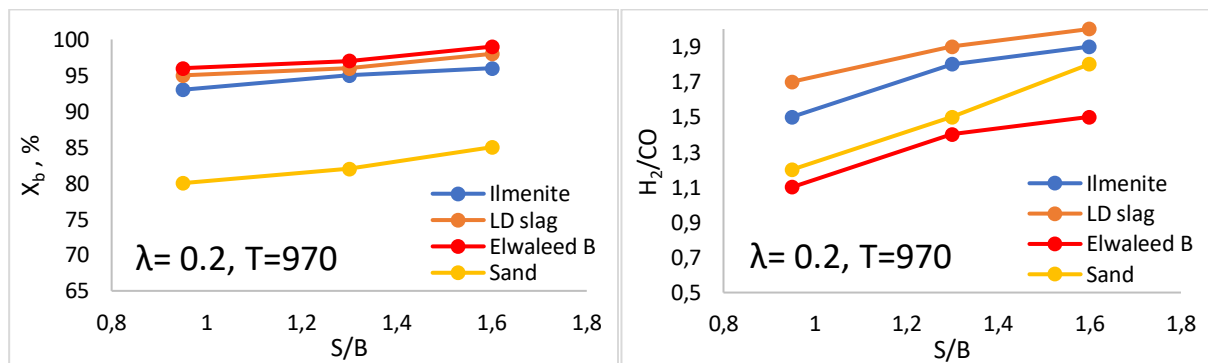

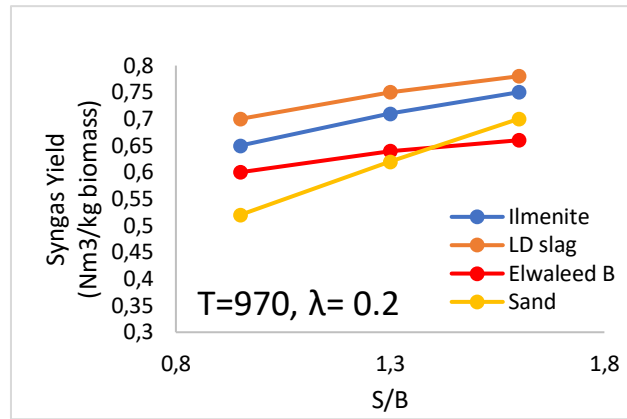**Figure 8. Effects of S/B ratio on CLG, T=970 ºC, λ= 0.2.**

Figure 8 (continued). Effects of S/B ratio on CLG, T=970 ºC, λ= 0.2.

- Effects of the air-to-fuel ratio, λ.

The most relevant parameter affecting syngas composition is obviously the oxygen-to-biomass ratio, λ. Figure 9 shows the results obtained with the selected oxygen carriers using PFR. The highest syngas yield and H_2/CO were obtained at low λ values. This is due to the increase of the combustion reactions over the gasification and reforming reactions at higher λ. However, it should be considered that autothermal CLG conditions should be reached and a preliminary study carried out showed that λ values in the range 0.2-0.4 are required. In general, very high biomass conversion, X_b, was obtained, with values above 85% in most of the cases and the conversion improved by increasing λ.
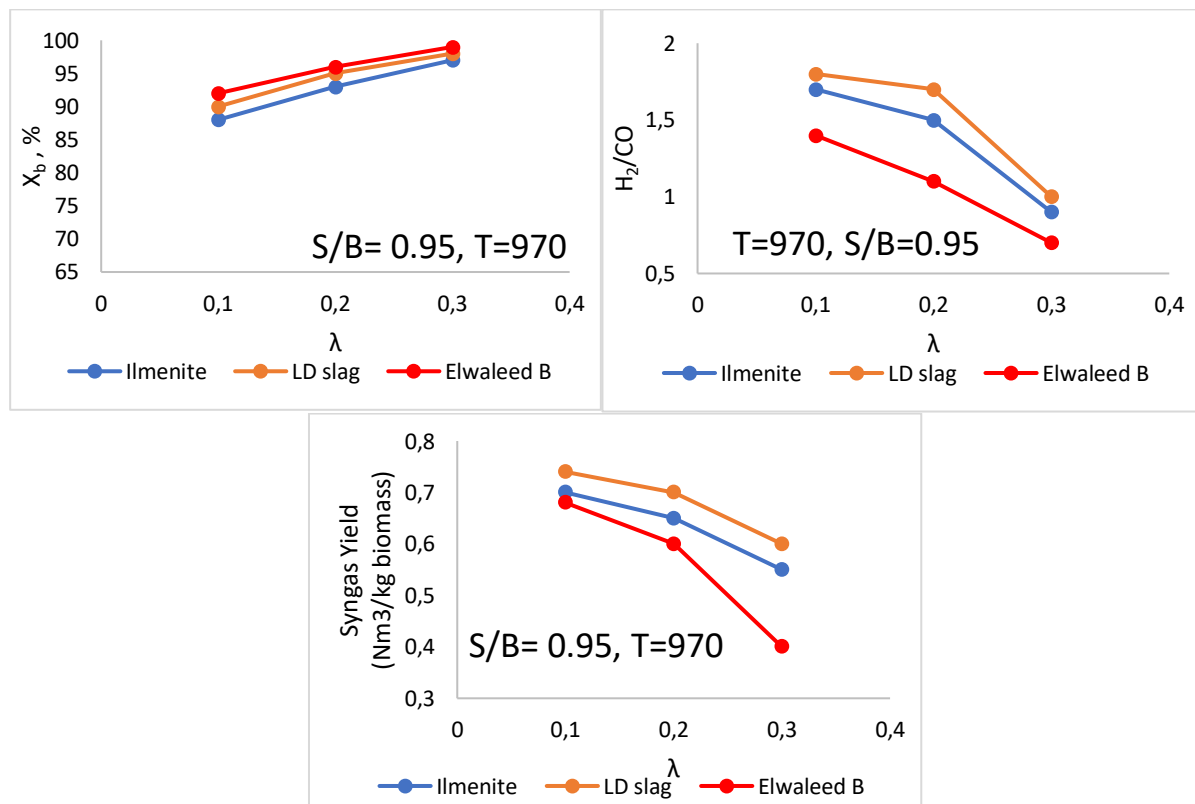

Figure 9. Effects of the air-to-fuel ratio, S/B= 0.95, T=970ºC

5.1.2 Tar generation with the different oxygen carriers

From the continuous CLG operation in 10 kW unit at CTH, it was observed that the most pronounced species of tars were the unbranched 6-carbon ring aromatics. Benzene was by far the most dominant species, followed by naphthalene and phenanthrene. This was observed for all bed materials, independent of having oxygen carrying properties or not. It was only at 870°C with a high load that significant amounts of more branched compounds, such as phenol, where detected. It was observed that the amount of tars where significant lower for LD slag compared to ilmenite and sand operated in similar conditions.

