



Chemical Looping Gasification for Sustainable Production of Biofuels

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Results of testing up to 100 kW_{th} scale using wood chips/pellets

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Abstract

The objective of this investigation was to demonstrate the feasibility of the Chemical Looping Gasification of wood chips/pellets under realistic conditions in small pilot plants. For this, the effect of the main operational variables (the fuel reactor temperature, the mean residence time of solids in the fuel reactor, and the oxygen-to-biomass ratio controlled by the oxygen fed into the air reactor), were investigated in two pilots; a 50 kW_{th} BCLG unit located at ICB-CSIC and a 100 kW CLG unit at Chalmers. Pelletized wood, mainly Pine Forest Residue (PFR), was used as main fuel in two different sizes, pellets and milled particles, for a total of 26 h of gasification in the 50 kW unit and 18 h in the 100 kW unit.

Results show that temperature and mean residence time of the oxygen carrier in the fuel reactor have a major impact on the char conversion of the fuel reactor, $X_{char,FR}$. This can be explained by an increase in temperature leading to increased reaction rates of all the reactions and an increase in the mean residence time of solids led to higher char conversion.

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 allow us to know the amount of oxygen that reacted 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 ($\Phi = \lambda_{eff,FR} / \lambda_{eff,AR} = 1$).

Previously, the use of ilmenite as oxygen carrier for the CLG process was investigated for 60 h using wheat straw pellets with additives as fuel in a 50 kW_{th} unit (Deliverable 3.5). In this report, the same batch of ilmenite was used for a total of 86 h of continuous CLG operation. Using ilmenite as oxygen carrier, it was possible to obtain syngas non-diluted with nitrogen with simultaneous high values of CO₂ capture.

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.

In order to consider the effect of particle size in the process, experiments with milled PFR pellets were also carried out in the 50 kW unit, in addition to those carried out using PFR pellets. It was observed that milled particles produced a quicker devolatilization of the biomass in comparison to the use of the same fuel in pellets shape, and led to increased amounts of volatile products in the gas produced and thus, slightly lower syngas yields were obtained.

In summary, to improve the syngas yield in CLG for Pine Forest Residue (PFR) or similar woody biomass fuels it is necessary to use long residence times in the fuel reactor, high temperatures and use the lower λ necessary to keep 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. Biomass Chemical Looping Gasification (BCLG) represents an innovative process that allows the generation of non-nitrogen diluted synthesis gas under autothermic 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 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 is reduced to a metal oxide of lower oxygen content, i.e. ($\text{Me}_y\text{O}_{x-1}$). In the air reactor, the oxygen carrier is re-oxidized by taking molecular oxygen from air.

For the current project, oxygen carrier material at multi-ton scale will be needed for demonstration of the BCLG technology at 1 MW scale at TUDA, using selected representative of commercial&densified biogenic feedstocks (Industrial wood pellets, IWP), forestry residues (Pine Forest residues, PFR) and agricultural residues (Wheat Straw pellets, WSP). 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 H_2 , 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 and do not suffer from agglomeration with the biomass fuels used. In milestone M3.1, ilmenite was selected as oxygen carrier for demonstrating BCLG in the 1 MW_{th} unit at TUD.

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 and in the 100 kW_{th} located at CTH, regarding the behavior and performance of ilmenite when using pine forest residue as fuel. The PFR pellets were supplied by CENER.

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, $\lambda_{\text{eff},FR}$ and $\lambda_{\text{eff},AR}$, 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-to-biomass ratio (controlled by the oxygen fed into the air reactor), on the process performance, the syngas yield and the tar generation using PFR as fuel. In addition, other aspects of the process were also investigated such as the evolution of the ilmenite reactivity along the process. Finally, a comparison between the two biomass fuels tested in the 50 kW_{th} unit was made, pine forest residue (PFR) and wheat straw pellets with additives (WSP_{add}).

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, FeTiO_3 , and it was crushed and sieved to obtain a sand-type material with particle size of +100-300 μm (80% <300 μm). 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 (Fe_2TiO_5) 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% Fe_2TiO_5 , 11.2 wt% Fe_2O_3 , 28.6 wt% TiO_2 and 5.5 wt% of inert compounds. The oxygen transport capacity for the calcined ilmenite ($R_{\text{O,ilm}}$), was 4.03 wt%. The main properties of calcined ilmenite used in the pilot unit were indicated in Table 1.

Table 1. Physical-chemical properties of calcined ilmenite.

Particle size	μm	100-300
True density	kg/m^3	4100
Oxygen transport capacity, $R_{\text{O,ilm}}$	%	4.0
Porosity	%	1.2
Crushing strength	N	65.0
XRD (main species)	Fe_2TiO_5 , Fe_2O_3 , TiO_2	

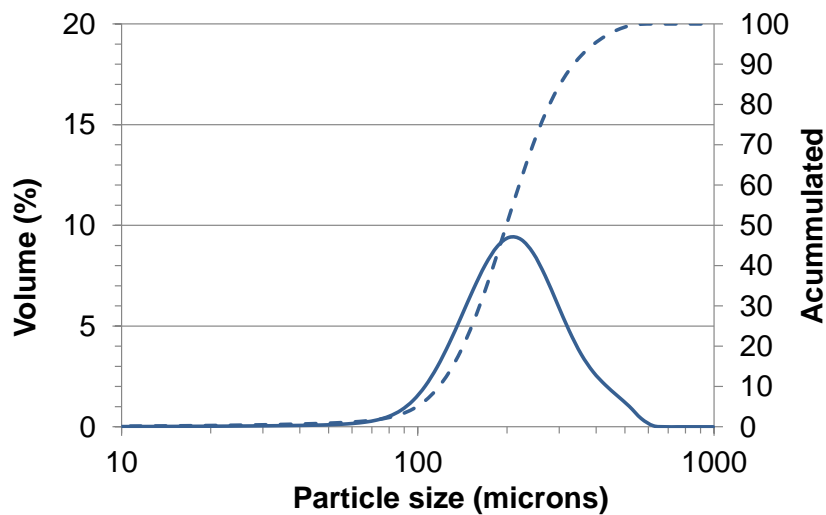


Figure 1. Particle size distribution of the ilmenite.

Pine Forest Residue (PFR) was used as fuel in two shapes: pellets of 6 mm diameter and 7-22 mm of length, density of 650 kg/m^3 , (see Figure 2) and milled pellets from 1 to 5 mm. These tests with PFR were carried out after the two experimental campaigns carried out using the Wheat Straw Pellets with additives (60 h of gasification) and using the same ilmenite inventory inside the unit. Table 2 shows the proximate and ultimate analysis of the PFR.

At Chalmers, the wood pellets could not readily be fed into the 100 kW unit. To allow feeding, the pellets had to be crushed and mixed another fuel, in this case steam-exploded wood of similar size, called “Black pellets”, or BP, which previously have been used successfully as fuel in the unit. Table 3 shows the fuels used in the 100 kW unit.

Table 2 Proximate and ultimate analysis of Pine Forest Residue (PFR).

