Flexible Dimethyl ether production from biomass gasification with sorption enhanced processes

Starting date: 1st November 2016
Duration: 48 months

WP 2 – Deliverable D2.1:

Characterisation of raw materials for sorption enhanced gasification

Dissemination level	PU Public CO Confidential, only for members of the consortium (including Commission Services)		PU
Written By	Ramón Murillo (ICB-CSIC) Gemma Grasa (ICB-CSIC) Isabel Martínez (ICB-CSIC)		April 26th, 2017 Revised on June 23rd, 2017
Due date	2017-04-30	Issue date	2017-06-23

Track changes

Version	DATE	Changes	CHECKED	APPROVED
V1	2017-04-26	First release	CSIC	Ramón Murillo
V2	2017-06-23	Revised version		
V3	2019-07-29	Acknowledgement section updated		

WP lead institution: CSIC

Authors' contacts

Author name	Organisation	e-mail address
Ramón Murillo	CSIC	ramon.murillo@csic.es
Gemma Grasa	CSIC	gga@icb.csic.es
Isabel Martínez	CSIC	imartinez@icb.csic.es

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Executive summary

This document describes the analytical techniques that were used and will be used along the project to perform the characterization of the different raw materials to be used in the gasification process. It includes the description of the techniques used for the characterization of fuels and those necessary to perform the characterization of sorbents. In addition, the full characterization of fuels and sorbents to be used in the project are also reported. It is concluded that the selected fuels can be processed in the available experimental rigs although some difference have been found between the natural biomass fuels and ECOH biomass. Regarding to the sorbents, their behavior has been similar to data found in the literature.

1   Analytical techniques description

1.1   Analytical techniques for fuels characterization

The fuels are characterized by using the following analytical techniques:

1.1.1   Proximate analysis

The proximate analysis of a fuel consists in the determination of the contents in humidity, ashes, volatile matter and fixed carbon.

Moisture content by indirect gravimetry is defined as the loss of mass until constant weight. In this analysis, samples are heated up to 107 °C in an oven under nitrogen or air atmosphere. The determination of moisture content in solid biofuels and refused derived fuel (RDF) is carried out according to the Standards UNE- EN 14774-3 and UNE-EN 15414-3 respectively. The analyses will be performed in a Thermoelectron-Heraeus oven which allows working until 150ºC with circulation of air and nitrogen.

Volatile content is defined as the mass loss (minus moisture) when 1 g of sample is heated to 900ºC for 7 minutes. The determination of volatile matter in solid biofuels and recovered solid fuels is performed according to UNE -EN 15148 and UNE -EN 15402. These tests will be performed in a CRN - 48 dee Hobersal oven. Samples will be stabilized in a desiccator with $CaCl_2$ and weighed in a Sartorius BP balance.

The ash content is determined by the total combustion of a certain amount of sample in a muffle at 875 °C (UNE-EN-14775). The residue obtained in the combustion is stabilized in a desiccator provided with $CaCl_2$ and then weighed on a balance.

Finally, the fixed carbon is calculated by difference.

1.1.2   Ultimate analysis

Ultimate analysis is defined as the determination of Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur in different materials, such as coal, solid biofuels, refused derived fuels, ash, graphite, liquid fuels, nanotubes, carbon fibers, zeolites, steel, etc. This determination is performed in a Thermo Flash 1112 (see Figure 1) which produces complete combustion of the sample inside a high temperature reactor followed by an accurate analysis of the flue gas.

Figure 1. Thermo Flash 1112 analyser

1.1.3   Calorific value

The higher heating value is defined as the energy released when a known amount of a fuel is burnt in an apparatus called calorimeter which is provided with an ignition system. Once the sample is inside the container, it is closed and filled with oxygen. The ignition system is activated and the sample is fully burnt. The energy released is transferred to a water bath whose temperature increases. Once the thermal equilibrium is achieved, the temperature increment is known and the heating value can be calculated. The samples will be analysed in a isoperibolic calorimeter IKA C-2000 (see Figure 2) which allows the determination of the high heating value of biofuels (UNE -EN 14918) and refused derived fuels (UNE -EN 15400).