Figure 10 shows the results tar evaluation for CLG operation in 10 kW at CTH using oxygen ilmenite and LD slag as and oxygen carrier and sand as a reference. Based on the results the ratio between higher carbons, 3-rings and 4-rings, towards sum of BTX (benzene, toluene and xylene) were highly affected by the oxygen carrier. The lowest amounts where observed for LD slag at 970°C with PFR as fuel. Comparing the 4-ring/BTX ratio using different bed materials at 8 kW load, ilmenite hade roughly 3 and sand 10 times higher ratio than LD slag. For the 3-ring/BTX ratio at the same experiments, ilmenite hade roughly 2 and sand 5 times higher ratio than LD slag.
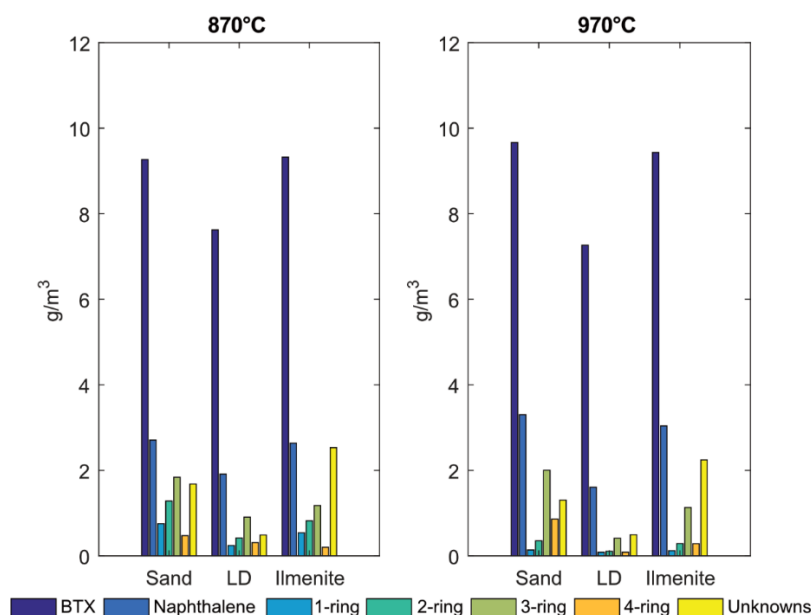

Figure 10. Measured and identified tar amounts for Sand, LD slag and Ilmenite used as bed materials for CLG operation in the 10 kW chemical looping reactor operated with PFR fuel with a load of 8 kW.

In Figure 11 the tar results from experiments with LD slag in the 10 kW unit at CTH are displayed. Two different fuels, PFR and BP, at two different fuel loads and at three different temperatures. It is observed that the tar amounts decrease with increased temperature and that higher load increases the amount of tars. BP generally generated higher amounts of tars compared to PFR.
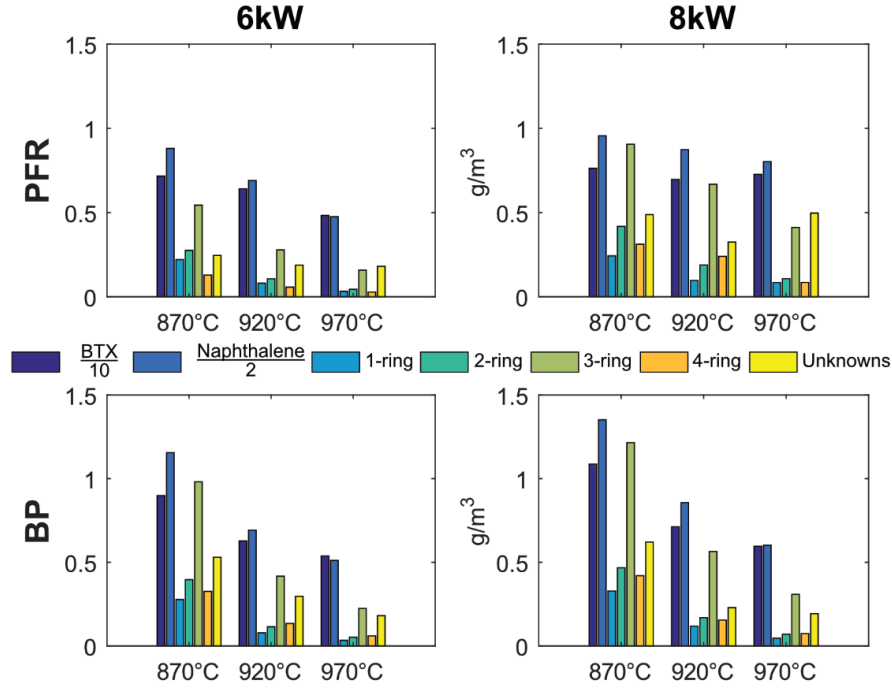
Figure 11. Measured and identified tar amounts using LD slag as bed material in 10 kW reactor. The temperature, fuel and fuel load are given in the table. Generally, the amount of tars where decreasing at higher temperatures. Observe that both BTX and naphthalene is divided with 10 respectively 2 to be able to see the other tar species better in the figure.

5.1.3　Summary of the results from CTH

Table 5 shows experimental data for the 4 materials tested at CTH. For a better comparison, the data has been normalized at S/B=0.95, T=970°C, λ=0.2, using PFR as fuel.

Based on the results in Table 5, using CLG of biomass with natural ores and waste materials as an oxygen carrier is viable for production of high purity syngas. High biomass conversion and carbon conversion efficiency were obtained at all operating conditions and for all oxygen carriers, with values above 90%. The syngas yield for CLG using all oxygen carriers were higher than steam gasification using sand. Also, the tar yield during CLG using oxygen carriers for gasification was significantly lower compared to steam gasification using sand. Among the oxygen carriers, LD slag has slightly higher H_2/CO ratio and syngas yield with the lowest tar yield. However, circulation problems were detected during operation with LD slag without heat pre-treatment. Therefore, calcination and sieving of LD slag prior to the operation is essential which is not necessary for ilmenite. Elwaleed B showed the lowest H_2/CO ratio and lifetime, compare to ilmenite and LD slag. Therefore, ilmenite is considered to be the best candidate for CLG operation at large scales considering syngas yield, lifetime, cost of pre-treatment.

Table 5: Comparison of oxygen carriers according to data obtained at CTH

Parameter	Unit	Oxygen Carrier			
		Ilmenite	LD slag	Elwaleed B	Sand
Gas composition					
CO_2	%vol	37	35	41	22
CO	%vol	22	20	24	27
H_2	%vol	29	34	26	32
CH_4	%vol	8	8	7	13
C2-C3	%vol	4	3	2	6
Biomass conversion, X_b	%	93	95	96	80
H_2/CO	-	1.5	1.7	1.1	1.2
Syngas yield, Y	m^3/kg dry biomass	0.65	0.70	0.60	0.52
Tar	g/Nm^3	8-18	4-10	NA	20-45
Lifetime	hour	850	800	370	NA

5.2 Work performed at CSIC

Selected oxygen carriers in Task 3.1 are evaluated at CSIC in parallel with CTH to collaborate with a comprehensive understanding and evaluation of the more suitable oxygen carriers for CLG under testing in continuous units (1.5 kW$_{th}$ at CSIC and 10 kW$_{th}$ units at CTH). The intention in this work is not to repeat the research, but rather to obtain complementary and more robust results and information for the selection materials to be used in Task 3.4 in small pilot plants (50 kW$_{th}$ at CSIC and 100 kW$_{th}$ units at CTH).