Proximate analysis		
Moisture content	3.3	wt.%; wb
Ash content	1.2	wt.%; wb
Volatile matter	77.2	wt.%; wb
Fixed carbon	18.3	wt.%; wb
Ultimate analysis		
C	51.5	wt.%; wb
H*	5.8	wt.%; wb
N	0.3	wt.%; wb
S	0.0	wt.%; wb
O (by diff.)	37.9	wt.%; wb
Lower heating value		
LHV	17.9	MJ/kg



Figure 2. Photography of the Pine Forest Residue pellets from CENER.

Table 3. Fuels used in Chalmers experiments, as-received basis.

Name	Abbreviation	Previous names	LHV (MJ/kg)	Size (mm)	Volatiles (%)	C-fraction (%)
German wood char	GWC	Schütte wood char	30	0.1-0.4 or 2-4	15.7	81
Black pellets	BP	Arbapellets	18.64	0.7-3.5	74.2	50
Pine forest residue	PFR	-	17.7	0.7-3.5	80	47
Torrefied wood	TW	-	18	0.7-3.5	80	

2.2 50 kW Biomass Chemical Looping Gasification unit

Figure 3 shows a diagram of the 50 kW_{th} CLG unit located at ICB-CSIC, consisting on 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 (CO₂, CO, and O₂) was analyzed in an on-line gas analyzer. The gas composition at the fuel reactor outlet (CO₂, CO, H₂, and CH₄) 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. 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 N₂ 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.

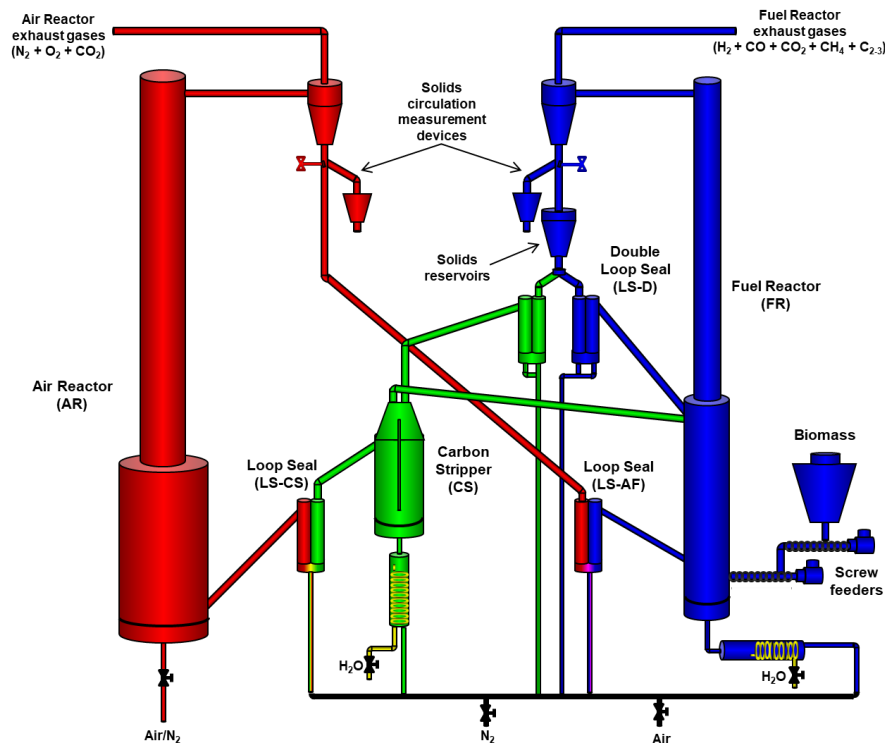


Figure 3. Scheme of the 50 kW_{th} BCLG unit at ICB-CSIC.

All the tests carried out with PFR were carried out after the modifications made in the 50 kW_{th} unit to reduce the time needed to reach the steady state for the solids in the unit and to improve the accuracy of the measurements taken in the unit.

The dimensions of the new configuration of the CLG unit were the following. 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 x 0.4 m height in the bottom and 0.08 m ID 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.

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 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.

Table 4. Operating variables used during the experimental tests at CSIC.

Power		kW _{th}	22
Solids inventory		kg	50
Solids circulation rate		kg/h	50-150
Fuel reactor	Temperature	°C	850-950
	Fluidizing gas		H ₂ O
	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		0.20 -0.45
	Steam to biomass ratio, S/B		0.5
Carbon stripper	Fluidizing gas		H ₂ O or N ₂
	Gas velocity	m/s	0.07-0.34
Air reactor	Temperature	°C	850 - 990
	Fluidizing gas		Air/N ₂ mixture
	Gas velocity (bottom)	m/s	0.5 - 0.8
	(riser)	m/s	4.0 - 6.7

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 later representing the oxygen fed into the air reactor with respect to the stoichiometric oxygen needed to fully burn the biomass.

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

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 by-passed 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 establishing the steady state in the overall unit.

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

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

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.

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

2.3 100 kW CLG unit at Chalmers

The 100 kW system, shown in Figure 4, 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 4. 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 re-oxidizes 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.

Table 5 shows operating variables used during the experimental tests at Chalmers.

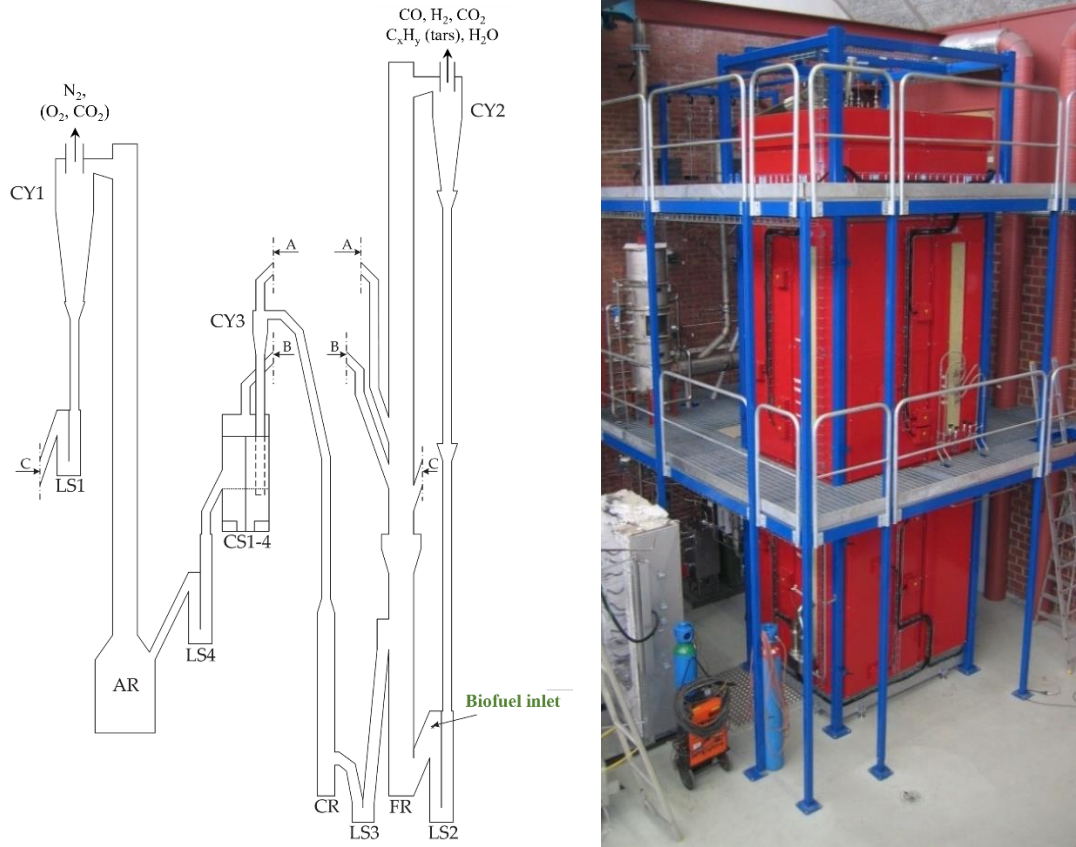


Figure 4. The Chalmers 100 kW CLC unit: a 2D sketch, drawn to scale (left), and the actual unit with oven enclosure (right).