Figure 2. IKA C-2000 calorimeter

1.1.4   Ash fusibility

This type of analysis will be performed in a SYLAB IF 2000 (see Figure 3) for determining the fusibility of ash coals both according to ASTM D – 1857 (triangular pyramids) and solid biofuels (UNE EN 15370) and refused derived fuels (UNE EN 15440) using right cylinders.

Figure 3. SYLAB IF 2000

1.1.5   Ash chemical analysis

The ash chemical composition will be analyzed by ICP-OES (Xpectroblue of AMETEK, see Figure 4). This technique allows to determinate the concentration of different elements in numerous types of samples such as ash coal, solid biofuels and solid recovered fuels. The concentrations that can be determined ranges between ppm scale to percentage scale. Samples must be in aqueous medium and with an appropriate concentration without the presence of precipitates or colloids.

Figure 4. ICP-OES apparatus Xpectroblue of AMETEK

1.1.6   Thermal analysis

Thermogravimetric analyses (TGA) are carried out in a Libra F1 thermobalance by Netzsch (see Figure 5). This TGA instrument allows to heat the sample under different gas mixtures (inert or oxidizing), from ambient temperatures up to 1100°C. The heating rate can be varied from 0.001 K/min to 200 K/min, with a resolution of 0.1 microgram and a measuring range of +2000mg. This analysis is used to study the devolatilization of the different fuels under realistic conditions.

Figure 5. Netzsch TGA system

1.2   Analytical techniques for sorbents characterization

The sorbents are characterized by using the following analytical techniques:

1.2.1   Particle size determination: laser diffraction

Particle size analyses are carried out in a LS13320 equipment by Beckman Coulter (see Figure 6). The equipment has three analysis units:

 -Tornado Dry Powder Module: dispersion liquid is not required in this module and it is possible to determine a minimum particle size of 0.4 microns.

 -Universal Liquid Module: this module allows to measure the particle size in different dispersion liquids and it is able to determine a minimum particle size of 40 nm.

-Micro Liquid Module: this module is suitable for small sample quantities in different dispersion liquids. The minimum particle size determined is 0.4 microns.

The laser diffraction analysis is performed according to ISO 13320:2009 Particle size analysis – Laser diffraction methods

Figure 6. Beckman Coulter apparatus for particle size distribution

1.2.2   Density: He pycnometer

Helium psychometry analyses are carried out in Accupyc 1340 by Micromeritics (see Figure 7). The equipment has a nominal cell volume of 10 cm^3 with multivolume option to analyze different sample amounts (1, 3.5 y 10 cm^3). In addition, it is provided with a temperature-control unit to perform analysis at different temperatures.

Figure 7. He pycnometer

1.2.3   Porosity: Hg porosimetry and physisorption

Total pore volume and pore size distribution in porous materials like the sorbents that will be used along the project are determined by physisorption and mercury porosimetry.

-Physisorption analyses are carried out in Micromeritics ASAP2020 (see Figure 8a). This equipment allows to obtain adsorption isotherms for mesoporous and microporous materials. The microporosity can be studied by using N_2 or CO_2 as adsorbate.

-Mercury porosimetry is performed in a Quantachrome POREMASTER (see Figure 8b). This analysis allows to determinate total pore volume and pore size distribution for mesoporous and macroporous materials.