5.2.1 Results obtained in the 1.5 kW$_{th}$ CLG unit

At CSIC, a systematic study of the CLG process has been carried out analyzing the effect of the main operating parameters. Below the gas composition and the parameters are shown indicating the efficiency of the process (biomass conversion, X_b; carbon conversion efficiency, η_{cc}; syngas yield, Y; and cold gas efficiency, η_g). Figures 13 to 16 shows the gas composition and the main efficiency parameters as a function of the different operating conditions for the four oxygen carriers: ilmenite, Tierga iron ore, LD slag and Gabon Mn ore.

- Effect of temperature. As a general rule, the temperature hardly affects the gas composition (dry and N_2 free basis), which agrees with the thermodynamic predictions. However, it is remarkable also the amount of hydrocarbons present in the gas phase, being CH_4 the most popular with amounts about 10 vol-%, and the rest, C2-C3 in the order of 1-2 vol%. No hydrocarbons higher than C3 were detected.

Biomass conversion showed always very high values, above 90% in most of the conditions and increased when the temperature ranged from 820 to 940 ºC as a consequence of the higher reaction rates of the reactions. This produced a slight increase in the syngas yield and cold gas efficiency. In addition, the higher gasification conversion in the FR led to less carbon transport to the AR, increasing in that way the carbon conversion efficiency, η_{cc}, which was always very high, above 90%.

- Effect of steam to biomass ratio, S/B. In the CLG process, water is used as gasifying agent and as fluidizing gas in the FR. At CSIC, a reference case using N_2 for fluidization was considered to better determine the effect of water in the process, and an S/B ratio of 0.6 was considered as usual for comparison reasons. Steam represents a relevant cost in the process and should be used as low amount as possible to improve process economy but maintaining high the biomass conversion.

As general rule, an increase in the S/B ratio produces an increase in the H_2 and CO_2 concentration and a decrease in CO, mainly due to the effect of the water gas shift equilibrium. The higher steam feeding also produces an increase in the gasification reaction rate, which leads to an increase in the biomass conversion and carbon conversion efficiency, reaching always very high values. In contrast, was observed a low effect of the H_2O addition on the reforming of CH_4 and other hydrocarbons and similar amounts of these compounds are found at the outlet of the FR. As a consequence, a small variation was observed in the syngas yield obtained with S/B ratio within the usual values here analysed (0-0.9).