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

Solids inventory		kg	140-300
Solids circulation rate		kg/min	1-35
Fuel reactor	Temperature	°C	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_2O 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

2.4 Data evaluation

The performance of the BCLG unit 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.

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

- 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.

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

- 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.

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

- The syngas yield, Y_{syngas} , shows the amount of H_2 and CO produced over the amount of dry biomass fed into the system, expressed in Nm^3/kg of dry biomass.

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

- 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.

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

- 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.

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

3 Results

3.1 Results from 50 kW unit at CSIC

The effect of different operating conditions on the process performance and on the syngas yield was analyzed in Task 3.4 using Pine Forest Residue as fuel and ilmenite as oxygen carrier. The first experimental campaign covers about 13 hours of continuous operation in a 50 kW_{th} BCLG unit using PFR pellets and after that, other 13 h of operation using milled PFR pellets.

Steam was fed as gasifying agent into the fuel reactor with a steam-to-biomass ratio of 0.5 kg/kg dry biomass. The most relevant variables affecting to the CLG process were the gasification temperature, the solids residence time in the fuel reactor, and the oxygen-to-biomass ratio (controlled by the oxygen fed to the air reactor). All of them have a significant effect on the process performance although having different effect depending on the parameter.

Table 6 shows the experimental conditions used in the experiments carried out with PFR as fuel. Table A1 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 PFR as fuel, including the use of pellets or milled particles.

Table 6. Operating conditions used in the experimental campaigns with PFR.

Test	Power kW	T _{FR} °C	S/B kg/kg d.b	λ mol/mol	m _{FR} kg/MW	CS LN/h	CS gas
PFR pellets							
9.1	21.6	888	0.51	0.44	447	5000	N ₂
9.2	21.6	850	0.51	0.44	178	5000	N ₂
9.3	21.6	916	0.51	0.44	380	2000	N ₂
9.4	21.6	920	0.51	0.44	579	5000	N ₂
9.5	21.6	935	0.51	0.25	265	5000	N ₂
9.6	21.6	947	0.51	0.25	359	1250	H ₂ O
9.7	21.6	944	0.51	0.25	319	2000	H ₂ O
9.8a	21.6	899	0.51	0.25	292	2000	H ₂ O
9.8b	21.6	904	0.51	0.25	299	2000	H ₂ O
9.9	21.6	849	0.51	0.25	295	2000	H ₂ O
Milled particles							
13.1	21.4	907	0.52	0.21	277	5000	N ₂
13.2	21.4	908	0.52	0.21	257	3000	N ₂
13.3	21.4	892	0.54	0.21	156	5000	N ₂
13.4	21.4	897	0.52	0.21	199	7000	N ₂
13.5a	21.4	916	0.54	0.21	312	5000	H ₂ O
13.5b	21.4	917	0.44	0.21	291	5000	H ₂ O
13.6a	21.4	923	0.35	0.21	136	5000	H ₂ O
13.6b	21.4	923	0.35	0.21	136	5000	H ₂ O
13.7	33.6	929	0.19	0.21	103	3500	H ₂ O

3.1.1 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. 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.

To carry out the evaluation with Pine Forest Residue as fuel, the temperature in the fuel reactor was varied in the usual range of gasification processes (800 - 980 °C).

Figure 5 shows the effect of temperature and mean residence time of the oxygen carrier in the fuel reactor on char conversion, using PFR in both pellets and sawdust (milled pellets) shape. The char conversion in the fuel reactor increased with the mean residence time of the oxygen carrier, $t_{mr,FR}$. Therefore, the residence time of char particles in the fuel reactor was being affected by the solids circulation rate of the oxygen carrier.

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% in the fuel reactor, the mean residence time of solids in the fuel reactor should be 200 s at 945 °C.

Figure 5 also shows the effect of the particle size on the char conversion. It was observed that higher char conversion was obtained as lower was the fuel particle size, for a given temperature. In fact, milled PFR particles tests reached higher values of $X_{char,FR}$ (70-90%) at a 915-935 °C and 100 s of residence time, even in comparison with tests carried out with PFR pellets at much higher temperature, 945 °C, where values of $X_{char,FR} \approx 60$ were obtained. As expected, reaction rate of the milled char particles is higher than those corresponding to pellets where diffusional effects are affecting the char conversion.

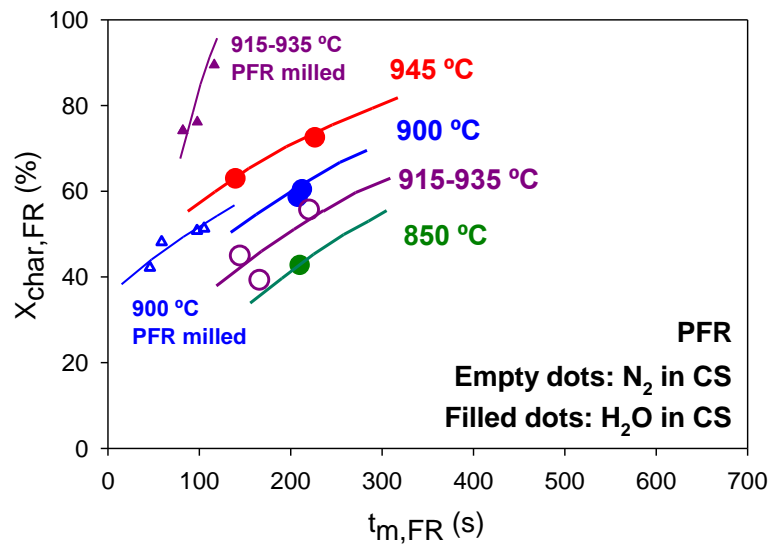


Figure 5. Effect of temperature and mean residence time on char conversion in the fuel reactor when using PFR in pellets or sawdust (milled PFR).

One of the advantages of the CLG process is the possibility to reach negative CO₂ emissions in the process, since most of the carbon present in the biomass is concentrated in the syngas stream. Thus, no CO₂ emissions through the AR are ideally reached. However, CO₂ 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. In this case, values of

η_{CC} above 95% were obtained in most of the cases and close to 100% in some of them, independently if pellets or sawdust shape was used.