Analyses for porosity determination are performed according to ISO 15901(1-2-3): Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption.
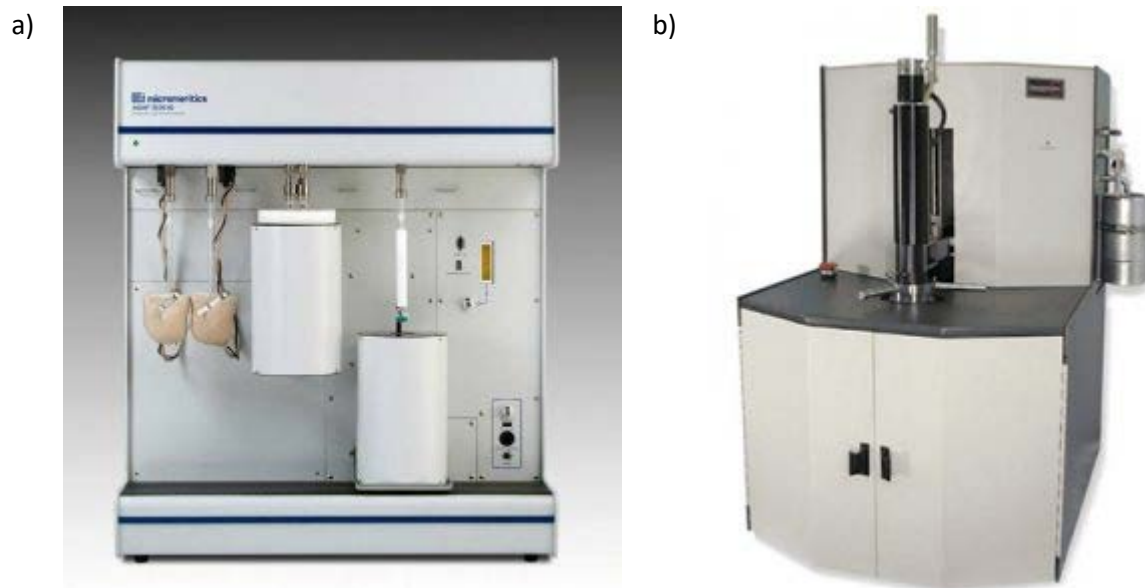
Figure 8. a) ASAP 2002 apparatus and b) POREMASTER apparatus

1.2.4   X-ray diffraction

X-Ray Diffraction analyses are carried out in a Bruker D8 Advance (see Figure 9) diffractometer (crystalline powder method). The diffractometer presents Bragg-Brentano theta-theta configuration for conventional powder samples and it is also equipped with a Göbel Mirror that converts the X-ray beam coming from the X-ray tube into a parallel beam. Grazing angle measurements are available too. X-Ray diffraction analysis are performed according to UNE-EN 13925 (1-2-3).

Figure 9. X-ray diffractometer

2   Results

2.1   Fuels characterization

Six different fuels have been characterized for being considered for the gasification experiments: A1 wood pellets, pine wood, straw, grape seeds, Ecohispanica biomass and two different biomasses obtained from the Ecohispanica one (i.e. RSU160 and ORGANIC70+PAPER). The different representative samples were allowed to stabilize in air until constant weight was reached. Subsequently they were ground to a particle size lower than 100 μm and finally were stored in sealed containers. Table 1 shows the ultimate and proximate analysis, as well as the calorific value and trace elements, of the different fuels.

Table1. Proximate analysis, ultimate analysis and calorific value of the different raw materials