In any case, the amount of the H_2O fed used in the gasification or reforming reactions is rather low and most of it goes out without reacting, acting only as fluidizing agent. This fact should be considered when the mass and heat balances were carried out since the heat necessary to steam production could be an important fraction of the heat needed in the global system.
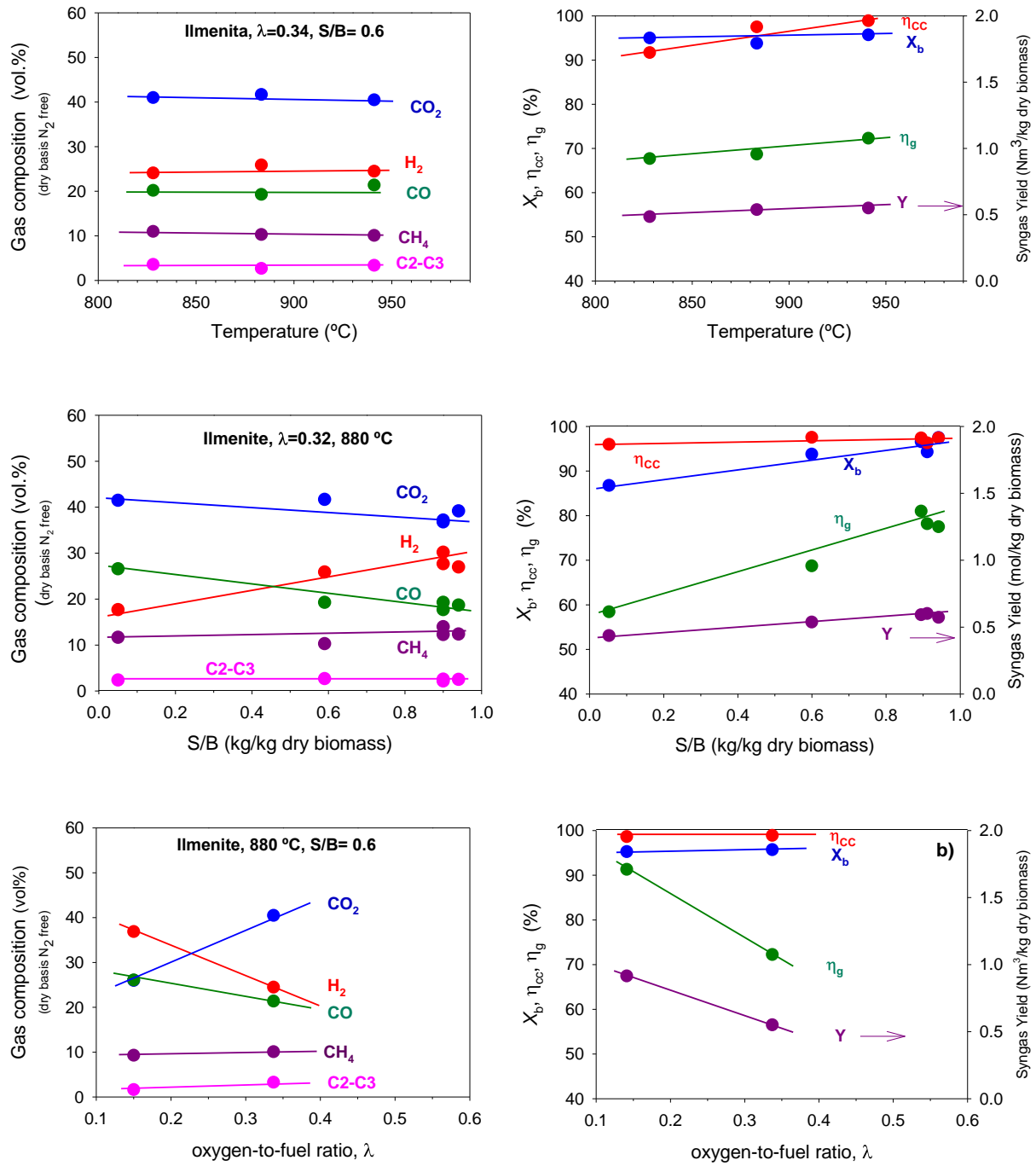
Figure 12. Effect of operating parameters on the syngas composition and on the gasification performance using ilmenite as oxygen carrier.
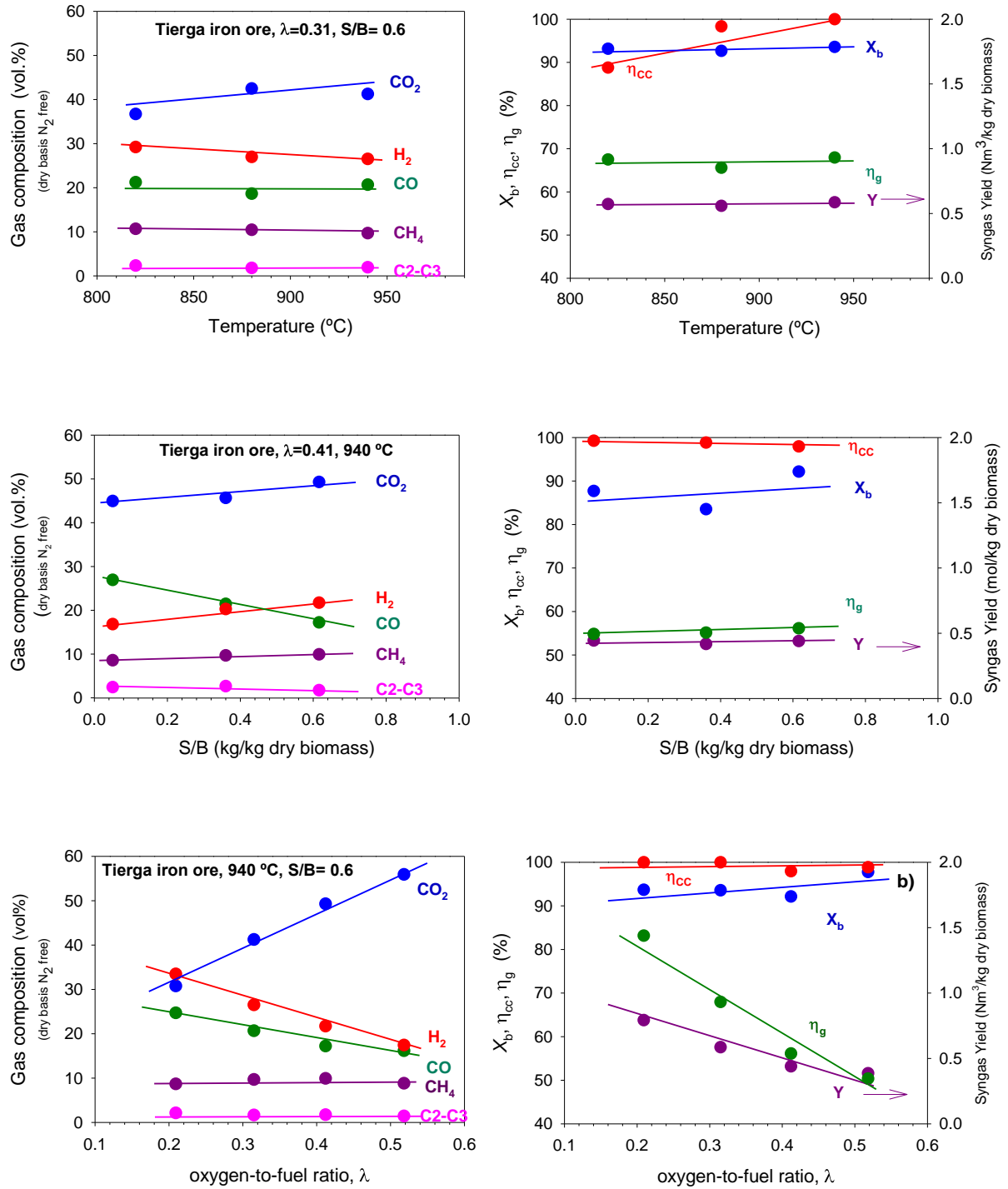
Figure 13. Effect of operating parameters on the syngas composition and on the gasification performance using Tierga iron ore as oxygen carrier.
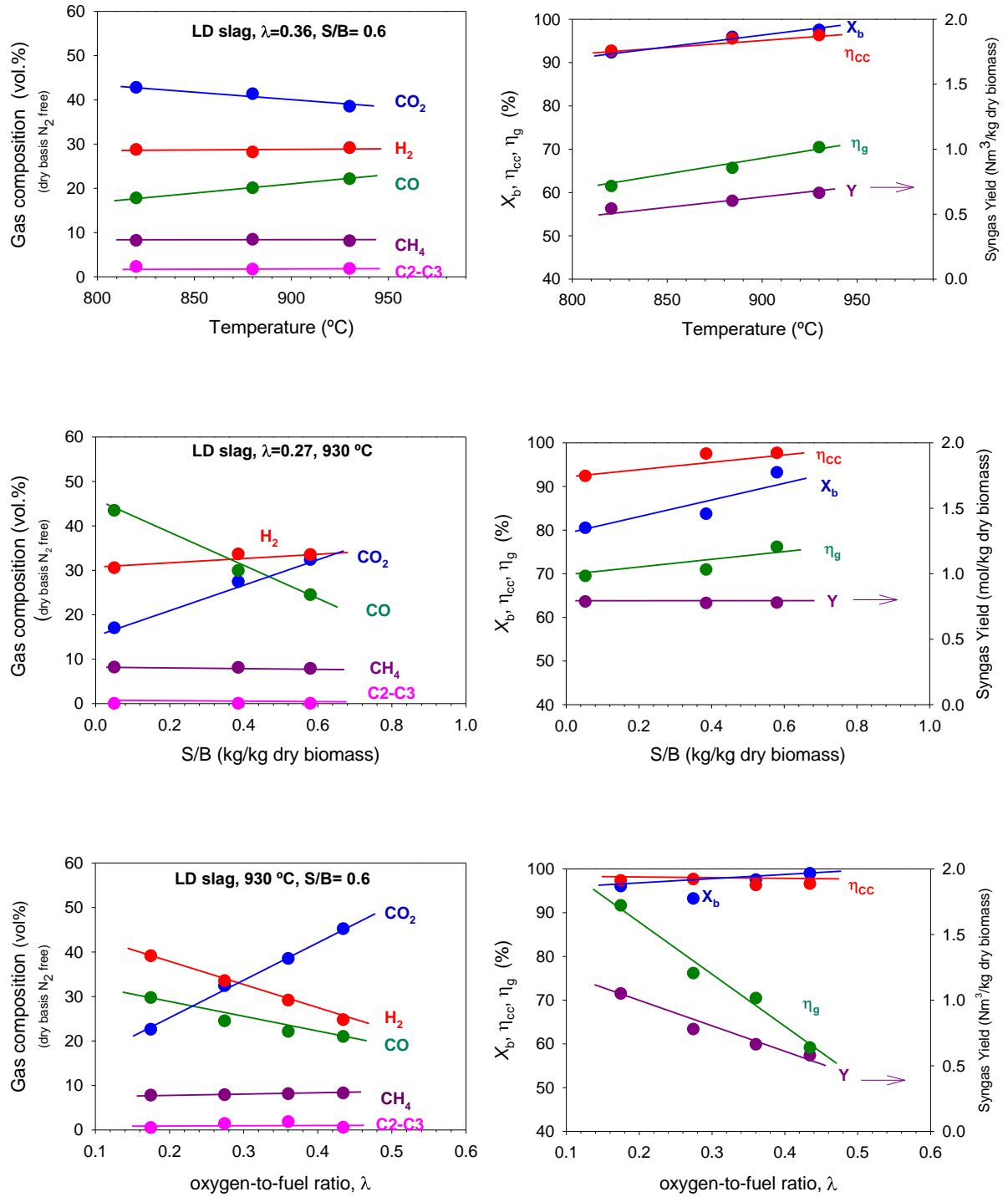
Figure 14. Effect of operating parameters on the syngas composition and on the gasification performance using LD slag as oxygen carrier.
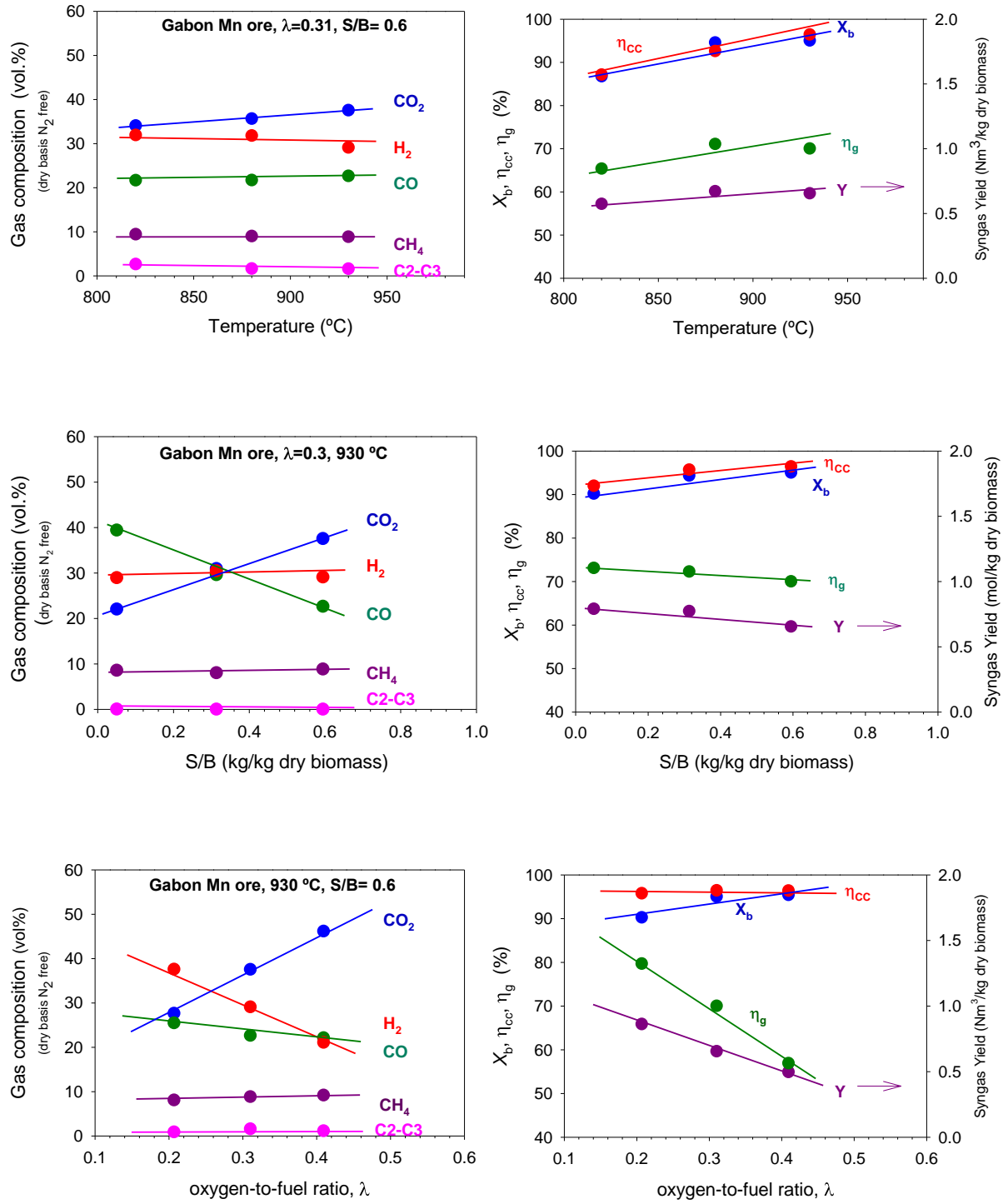
Figure 15. Effect of operating parameters on the syngas composition and on the gasification performance using Gabon Mn ore as oxygen carrier.