3.1.2 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 auto-thermal 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 N_2 , 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 autothermal 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 CO_2 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 6 shows the graph with the different tests carried out with the PFR. The diagonal represent points at steady state since $\lambda_{eff,AR} = \lambda_{eff,FR}$ or $\Phi = 1$. The discontinuous lines represent the conditions with an error below 15% of that condition. The zone above the diagonal represents conditions where more oxygen is transferred in AR than in FR, and thus, the ilmenite is being oxidized during the process. In contrast, the zone below the diagonal corresponds to conditions where more oxygen is transferred in the FR with respect to the AR, and thus, more carbon is being gasified, and the additional oxygen produced a higher reduction of the ilmenite.

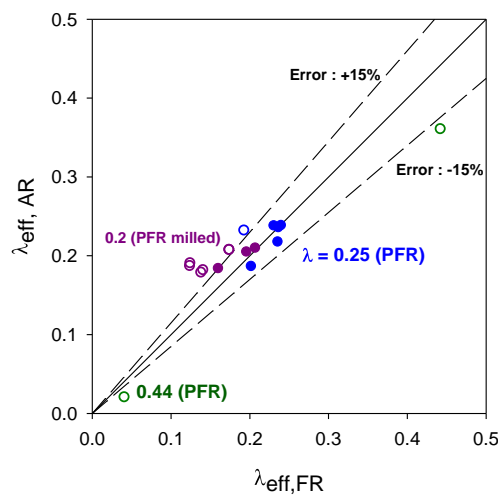


Figure 6. Relationship between effective oxygen-to-biomass ratios in fuel and air reactors, $\lambda_{eff,AR}$ and $\lambda_{eff,FR}$, respectively. Solids points represent steady state conditions. Empty points represent transitory states.

Among the three oxygen-to-biomass ratio defined by equations (1-3), the effective oxygen-to-biomass ratio in the fuel reactor, $\lambda_{eff,FR}$, had a direct influence on the syngas yield. Figure 7 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 CO_2 and H_2O . As a consequence, ilmenite released a larger amount of lattice oxygen in the fuel reactor. Thus, the concentration of CO_2 increased while the concentration of H_2 and CO decreased.

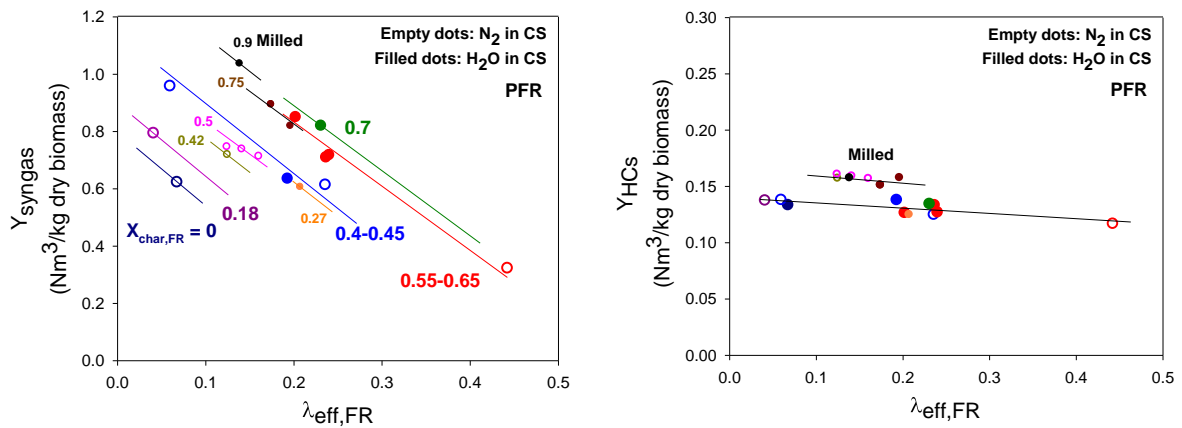


Figure 7. Effect of the effective oxygen-to-biomass ratio in the FR, $\lambda_{eff,FR}$, on the syngas yield, Y_{syngas} , and yield to HCs, Y_{HCs} , for different char conversions in the FR, $X_{char,FR}$.

On the other hand, it can be seen in Figure 7 that the yield to light hydrocarbons (CH_4 and $\text{C}_2\text{-C}_3$ 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 CH_4 . In CLG, the conditions of the fuel reactor are deficient in oxygen and it was likely to react mainly with H_2 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. These results agree with the obtained previously during operation in a 1.5 kW_{th} CLG unit [Condori et al., 2021a, 2021b], and also during the tests carried out with wheat straw pellets in this unit [Deliverable D3.5].

However, an interesting result was obtained when a comparison between the use of pellets or milled particles. It was observed that milled particles produced a higher yield to HCs (15% superior) in comparison to the use of pellets. It seems that small particles produced a quicker devolatilization inside the fluidized bed and the volatiles plume reaches the gas outlet without being in contact with the oxygen carrier, and thus without reacting. In contrast, devolatilization in pellets is slower and the volatiles produced have more time to react with the oxygen carrier, increasing their conversion inside the dense bed of the reactor. However, although the differences found in Y_{HCs} were small; this fact also produced a slight decrease in the syngas yield.

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 Nm^3/kg of dry PFR can be obtained. With high char conversion $\approx 90\%$, syngas yields higher than 0.8 Nm^3/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 at high temperatures in the fuel reactor with high char conversion and λ values near to the auto-thermal value.

Carbon losses by the air reactor are 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 8 shows that carbon losses by the air reactor increased with λ value. Carbon losses during the tests carried out with the PFR were very low because the contact time in AR after the unit modification was lower than previously by the decrease in the AR solids bed inventory and thus, in the residence time of char particles in this reactor. At the same time, carbon lost when using milled particles was lower due to the higher char conversion reached in the FR.

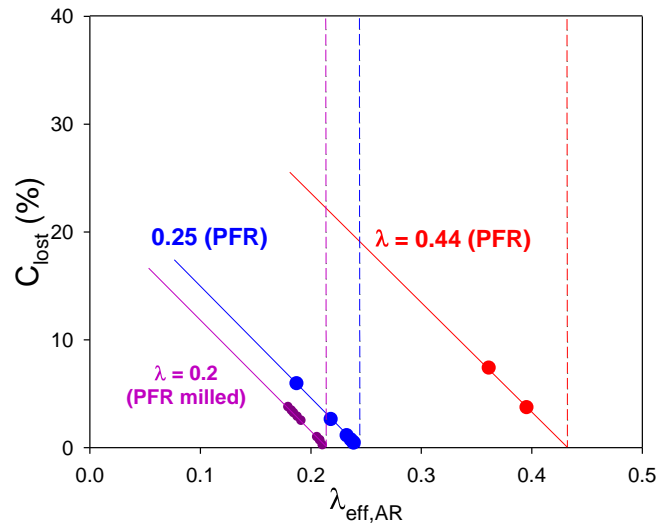


Figure 8. Carbon losses by the air reactor as a function of $\lambda_{eff,AR}$.