PROXIMATE ANALYSIS						
%wt.	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70+ PAPER30	GRAPE SEEDS
% moisture	5.55	8.09	7.06	6.56	2.51	2.79	6.30
% ash	0.36	1.30	4.39	32.47	38.54	37.81	4.30
% volatile matter	78.80	72.94	71.04	53.63	53.26	53.38	65.12
% fixed carbon	15.29	17.67	17.51	7.34	5.69	6.02	24.28
ULTIMATE ANALYSIS						
	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70+ PAPER30	GRAPE SEEDS
% C	49.28	49.15	44.80	36.46	34.06	34.21	53.92
% H**	6.30	5.83	5.97	5.19	4.56	4.40	6.58
% N	0.10	0.14	0.38	1.36	1.65	1.60	2.20
% S	0.02*	0.05*	0.11*	0.21	0.40	0.40	0.12
% O	40.77	39.53	40.29	29.24	25.45	25.83	32.35
%Cl	0.00	0.01	0.06	0.56	0.67	0.61	0.06
CALORIFIC VALUE						
	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70+ PAPER30	GRAPE SEEDS
HHV (MJ/kg)	19.05	18.05	17.26	14.74	13.85	13.85	22.07
LHV (MJ/kg)	17.59	16.69	15.80	13.47	12.81	12.83	20.51
TRACE ELEMENTS						
	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70+ PAPER30	GRAPE SEEDS
F (ppm)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al (ppm)	37	163	95	9984	9796	9359	357
Ca (ppm)	741	3367	3332	52214	62426	62617	8313
Fe (ppm)	43	119	37	3248	8526	7799	313
K (ppm)	489	487	7631	9515	7269	7232	8639
Mg (ppm)	136	209	625	5033	4913	4932	781
Mn (ppm)	37	10	11	164	200	189	54
Na (ppm)	15	41	68	13393	17684	17893	86
P (ppm)	41	60	322	3046	3226	3287	2094
Si (ppm)	135	782	10528	65222	81408	79708	1359
Ti (ppm)	3	10	5	1129	1046	1038	13

*This number was determined by ionic chromatography since this technique is able to determine low amounts of S in the samples
** Includes H in the moisture

It is interesting to highlight that the sum of the % of each element determined in the ultimate analysis (i.e. C, H, N, S, O and Cl) do not make 100% in any of the biomasses analysed, being this sum closer to 100% as the content of ashes decreases. This is due to the fact that the mineral fraction of the biomass (i.e. the ashes) is fully oxidized during the ultimate analysis determination procedure (explained in section 1.1.2) and remains as a solid, and so it is not determined through the flue gas as done for the C, H, N, S and O. For this reason, as the ash content increases, the sum of the different elements in the ultimate analysis becomes lower than 100%.

Moreover, as it was expected, the ash content of the different biomass fuels is low except for the Ecohispanica biomasses (i.e. ECOH biomass, RSU160 and ORGANIC70+PAPER30 given in Table 1) that was over 30%, which makes the calorific value of these biomasses be low compared to the other fuels included in the table. Moreover, these biomasses as well as the GRAPE SEEDS biomass showed a relatively high Sulphur content and H_2S formation during gasification is expected. Regarding to trace elements, the typical metals found in the soil were detected for the Ecohispanica biomasses (Si, Ca, K, etc), as well as Cl whose content is high, especially in the ORGANIC70+PAPER30 one, probably due to the presence of PVC. The Cl content was also high for the straw because it is a fast growing biomass.

With the aim of being implemented in the simulation models developed within FLEGDED, a normalized 'daf' composition (i.e. dry-ash free) has been calculated for each biomass characterized. Table 2 shows the 'daf' composition calculated for each biomass from the information given in Table 1. This composition is calculated from the ultimate analysis, considering that the remaining fraction until 100% is made of moisture and ashes (ASTM D3180-89) and so normalizing to 100% with these components.

Table 2. Normalised composition of the biomasses for simulation purposes

NORMALISED COMPOSITION						
%wt. daf	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70+ PAPER30	GRAPE SEEDS
% C	51.41	52.39	49.33	50.43	51.21	51.26	57.04
% H	5.93	5.26	5.71	6.17	6.44	6.13	6.22
% N	0.10	0.15	0.42	1.88	2.48	2.40	2.33
% S	0.02	0.05	0.12	0.29	0.61	0.60	0.13
% O	42.53	42.14	44.36	40.45	38.26	38.70	34.22
%Cl	0.00	0.01	0.06	0.77	1.01	0.91	0.07
%moisture	5.55	8.09	7.06	6.56	2.51	2.79	6.30
%ash	0.36	1.30	4.39	32.47	38.54	37.81	4.30

Table 3 shows the ash fusibility for the different fuels in two different environments: oxidant and reductant. It is observed that, regardless the environment, ash melting takes place at very high temperature, much higher than the typical operational temperature of the process. For the GRAPE SEEDS biomass, the initial deformation temperature was not reached at the maximum temperature of 1550ºC of the apparatus used for determining the ash fusibility (described in section 1.1.4), and therefore information for the temperatures of initial deformation, hemisphere and melting has not been given in Table 3. Consequently, the melting of its ashes would occur at a higher temperature than that maximum value.