- Effect of the air-to-fuel ratio, λ. The air-to-fuel ratio is the main operating variable affecting to the syngas yield since represents the amount of oxygen used for the syngas production. It is seen than CO and H_2 concentration decrease with increasing λ. In contrast, CO_2 concentration significantly increases because more oxygen reacts with biomass and therefore, more biomass is used for combustion instead of producing syngas. It is also remarkable that the amount of CH_4 and other hydrocarbons remain almost constant in spite of the very different lattice oxygen present in the fuel reactor. This is likely due to the bad contact between volatiles and oxygen carrier in the fluidized bed, the low reaction reactivity of the oxygen carrier with respect to these compounds, or the fact that the contact time with the oxygen carrier in this unit is not enough to burn or reform them with H_2O in this CLG unit. However, it is probable that the amount of these compounds will be lower when operating in a circulating CLG unit operating at higher gas velocities.

Obviously, the cold gas efficiency and syngas yield decrease for higher values of λ because more biomass is burned in FR instead of producing syngas. In contrast, an increase in the biomass conversion and carbon conversion efficiency was observed with increasing λ values, reaching always very high values, above 90% in the majority of the operating conditions.

After more than 200 h of continuous operation with the different oxygen carriers it was concluded that the method for controlling lattice oxygen used in this work resulted to be an easy and accurate method for the operation of the CLG process, since the solids circulation rate can be fit at the optimum values independently of the oxygen transported between reactors.

However, a relevant advantage of the CLG process with respect to other gasification processes is due to the heat balance in the fuel and air reactors, in such a way that the hot solids coming from the AR should be enough to give the heat necessary for the endothermic reactions taking place in the FR, with the possibility to reach an autothermic process in the whole system. Preliminary heat balances made at ICB-CSIC indicate that this autothermic process is reached at λ values between 0.3 and 0.4, depending on the assumptions made and on the amount of CH_4 considered.