3.1.3 Effect of the type of biomass on the BCLG process

After the 86 h of BCLG operation accomplished with the same batch of ilmenite, a comparison between the two types of biomass used in the 50 kW_{th} unit, Wheat Straw with additives (WSP_a) and Pine Forest Residue (PFR), was made. Figure 9 shows the effect of the mean residence time of the solids in the fuel reactor on the char conversion for both fuels. For a better comparison, those tests obtained when using N₂ as fluidizing agent in the CS were selected. It was observed that WSP_a reached higher char conversion than PFR for similar operating temperatures. As an example, X_{char} values of 75% (Test 10.4c) and 56% (Test 9.4) were obtained for the WSP_a and PFR, respectively, for a residence time of 200 s and a temperature of 930 °C. This indicates that WSP_a pellets exhibited a higher reactivity than PFR.

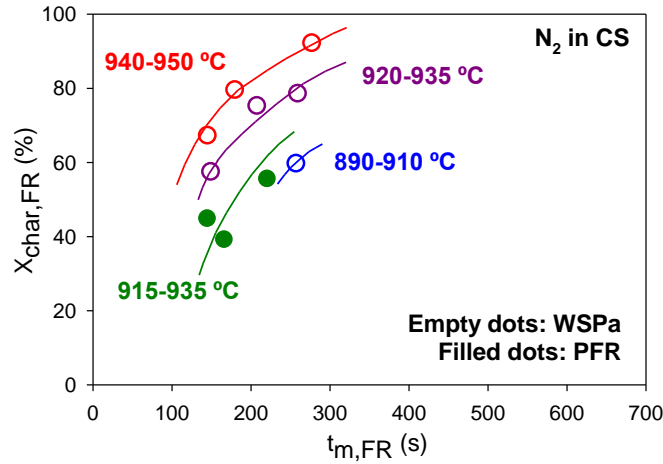


Figure 9. Comparison of the type of fuel for the char conversion as a function of the mean residence time.

Another comparison was made considering the syngas yield obtained with both pelletized biomasses. Figure 10 shows the results obtained as a function of $\lambda_{\text{eff,FR}}$. These data includes tests carried out at very different conditions regarding temperature, residence time, and oxygen-to-fuel ratio. Obviously, the syngas yield obtained was higher as lower was the value of $\lambda_{\text{eff,FR}}$ for both biomasses. As it can be observed, slight differences were found for WSPa and PFR considering the same value of char conversion. However, it should be remembered that the latter depends on the type of biomass (see Figure 9).

Regarding hydrocarbon yield, no effect of the $\lambda_{\text{eff,FR}}$ was found for any of the biomasses, reaching values about 12-14% in the whole range of $\lambda_{\text{eff,FR}}$ independently of the biomass used for gasification.

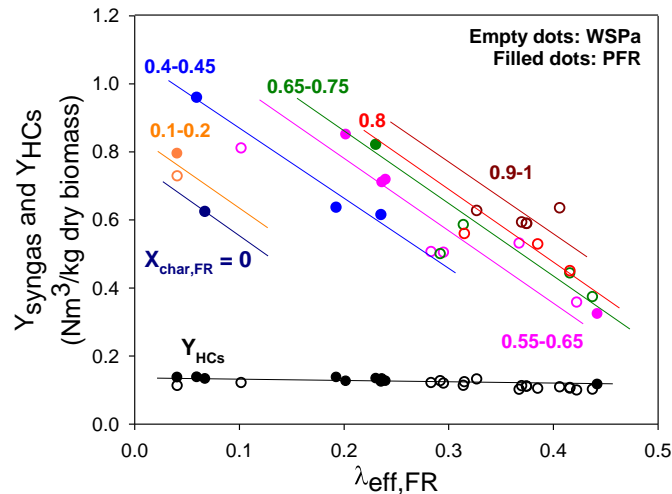


Figure 10. Comparison of the type of fuel on the syngas and HCs yield as a function of char conversion.

3.1.3 Tar emissions

The European tar protocol was used to determine the amount of tar present at the fuel reactor outlet in some experiments carried out with PFR as fuel, both in pellet and sawdust size.

Figure 11 shows the total amount of tar present in the syngas at some selected conditions. For comparison reasons, data corresponding to the tests previously carried out using Wheat Straw Pellets with additives as fuel (see Deliverable D3.5) were also included. Typical values of ≈ 4.5 g/kg biomass (≈ 3 g/Nm³ dry syngas) were obtained for the PFR, independently on the size. These values are somewhat superior to the obtained with WSPa, which reached values ≈ 3 g/kg biomass (2-3 Nm³/kg biomass). Therefore, it seems that particle size of the fuel was not affecting the tar content in the syngas, and this is slightly dependent on the type of fuel used. In any case, these values obtained in BCLG process are lower than the obtained in the typical gasification process with steam.

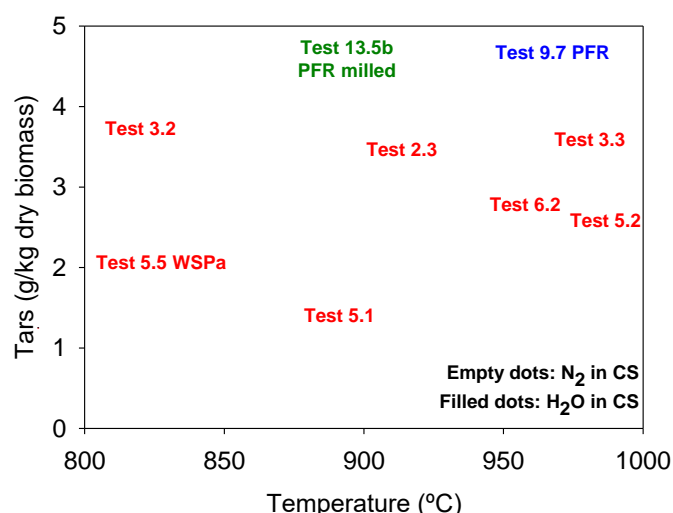


Figure 11. Comparison of tar content as a function of temperature for the two biomasses.

In addition, speciation of recovered tars was made by gas chromatography coupled to mass spectroscopy. In this case, an interesting result was obtained (see Figure 12). The main component found when using PFR as fuel was naphthalene with lower amounts of benzene and indene in contrast to the results obtained when using WSPa (see Deliverable D3.5) where the main tar component was benzene.

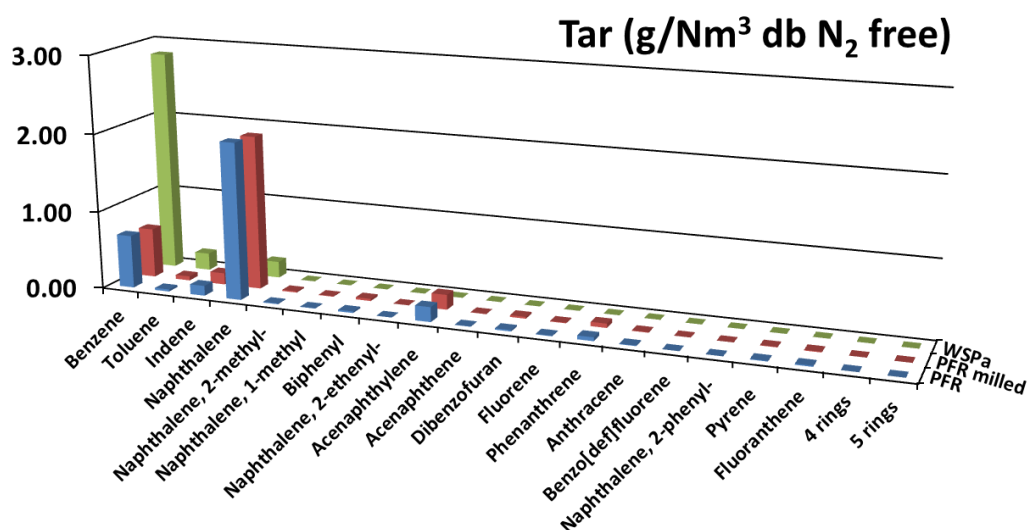


Figure 12. Distribution of tar compounds for different tests carried with wheat straw pellets.