Table 3. Ash fusibility of the different raw materials

Oxidant conditions							
	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70 +PAPER30	GRAPE SEEDS
Shrinking T (ºC)	1019	982	765	1155	1142	1126	731
Initial deformation T (ºC)	1404	1530	885	1191	1164	1158	--
Hemisphere T (ºC)	1482	1538	1061	1203	1196	1186	--
Melting T (ºC)	1493	1540	1080	1215	1204	1198	--
Reductant conditions							
	Wood pellets	Pine wood	Straw	ECOH biomass	RSU160	ORGANIC70 +PAPER30	GRAPE SEEDS
Shrinking T (ºC)	772	802	723	1122	1105	1096	719
Initial deformation T (ºC)	1470	>1560	829	1133	1149	1135	--
Hemisphere T (ºC)	1513	>1560	1032	1201	1188	1177	--
Melting T (ºC)	1522	>1560	1084	1214	1210	1199	--

2.2   Sorbents characterization

Two different natural CaO based sorbents have been selected for the experimental testing in the bubbling fluidized bed gasifier/combustor. These materials, a natural limestone and a dolomite have been characterized and tested in an atmospheric TGA apparatus to determine their CO_2 carrying capacity. Table 4 shows the ICP- OES results those represent the % in weight of representative elements in the calcined sorbents.

Table 4. Properties of the analyzed sorbents

	Limestone-1	Dolomite
% weight loss upon calcination	46.5	52.2
CaO (% wt in residue)	98.25	58.18
Al_2O_3 (% wt in residue)	0.145	0.20
Fe_2O_3 (% wt in residue)	0.002	0.07
K_2O (% wt in residue)	<0.001	<0.001
MgO (% wt in residue)	0.183	41.29
Na_2O (% wt in residue)	<0.001	<0.001
SiO_2 (% wt in residue)	0.132	0.27

As it can be seen, the limestone presents a high purity with more than 98 % wt. CaO after calcination. Minor impurities are Al_2O_3 and MgO. With respect to the dolomite, CaO represents the 67.02 % and MgO the 37.64 % wt. from the calcined solid. The materials have been also texturally characterized, and their porosity, BET surface area and true density are compiled in Table 5.

Table 5. Textural characterization of the calcined of the two natural sorbents

	Porosity	S_{BET} (m^2/g)	ρ_{true} (kg/m^3)
Calcined Limestone	0.52	8.8	3139
Calcined Dolomite	0.64	17.9	2704

Comparing both materials, the calcined dolomite presents higher porosity and larger BET surface area than the calcined limestone. As a consequence of the dolomite composition, it presents lower true

density than the calcined limestone. It is important to highlight that the values presented in Table 5, all fall in the typical range expected for CaO-based natural sorbents.

Figure 10 shows the pore size distribution of the calcined materials: limestone and dolomite. After the first calcination the materials both present, unimodal pore size distribution. As reported in Table 5, calcined dolomite presents a higher porosity (area under the curve in the Figure) and an average pore size slightly higher than 50 nm diameter. The calcined limestone presents a slightly wider pore size distribution and an average pore diameter of around 80 nm.
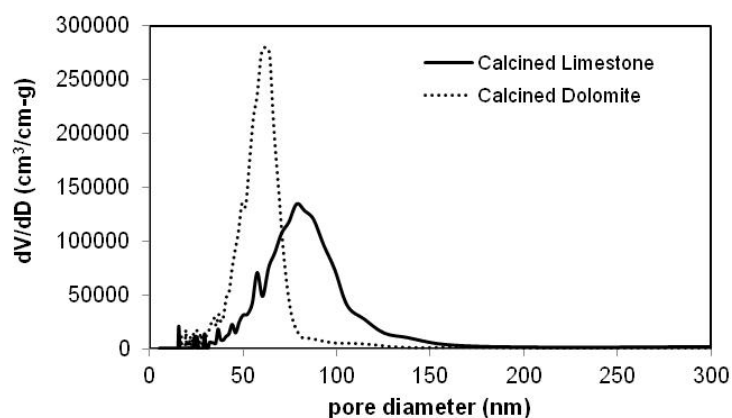