For a better comparison among oxygen carriers in order to select the most promising materials to be tested at higher scale in the Task 3.4, the same operating conditions were selected for all of them: λ =3.5, S/B=0.6, and a range of temperature 900-940 ºC. Figure 16 and Figure 17 shows the gas composition and efficiency parameters for the four oxygen carriers tested at CSIC.
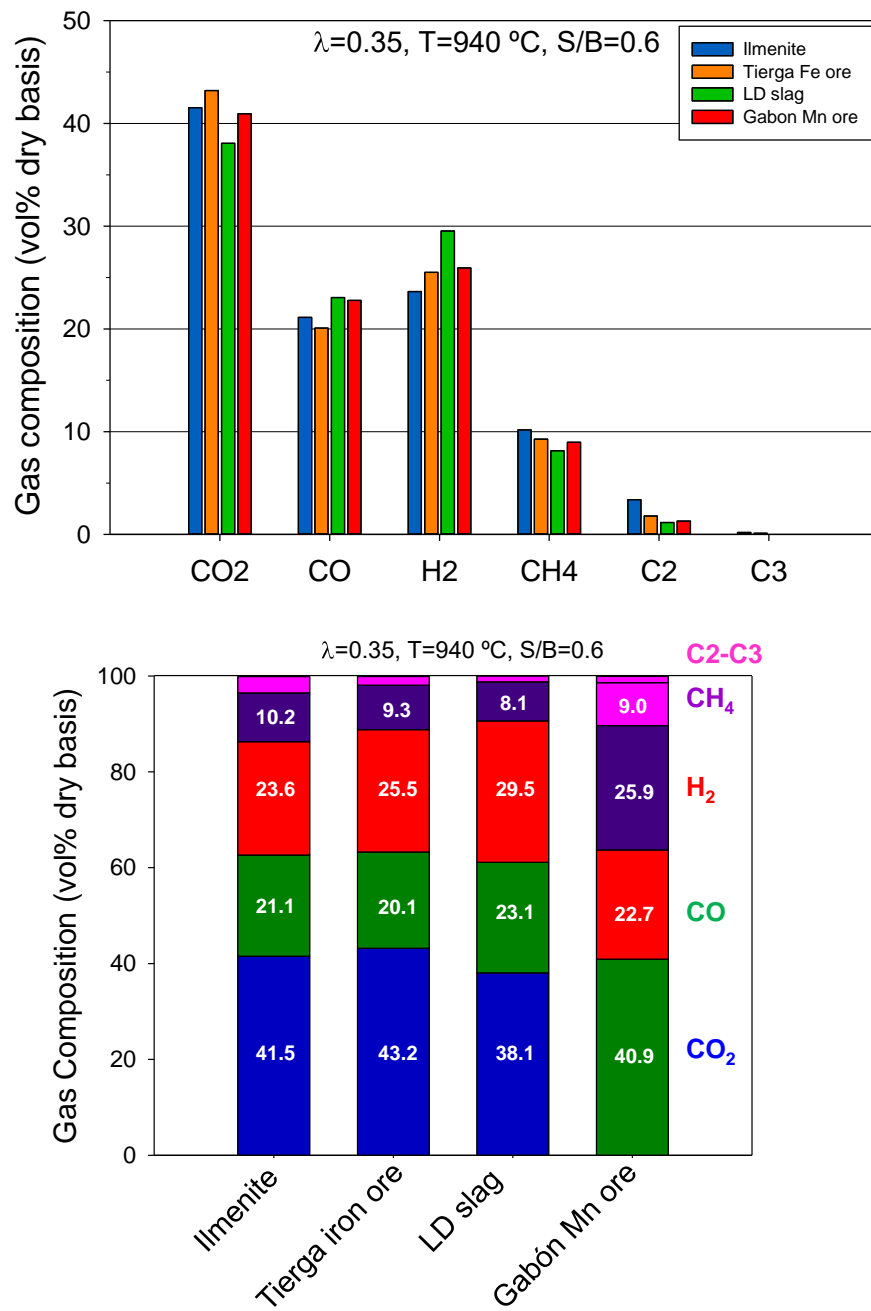
Figure 16. Comparison of gas composition normalized at λ=0.35, S/B=0.6 and T=940ºC for the different oxygen carriers tested at CSIC.

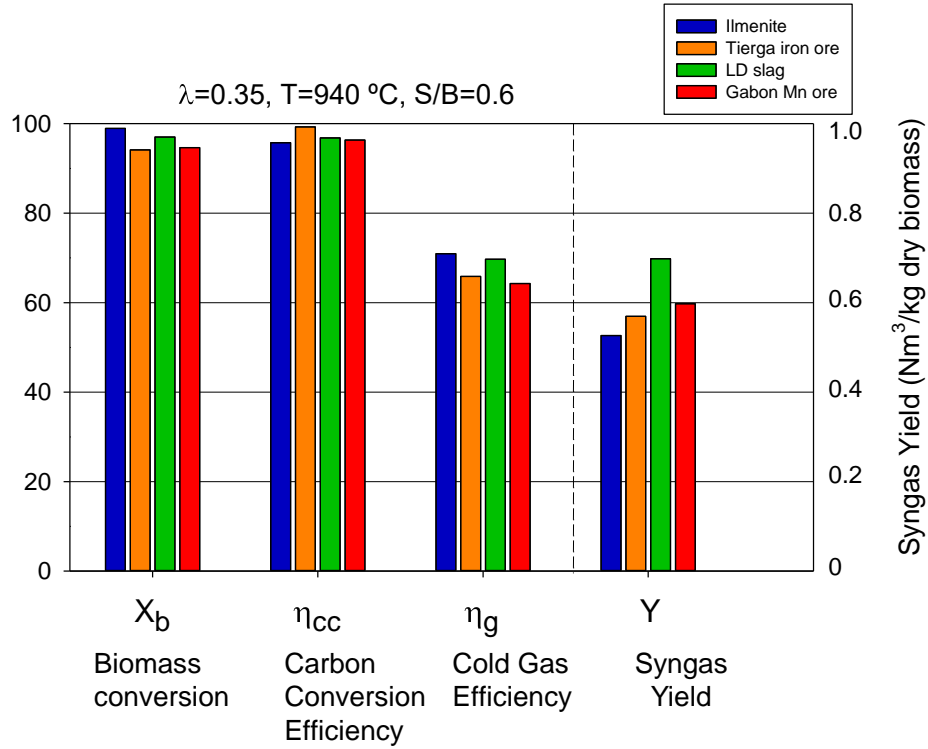**Figure 17. Comparison of gasification performance normalized at λ=0.35, S/B=0.6 and T=940°C for the different oxygen carriers tested at CSIC.**

5.2.2 Fluid-dynamic behavior of the oxygen carriers

The fluid-dynamic behavior of the materials used in the fluidized bed represents an important indicator of the suitability of the material to be used in a CLG process. It should be remembered that, according to the method herein used to control the oxygen used in the syngas production, the oxygen carrier is highly reduced in the FR. This could have relevant consequences in some oxygen carriers if the reduced materials are prone to agglomerate. However, it is remarkable that no defluidization or agglomeration was observed for any of the experiments carried out with any of the materials tested.

Another relevant aspect to consider in the CLG process is the lifetime of the oxygen carrier particles considering its special feature. Figure 18 shows the attrition rate obtained for the four oxygen carriers tested at CSIC during the continuous operation in the 1.5 kW$_{th}$ unit. The x-axis corresponds to the total operation time circulating at hot conditions, most of them corresponding to gasification conditions at steady state. Values between 0.16 and 0.62 were found, which corresponds to lifetime values in the range from 165 h to 625 h obtained for LD slag and ilmenite, respectively. These values are lower than the normally obtained during operation at combustion conditions, as can be seen, for example, for ilmenite where a lifetime of 1300 h was obtained under CLC conditions in the same unit. This is probably due to the more extreme conditions that the oxygen carrier should endure in CLG with respect to CLC.
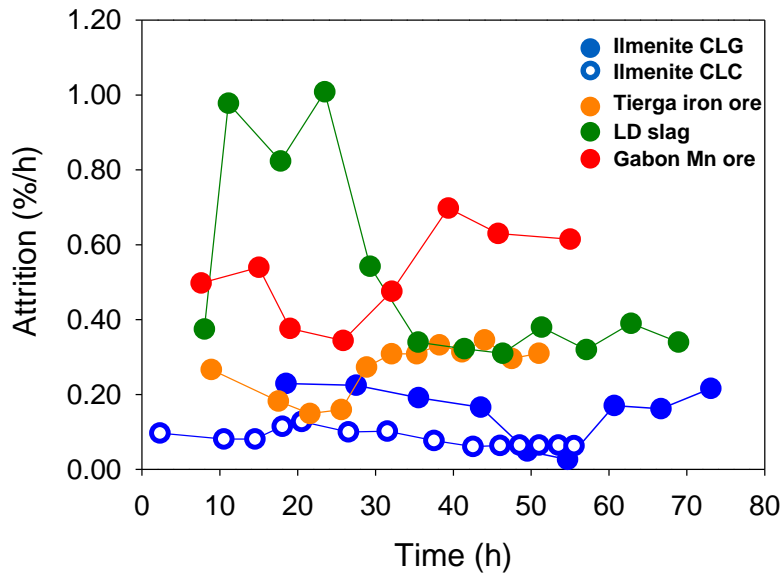
Figure 18. Attrition rate during the continuous operation with the different oxygen carriers.