3.2 Results from 100 kW CLG unit at Chalmers

The 100 kW unit was operated at hot conditions ($>800^{\circ}\text{C}$) for more than 60 h, of which 17 h were CLG operation with fuel, either wood pellets or wood char, separated over 4 days. Table 7 summarizes the operation.

Important findings summarized:

- Carbon capture efficiency was close to 100% in all tests.
- No agglomeration observed during the tests, except at first heat up.
- Duration of hot circulation: 85 h.
- Stable operation could be reached with all fuels except PFR, which has to do with the texture of the crushed PFR pellets. In order to feed them in the 100 kW unit, they had to first be crushed, but when crushed, they were too fibrous and feeding quickly led to build-up of “cakes”, or fuel agglomeration in the feeding system.
- Tar samples were taken and will be analyzed later.

Table 7. 100 kW campaign with wood pellets and wood char as fuels.

Day	AR flow (Ln/min)	Duration of fuel op. (h:min)	Fuel flow (kg/h)	Fuel power (kW)	Fuel
1	1000-2500*	05:00	8.9	47	BP
2	1300-1400	00:28	21.0	175	GWC
	1200-1300	00:20	12.0	100	GWC, 2-4 mm
3	1200-1300	02:24	12.1	63	BP
	1200	01:04	14.0	71	BP+PFR
4	1200	02:33	8.4	70	GWC, 2-4 mm
	900-1000	02:10	7.0	35	TW
	900	02:20	9.0	75	GWC, 2-4 mm
	600-900	01:28	8.5	42	TW+PFR
Total time of operation (h)		17:45			

*Some of these tests were CLC, where the air flow was high, i.e. up to 2500 Ln/min.

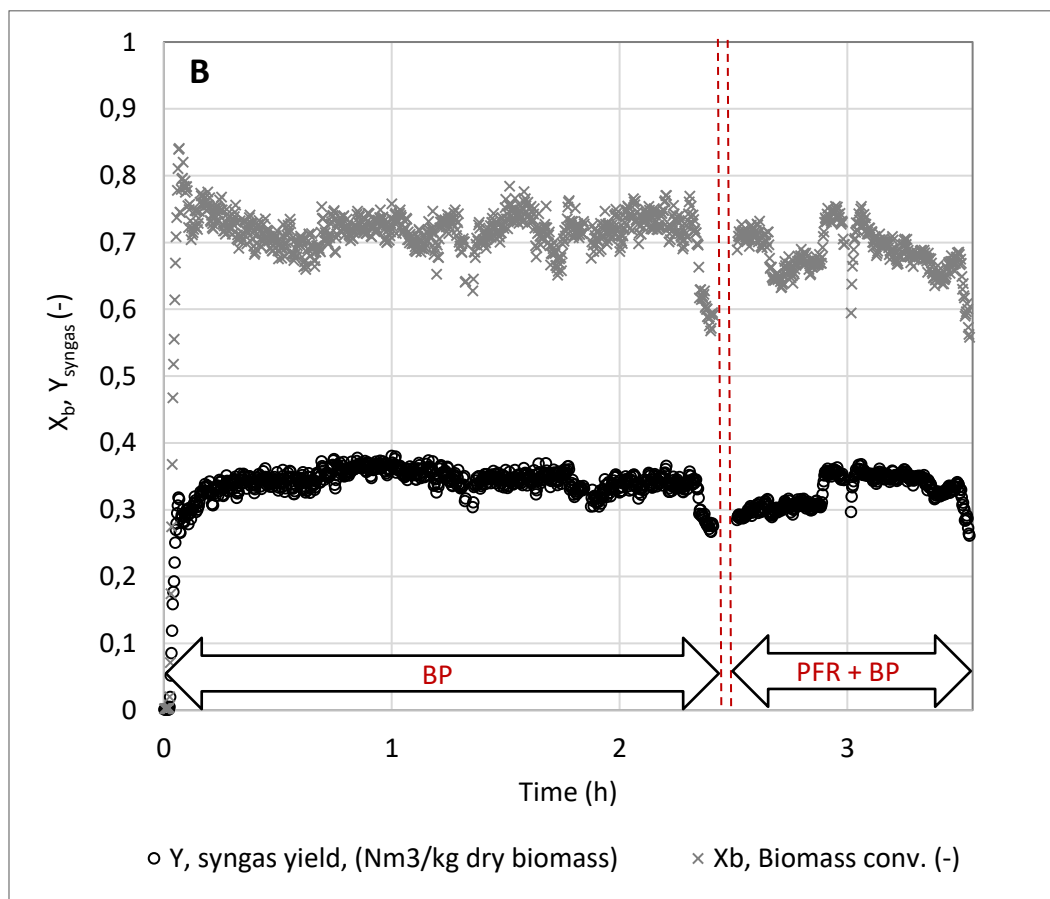
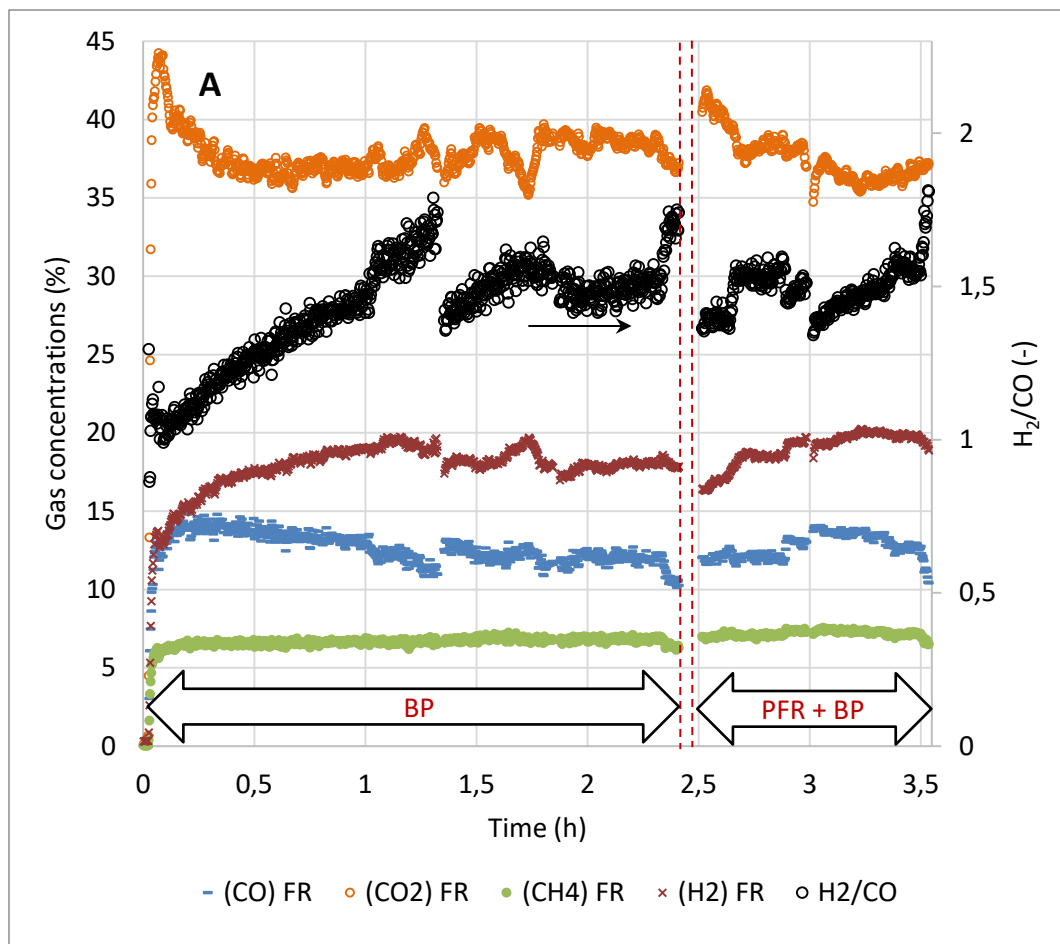