Figure 10. Pore size distribution of CaO from the two sorbents after a first calcination.

The evolution of materials CO_2 carrying capacity with the number of reaction cycles has been assessed in an atmospheric TGA apparatus especially designed for high temperature multi-cycle testing. The TGA, consisted of a quartz tube placed inside a two-zone furnace capable of working at temperatures up to 1000 º C. The temperature and sample weight were continuously recorded on a computer. The reacting gas mixture (CO_2, O_2/air) was regulated by mass flow controllers and fed into the bottom of the quartz tube. A special characteristic of this TGA is the presence of two zones in the furnace capable of working at different temperatures. The furnace can be moved up and down by means of a pneumatic piston. Its position with respect to the platinum basket alternates between calcination conditions (> 850 ºC) or carbonation conditions (around 650 ºC). Preliminary experiments were carried out to determine the total gas flow needed to eliminate external diffusion effects around the sample pan (this was finally set to $4*10^{-6}$ m³/s i.e. about 0.06 m/s of superficial gas velocity around the sample pan at 650 ºC and 0.08 m/s at 950 ºC). CaO conversion vs. time for each cycle was calculated by measuring the weight losses and assuming that the CaO was converted to $CaCO_3$ during carbonation. Although the TGA has been designed to allow for fast changes in temperature around the sample holder, there is still a delay in the order of 30-60 s before the desired carbonation temperature is reached after the calcination step. In order to stop the carbonation reaction during this temperature stabilisation period, the flow of CO_2 was switched off until the carbonation temperature was stable within a ±5 K difference with respect to the pre-configured temperature [Grasa et al. 2009]. The experimental cycles consisted of a calcination stage performed at 900 ºC in air (5 minutes stage) and a carbonation staged performed at 710 ºC in a 15 % v. CO_2 in air for (5 minutes). Figure 11 shows the evolution of CO_2 carrying capacity of both calcined materials expressed in two different units.
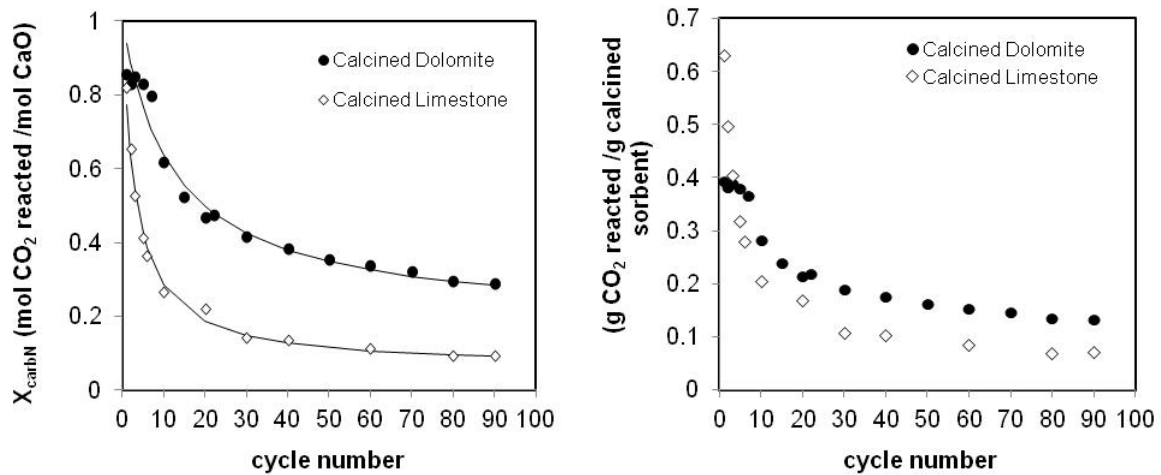
Figure 11. Evolution of calcined materials CO$_2$ carrying capacity expressed as: left) mol CO$_2$ reacted/mol CaO; solid lines represents predictions according to Equation (1); right) g CO$_2$ reacted/g calcined sorbent.