5.2.3   Tar generation with the different oxygen carriers

As explained above, the tar protocol was used for tar recovery and a Gas Chromatograph coupled to a Mass Spectrometer was used for the quantification of the different compounds. Tar concentration in the gas product decreased with fuel reactor temperature, the air to fuel ratio and the steam to biomass ratio.

Figure 19 shows a comparison of the tar generation as a function of gasification temperature for the different oxygen carriers in 1.5 kW unit at CSIC. This graph includes data corresponding to different λ values, although the effect of this parameter was low. The largest tar content was obtained with the Gabon Mn ore. The tar content was lower for the other materials based on iron, due to the catalytic effect of Fe on tar reforming. The lowest values were found for ilmenite and LD slag, with values ranging from 0.9 and 3.5 g/Nm^3.

In all operating conditions and for all materials, the major compounds detected were always naphthalene, indene, biphenyl and phenanthrene. Benzene was detected, but in small amounts. As an example, Figure 20 shows, as an example, the distribution of these compounds using ilmenite as oxygen carrier.
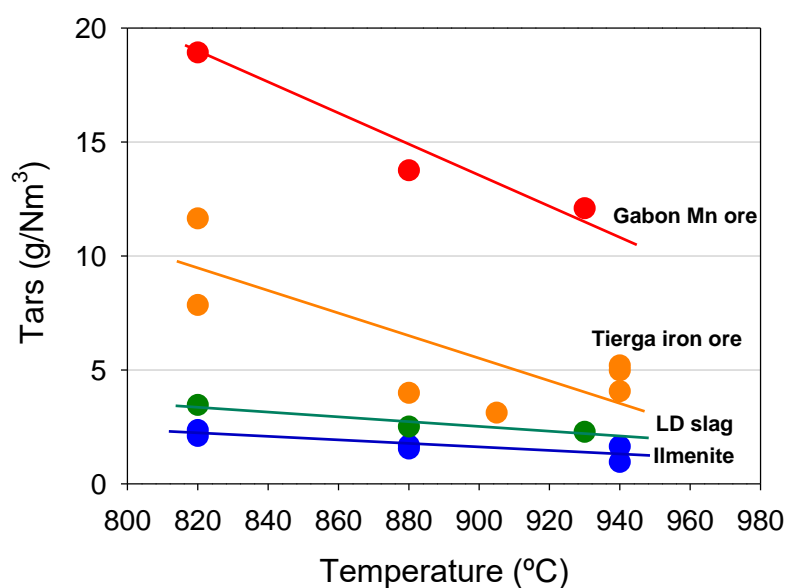
Figure 19. Comparison of tar generation as a function of temperature for the different oxygen carriers. S/B=0.6. λ= 0.2-0.4.
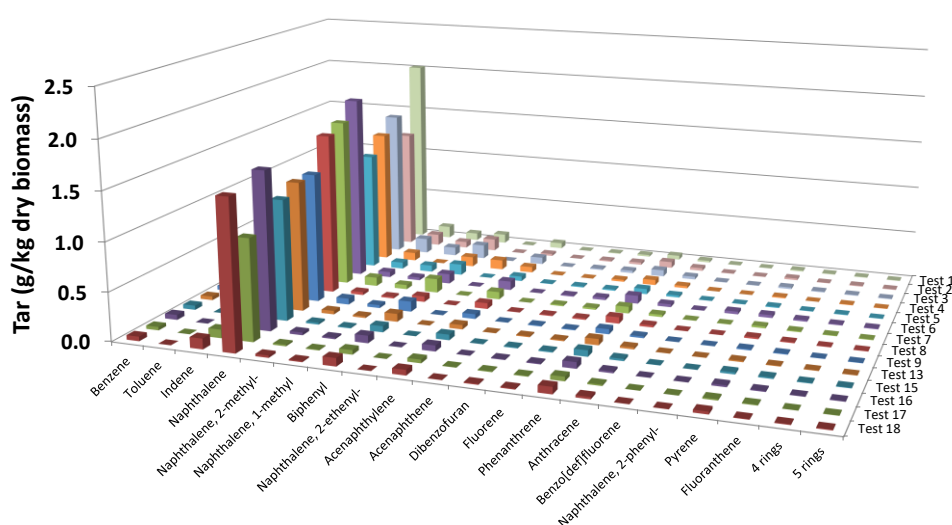

Figure 20. Tar compounds obtained during the CLG tests carried out in the continuous unit using ilmenite as oxygen carrier.

5.2.4   Summary of the results from CSIC

The selection of the most promising oxygen carriers to be used in Task 3.4 at higher scales, should be based on different parameters including composition and process efficiency, tar generation, lifetime and cost of the oxygen carriers including mineral ores and wastes.

Table 6 shows the experimental data for the 4 materials tested at CSIC. For a better comparison, the data has been normalized at λ=0.35, S/B=0.6 and a range of temperature between 900 and 940 ℃.

32

Table 6: Comparison of oxygen carriers according to data obtained at CSIC

Parameter	Units	Oxygen Carrier			
Gas composition		Ilmenite	Tierga iron ore	LD slag	Gabón Mn ore
CO_2	vol%	41.5	43.2	38.1	40.9
CO	vol%	21.1	20.1	23.1	22.8
H_2	vol%	23.6	25.5	29.5	25.9
CH_4	vol%	10.2	9.3	8.1	9.0
C2-C3	vol%	3.4	1.9	1.2	1.4
Biomass conversion, X_b	%	98.9	94.1	97.0	94.7
Carbon conversion ef.,η_{cc}	%	95.8	99.3	96.8	96.4
Cold gas ef., η_g	%	70.9	65.9	69.7	64.3
Syngas yield, Y	Nm^3/kg db	0.53	0.57	0.70	0.60
Tar	g/Nm^3	1--2	4--5	2--3	7--14
Lifetime	h	630	300	275	160
Cost	$/ton	≈200	≈100		≈5

The tests demonstrated that it is possible to obtain a high purity syngas, with low tar production with the ores and wastes tested. High hydrocarbons contents were found, especially CH_4, where values up to 10% were usual. However, in the continuous circulating fluidized bed units (50 kW$_{th}$ CSIC, 100 kW$_{th}$ CTH, and 1MW$_{th}$ TUD) it is expected a better gas-solid contact and a higher CH_4 and hydrocarbon reforming. High biomass conversion and carbon conversion efficiency were obtained at all operating conditions and oxygen carriers, with values above 90%, which reinforces the validity of the process.