Figure 13. CLG operation on Day 3 using first black pellets (BP) as fuel, 0 – 2.45 h, followed by a mixture of black pellets and pine forest residue (PFR + BP), 2.5 – 3.55 h. $T_{FR} = 910-930^{\circ}\text{C}$; $\lambda = 0.1-0.25$; $P_{fuel} = 63-71\text{ kW}$. 13A shows concentrations of H_2 , CO , CO_2 and CH_4 , and H_2/CO ratio; 13B shows biomass conversion, X_b , and syngas conversion, Y .

Figure 13A shows gas concentrations and the H_2/CO ratio during the tests on Day 3 using two fuels, first black pellets (BP) and then a mixture of black pellets and pine forest residue (PFR + BP) as shown in the figure. During the first minutes of the experiments, the oxygen carrier is fully oxidized and the atmosphere in the FR is hence more oxidizing than during the later stages. Consequently, the syngas yield is very low at the outset of the experiments, and the CO_2 is high, peaking at 44%. Other hydrocarbons species, C_2H_4 , C_2H_6 , and C_3H_8 , were measured with a gas chromatograph, but they were below the detection limit or very close to 0 throughout the testing period.

The methane concentration is stable throughout the testing period, which is due to the low reactivity of methane relative to syngas. In fact, most of the methane proceeds through the bed without reacting with the oxygen carrier. Hence, the concentration of methane is a good indicator of the stability of the fuel flow.

The H_2/CO ratio is around 1 at the outset of the experiments, and then slowly increases during 1.3 h when it reaches 1.8. There is a change in H_2/CO ratio after 1.3 h, going from 1.7 to 1.3, the reason for this is not fully understood at this point.

Figure 13B shows biomass conversion, X_b , and syngas conversion, Y_{syngas} . Both these performance indicators are quite stable throughout the experiments. The biomass conversion is actually highest at the start of the experiments, when the oxygen carrier is fully oxidized, i.e. before moving into CLG conditions. The syngas yield is low at the very start of the tests, but then settles around $0.35\text{ m}^3/\text{kg}$ dry biomass.

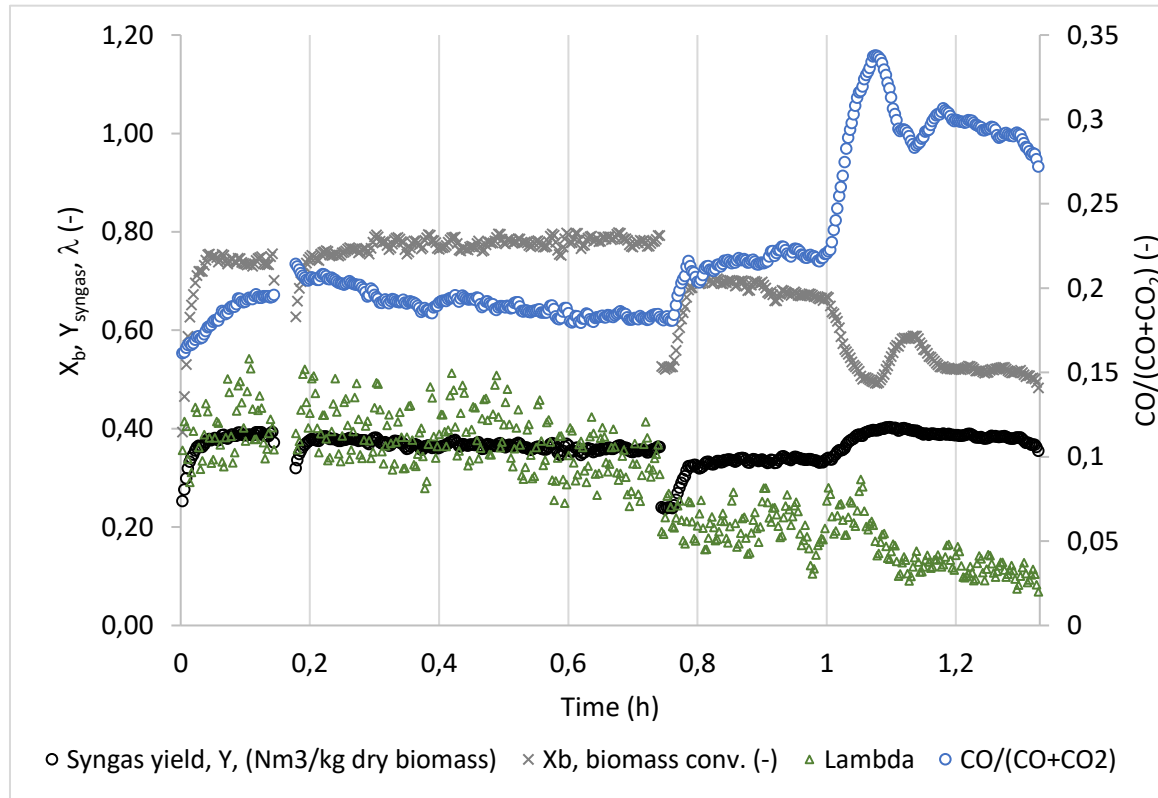


Figure 14. CLG operation on Day 4 using a mixture of pine forest residue and torrefied wood (PFR + TW). $T_{FR} = 885-915^{\circ}\text{C}$; $P_{fuel} = 42\text{ kW}$. X_b (biomass conversion), Y_{syngas} , H_2/CO ratio and λ plotted versus time.