Figure 11 left) represents materials CO$_2$ carrying capacity expressed as mol CO$_2$ reacted/mol CaO in the material. Both materials present the typical decay in CO$_2$ carrying capacity that experience natural CaO-based sorbents. On view of the experimental results, and in agreement with results shown in the literature, calcined dolomites present a higher CaO utilization than calcined limestones. CaO utilization is slightly below 30 % up to 100 reaction cycles compared with the 10 % CaO utilization that present the calcined limestone. [1]. Given the composition of the dolomite, there is an important fraction of the material (MgO) that will act as an inert for the CO$_2$ capture in the range of operation temperatures of the Fledged Project. In this way, the comparison of materials performance can be better represented by Figure 12 right that shows the evolution of CO$_2$ carrying capacity as g CO$_2$/ g calcined sorbent. According to this Figure, the calcined dolomite tested is able to capture a 13 % wt. of CO$_2$ in the long term performance with respect to the 7 % wt. that is able to capture the calcined limestone.

Several equations have been proposed in the literature to fit the experimental data reported on sorbents CO$_2$ carrying capacity [2]. In this project, Equation (1) that has been successfully used to fit experimental curves of CaO based sorbents will be adopted to predict the evolution of materials CO$_2$ carrying capacity under meaningful conditions for the Fledged project. This Equation includes two parameters: k, that is defined as sorbent deactivation constant and Xr that would correspond to the sorbent residual capacity for an infinite number of cycles [1].

$$X = \frac{1}{\frac{1}{(1-X_r)}+kN} + X_r \qquad\qquad (1)$$

The parameters those fit the experimental curves in Figure 11 left) are: k=0.09 and Xr=0.18 for the calcined dolomite and k=0.33 and X$_r$=0.06 for the calcined limestone.

The results obtained show that the limestone tested behaves as a standard limestone, and its CO$_2$ carrying capacity falls in the range of data widely reported in the literature. The calcined dolomite presents slightly better sorption capacity than the calcined limestone, but its attrition resistance needs to be assessed. This might not be a critical parameter for the bubbling fluidized bed gasifier at ICB, and the reason to include a dolomite material in the testing campaign was to assess the effect that the sorbent material had on tar production in the gasifier.

3   Conclusions

The different fuels that will be used in the project where characterized according to the requirements established in WP2 description. It has been found that the three natural biomass fuels are very similar with low ash content and a relevant calorific value (especially A1 pellets). However, the three Ecohispanica biomasses are quite different as a consequence of their particular origin. Although the ash content is significantly higher compared to the natural biomass fuels, the calorific value of these raw materials is not so different. This is probably due to the presence of plastic materials which usually have very high calorific values. In fact, it is observed the presence of Cl probably due to PVC mixed with the biomass. Regarding to the ash fusibility, it is observed that it is above the operating temperatures of the gasifier and calciner and no problems at this respect are expected.

With respect to the sorbents characterization, the results obtained show that the limestone tested behaves as a standard limestone, and its CO_2 carrying capacity falls in the range of data widely reported in the literature. The calcined dolomite presents slightly better sorption capacity than the calcined limestone, but its attrition resistance needs to be assessed. This might not be a critical parameter for the bubbling fluidized bed gasifier at ICB, and the reason to include a dolomite material in the testing campaign was to assess the effect that the sorbent material had on tar production in the gasifier.

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5   Acknowledgment

http://ec.europa.eu