The worst parameters were obtained for the Gabon Mn ore, which presented low lifetime and the highest tar generation. Tierga iron ore exhibited medium values both in syngas yield, tar generation and lifetime. In addition, circulation problems were detected during operation in some tests as a consequence of fines generation. LD slag showed the highest syngas yield, with values about 0.7 Nm^3/kg dry biomass, and low tar generation but exhibited low lifetime. Ilmenite exhibited lower syngas yield than LD slag but better tar generation and lifetime. In summary, ilmenite and LD slag are considered as promising materials to continue with the testing at higher scale. Taking into account the differences found in the performance parameters referred to syngas yield, lifetime and oxygen carrier cost, a compromise between syngas generated and oxygen carrier replacement cost is needed.

6 Conclusions

Six iron and manganese ores and one by-product from the steel industry had been preselected as oxygen carriers for chemical looping gasification (CLG). The primary focus was on cheap, readily available oxygen carriers suitable for CLG, as it was judged to be the only accessible way to obtain the amounts needed during the final demonstration at TUDA (WP5). The selected oxygen carriers have been evaluated at different scales at CTH and CSIC to develop a comprehensive understanding and establish a portfolio of suitable oxygen carriers for CLG. A range of methods has been utilized in order to study most of the sourced materials. The aspects considered for the selection of the suitable oxygen carriers for CLG are:

1. Availability at multi-ton scale
2. Propensities to convert methane
3. Selectivity towards CO and H_2
4. Syngas yield
5. Ability for reducing tar formation
6. Attrition behavior and lifetime
7. Pretreatment of raw materials before using in CLG
8. Cost

A total number of 300 hours experiments has been done in a prescreening step, i.e. Task 3.1, and five oxygen carrier selected for continuous operation in Task 3.3. The selected oxygen carriers from prescreening were Ilmenite, Tierga, LD slag, Elwaleed B, and Moanda. For evaluation of these selected oxygen carriers, a total of 600 hours of continuous CLG operation has been done in 10 kW_{th} reactor at CTH and 1.5 kW_{th} reactor at CSIC. After a vast experimental evaluation at CTH and CSIC, it has been confirmed that using oxygen carrier in CLG has a positive effect on gasification of biomass by reducing tar formation, increasing syngas yield, biomass conversion and H_2/CO ratio compared to conventional steam gasification using sand as bed. Among the tested oxygen carriers, Ilmenite and LD slag have better biomass gasification performance compare to Mn ores (Elwaleed B and Moanda) and Tierga ore. LD slag has a lower lifetime than ilmenite and needs heat pretreatment, but a higher syngas yield and H_2/CO. Therefore, ilmenite has been selected for Task 3.5 and the final demonstration at TUDA (WP5). This was decided during the GA meeting on November 10th and 11th, 2020, considering the operational performance, availability of the material at multi-ton scale, lifetime and pretreatments required for the material prior to CLG operation. Nonetheless, LD-slag is an oxygen carrier showing auspicious characteristics in terms of syngas yields, tar reduction, and biomass conversion. Moreover, initial experiments at CTH showed that pre-treatment of the OC (calcination and sieving) can improve the lifetime of the OC during CLG. Therefore, the CLARA consortium encourages future investigations of LD-slag during CLG operation, to further analyse the potential of valorizing this waste material from the steel industry in CLG applications.

7 References

[1] O. Condori, F. García-Labiano, L.F. de Diego, M.T. Izquierdo, A. Abad, J. Adánez, Biomass chemical looping gasification for syngas production using ilmenite as oxygen carrier in a 1.5 kWth unit, Chem. Eng. J. 405 (2021) 126679. https://doi.org/10.1016/j.cej.2020.126679.

[2] P. Dieringer, F. Marx, F. Alobaid, J. Ströhle, B. Epple, Process control strategies in chemical looping gasification-A novel process for the production of biofuels allowing for net negative CO2 emissions, Appl. Sci. 10 (2020). https://doi.org/10.3390/app10124271.

[3] I. Gogolev, A.H. Soleimanisalim, C. Linderholm, A. Lyngfelt, Commissioning, performance benchmarking, and investigation of alkali emissions in a 10 kWth solid fuel chemical looping combustion pilot, Fuel. 287 (2020) 119530. https://doi.org/10.1016/j.fuel.2020.119530.

[4] M. Israelsson, M. Seemann, H. Thunman, Assessment of the Solid-Phase Adsorption Method for Sampling Biomass-Derived Tar in Industrial Environments, Energy & Fuels. 27 (2013) 7569–7578. https://doi.org/10.1021/ef401893j.

[5] P. Simell, P. Ståhlberg, E. Kurkela, J. Albrecht, S. Deutsch, K. Sjöström, Provisional protocol for the sampling and anlaysis of tar and particulates in the gas from large-scale biomass gasifiers. Version 1998, Biomass and Bioenergy. 18 (2000) 19–38. https://doi.org/10.1016/S0961-9534(99)00064-1.

8　Nomenclature

F_b　　　　　flow of dry biomass fed into the system, (kg/h)

$F_{C,b}$　　　　flow of carbon in the biomass, (mol/h)

$F_{C,elut}$　　　flow of carbon elutriated in the system, (mol/h)

$F_{C,FR,out}$　　flow of carbon at the FR outlet stream, (mol/h)

$F_{C,AR,out}$　　flow of carbon at the AR outlet stream, (mol/h)

$F_{g,AR,out}$　　flow of gas at the AR outlet stream, (mol/h)

F_i　　　　　molar flow of gas i in a stream, (mol/h)

$F_{O2,ARin}$　　Molar flow of O_2 afed into the AR, (mol/h)

$F_{CO2,ARout}$　Molar flow of CO_2 at the AR outlet stream, (mol/h)

G_{CO}　　　　Gas flow of CO at the FR outlet stream (Nm^3/h)

G_{H2}　　　　Gas flow of H_2 at the FR outlet stream (Nm^3/h)

LHV_g　　　Low Heating Value of the gas (kJ/Nm^3)

LHV_b　　　Low Heating Value of the dry biomass (kJ/kg dry biomass)

L_f　　　　　The loss rate of fines that have a size smaller than 63 µm (wt%·h^{-1})

Y　　　　　Syngas yield, (Nm^3/kg dry biomass)

Y_{H2}　　　　Syngas yield of H_2, (Nm^3/kg dry biomass)

Y_{CO}　　　　Syngas yield of CO, (Nm^3/kg dry biomass)

S/B　　　　Steam-to-biomass ratio, (kg/kg dry biomass)

T　　　　　Temperature, (ºC)

t_{life}　　　　Life time, (hour)

X_b　　　　　Biomass conversion, (%)

x_i　　　　　Content of the i component in the biomass, (wt%)

η_{CC}　　　　Carbon conversion efficiency, (%)

η_g　　　　　Cold gas efficiency, (%)

Ω_{bio}　　　the oxygen demand for the full combustion of the biomass, (mol O/kg biomass)

λ　　　　　oxygen-to-biomass ratio, (mol/mol)