Figure 14 shows X_b (biomass conversion), Y_{syngas} , $CO/(CO+CO_2)$ ratio and λ during Day 4, using a mixture of pine forest residue and torrefied wood (PFR + TW). λ decreases throughout the testing period, from around 0.4 to 0.1, reflecting a gradual decrease in circulation, or oxygen supplied by the oxygen carrier.

It is interesting to see that as λ decreases, and less oxygen is supplied to the FR with the oxygen carrier, the syngas yield remains more or less constant, even though more syngas is produced relative to total gas production, here shown as the $CO/(CO+CO_2)$ ratio. However, the total biomass conversion decreases. Thus, in this case, the overall conversion of the fuel to gas is largely affected by the oxygen supply.

4 Conclusions

One of the objectives of the CLARA project is the use of different type of biomasses including commercial and densified biogenic feedstocks (e.g. Industrial wood pellets, IWP), forestry residues (Pine Forest residues, PFR) and agricultural residues (Wheat Straw pellets, WSP). This deliverable compiles the results obtained after the use of Pine Forest Residue delivered by CENER during CLG operation in the 50 kW_{th} unit located at ICB-CSIC and 100 kW_{th} unit at CTH. 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.

Increasing λ caused a decrease in the syngas yield as more lattice oxygen reacted for combustion in the fuel reactor. In addition, it was observed that the variation of λ had low impact on the production of CH_4 and light hydrocarbons and high amounts of CH_4 and C_2-C_3 were always detected.

The tests in the 50 kW CLG unit account for 13 h of gasification carried out with PFR pellets and another 13 h of gasification using milled PFR as fuel to analyze the effect of particle size in the process. These tests were carried out after those accomplished during 60 h of operation with Wheat Straw Pellets with additives (see D3.5) and using the same particles of ilmenite. In summary, the same batch of ilmenite particles was used for about 86 h of CLG operation with very satisfactory results since no agglomeration was detected at any operating condition, with low attrition rate and maintains a high reactivity after the operation.

The effect of using pellets instead milled PFR was slightly beneficial since the slower devolatilization process leads to lower formation of hydrocarbons. As a consequence, slightly higher syngas yields were obtained for PFR pellets.

A comparison between the results obtained here with PFR and those obtained with straw pellets (D3.5), shows that straw produced higher char conversion, X_{char} , than PFR for the same operating conditions of temperature and mean residence time. In contrast, similar syngas and HCs yields were obtained for both biomasses when the same char conversion is used for comparison.

In summary, to obtain high syngas yield in the CLG process with wood pellets such as PFR, it is necessary to use high residence times in the fuel reactor, high temperatures and low λ .

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.

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7 Annex 1

Table A1 Operating variables, performance parameters and gas composition for the tests with the Pine Forest Residue.

Test	Operating variables									Process performance							Gas composition (vol%)				
	Power kW	T _{FR} °C	S/B -	CS gas	λ -	Θ -	m _{FR} kg/MW	CS LN/h	t _{mr,FR} s	X _b %	Char _{rel} %	X _{char,FR} %	η_{CC} %	C _{lost} %	Y _{syngas} Nm ³ /kg	Y _{HCS} Nm ³ /kg	CO ₂	CO	H ₂	CH ₄	C _x H _y
PFR pellets																					
9.1	21.6	888	0.51	N ₂	0.44	1.92	447	5000	694 ₅	70.7	82.6	17.4	100.0	0.0	0.80	0.14	21.2	23.7	43.4	9.0	2.6
9.2	21.6	850	0.51	N ₂	0.44	0.37	178	5000	691	68.9	87.6	0.4	93.8	4.3	0.62	0.13	23.2	24.7	38.6	10.0	3.5
9.3	21.6	916	0.51	N ₂	0.44	0.15	380	2000	144	84.2	44.5	45.0	95.6	3.7	0.96	0.14	19.8	26.4	43.7	8.1	2.0
9.4	21.6	920	0.51	N ₂	0.44	1.22	579	5000	220	91.7	23.5	55.7	91.9	7.4	0.32	0.12	54.5	17.1	16.3	9.7	2.3
9.5	21.6	935	0.51	N ₂	0.25	1.08	265	5000	166	81.1	53.3	39.3	96.7	2.6	0.62	0.13	33.5	23.2	32.1	9.3	2.0
9.6	21.6	947	0.51	H ₂ O	0.25	1.08	359	1244	139	92.8	20.2	63.0	93.6	6.0	0.85	0.13	28.6	23.6	38.6	7.8	1.5
9.7	21.6	944	0.51	H ₂ O	0.25	0.97	319	1991	226	90.7	26.1	72.5	99.5	0.5	0.82	0.13	32.3	20.1	38.1	8.0	1.6
9.8a	21.6	899	0.51	H ₂ O	0.25	1.00	292	1991	208	85.8	40.1	58.7	99.5	0.5	0.72	0.13	34.5	19.1	36.5	7.8	2.1
9.8b	21.6	904	0.51	H ₂ O	0.25	1.00	299	1991	212	86.7	37.5	60.4	99.1	0.7	0.71	0.13	34.4	19.3	35.9	8.2	2.2
9.9	21.6	849	0.51	H ₂ O	0.25	0.83	295	1991	210	80.8	54.0	42.8	98.6	1.1	0.64	0.14	34.2	18.2	35.9	8.7	3.0
Milled PFR																					
13.1	21.4	907	0.52	N ₂	0.21	0.87	277	5000	105	85.9	39.6	51.3	96.2	3.2	0.72	0.16	28.8	23.1	35.3	10.6	2.2
13.2	21.4	908	0.52	N ₂	0.21	0.77	257	3000	97	86.0	39.5	50.8	96.0	3.5	0.74	0.16	27.4	23.5	36.3	10.6	2.3
13.3	21.4	892	0.54	N ₂	0.21	0.65	156	5000	46	82.0	50.7	42.2	96.9	2.5	0.72	0.16	26.6	23.7	36.5	10.8	2.4
13.4	21.4	897	0.52	N ₂	0.21	0.66	199	7000	59	84.5	43.7	48.1	96.6	2.9	0.75	0.16	26.3	23.9	36.8	10.7	2.4
13.5a	21.4	916	0.54	H ₂ O	0.21	0.77	312	4978	116	100.0	0.0	89.5	96.2	3.8	1.04	0.16	27.6	19.2	43.6	8.1	1.5
13.5b	21.4	917	0.44	H ₂ O	0.21	0.95	291	4733	98	92.5	21.0	76.1	98.9	1.0	0.82	0.16	32.5	17.5	39.1	9.2	1.7
13.6a	21.4	923	0.35	H ₂ O	0.21	0.83	136	4733	82	91.5	23.9	74.1	99.2	0.7	0.90	0.15	29.0	20.6	40.2	9.0	1.3
13.6b	21.4	923	0.35	H ₂ O	0.21	0.83	136	4733	82	91.5	23.9	74.1	99.2	0.7	0.90	0.15	29.0	20.6	40.2	9.0	1.3
13.7	33.6	929	0.19	H ₂ O	0.21	0.98	103	3489	63	74.3	72.4	26.8	99.6	0.3	0.61	0.13	32.3	22.5	33.6	10.2	1.4