CO_2 gasification of dairy and swine manure: a life cycle assessment approach.

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ABSTRACT

CO_2 gasification of three different chars obtained from the pyrolysis of two dairy manure samples and a swine manure sample was evaluated. Dairy samples were firstly pretreated by anaerobic digestion process and swine sample by bio-drying process. Subsequently, manure samples were pyrolyzed between 30 ºC and 980 ºC obtaining a solid fuel (biochar), which was later gasified using different vol.% CO_2 (15 to 90 %) which was the gasifying agent. Gasification was conducted at 900 ºC. Thermal behavior and gasification characteristics were studied by means of the thermogravimetric-mass spectrometric analysis. In this sense, the reactivity of the samples was influenced by the catalytic activity of the mineral matter contained in the remaining biomass ashes. On the other hand, the viability of the manure gasification process vs the traditional use of manure as fertilizer was studied by means of the life cycle assessment (LCA)

methodology. Two different scenarios were analyzed: gasification of manure sample before anaerobic digestion (Pre) and gasification of manure after anaerobic digestion (Dig R). According to the results obtained, the gasification of char Pre was the most viable scenario from the economic and environmental viewpoints whereas the gasification of char Dig R was the best energetic option.

Keywords: CO_2, gasification, manure, LCA, TGA-MS.

1. INTRODUCTION

The accumulation of livestock manure (LSM) has associated some hygienic and environmental problems due to its high potential for pollution and high production. In this sense, subterranean and surface water, ground and air contamination, odors and greenhouse gases and ammonia emissions are some of the problems of LSM accumulation. LSM also is a potential source of pathogens [1]. Traditional uses of LSM, as a fertilizer and landfill, have to be changed due to land limitations and more strict regulations [1]. Currently, there is an increasing interest in the valorization of manure as a solid fuel. Therefore, the utilization of this surplus of manure for waste-to-bioenergy generation could be a sustainable choice since it is considered a zero-cost feedstock [2].

Generally, the conversion of biomass waste into energy could be carried out through biological or thermochemical processes. One of the most common biological processes is the Anaerobic Digestion (AD). AD is usually used for odor control, manure stabilization, resulting in the generation of biogas and residual digested [3]. On the other hand, among the different thermochemical processes such as pyrolysis, combustion and thermal liquefaction, the biomass gasification is one of the key technologies to convert biomass waste into syngas as well as fuel gas, which can be used for feeding gas

45 engines and gas turbines [4]. Biomass gasification can be defined the as the conversion
46 of biomass into a gaseous fuel by heating in a partial oxidation atmosphere.
47 Specifically, the gasification of the char has a special interest because it is the rate-
48 controlling step in the gasification process [5].

49 Guizani et al. (2013) studied the mixtures of steam and carbon dioxide as a gasifying
50 agent with a biomass feedstock of beech wood chips [6]. Valin et al. (2015) investigated
51 the influence of using H_2O/CO_2 during the wood chips gasification process on the
52 products yield and the remaining solid characteristics [7]. On the other hand, Scala
53 (2015) studied the char gasification using both H_2O and CO_2 as gasifying agent, a
54 kinetic model of the process being proposed based on experimental data [8]. The oxy-
55 fuel combustion is also being studied currently. This kind of process consists of using a
56 mixture atmosphere in which steam, oxygen and carbon dioxide are mixed in different
57 proportions. Su et al. (2015) focused their study on the oxy-fuel combustion with CO_2
58 of a bituminous coal and the effect of the presence of carbon dioxide on the
59 characteristics of the char formed [9].

60 Therefore, the nature of the gasifying agent and its proportion has a great influence on
61 the gasification process. In addition, the use of CO_2 would contribute to a reduction of
62 its concentration in the atmosphere [6]. Carbon dioxide used in this type of reaction
63 could be part of either an effluent stream coming from anaerobic digestions or coming
64 from a flue gas from any combustion or gasification plants [10].

65 Life Cycle Assessment (LCA) is an appropriated tool for studying these
66 thermochemical processes from an energetic, environmental and economic point of
67 view [2]. In this sense, Iribarren et al. (2013) studied the life-cycle assessment of an
68 energy conversion system for the coproduction of fuels and electricity from a

69 gasification-based biosyngas feedstock via Fischer–Tropsch synthesis coupled with a
70 combined-cycle process [11]. Furthermore, Susmozas et al. (2013) evaluated the
71 hydrogen production via indirect gasification of poplar biomass, following a LCA
72 approach [12]. Specifically, Wu et al. (2013) compared the management of manure by a
73 gasification process to its land application, through a LCA methodology [13].

74 In this work, the gasification process and the gases evolved of two different manure
75 chars (dairy and swine manure) were studied by thermogravimetric analysis (TGA)
76 coupled with mass spectrometry (MS). The influence of the amount of CO_2 in the
77 gasification process was carried out by varying the concentration of CO_2 from 15 to 90
78 vol.%. Furthermore, the effect of AD pretreatment on the thermal behavior of dairy
79 manure sample was evaluated. Finally, a LCA was performed to estimate and compare
80 the gasification of the different chars considered from the viewpoint of the energy
81 requirements, the greenhouse gas (GHG) emissions and the economic feasibility.

82 ## 2. MATERIALS AND METHODS

83 ### 2.1. Char preparation

84 Two samples of biomass were used in this investigation. Swine (SW) and dairy samples
85 were solid animal wastes obtained from the province of Québec (Canada). They were
86 treated by bio-drying and anaerobic digestion, respectively. To evaluate the changes
87 during the biological process, two dairy samples were studied: the storage tank output
88 (Pre) and the digester output (Dig R) [2].
89 Ten grams of these manure samples were pyrolyzed in a tubular reactor in order to
90 obtain the manure char for the gasification process. The samples were devolatilized
91 under a continuous He flow of 200 Nml/min from room temperature to 980 ºC, using a
92 heating rate of 10 ºC/min. The samples were kept around 980 ºC for 1 h. He flow was

maintained until the temperature dropped to ambient in order to prevent reaction with air. Once the different chars were obtained, they were sieved to an average particle size between 50 and 100 μm.

2.2. TGA-MS analysis

The gasification of manure samples were carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO). Previous to the gasification process, a pyrolysis process was required. Firstly, a pyrolysis step was performed in a tubular furnace as it was explained in section 2.1. Secondly, a pyrolysis stage was performed at 900 ºC in the termobalance, being just a heating of the pyrolyzed sample under an inert gas to reach to the gasification temperature. Sample weight was fixed at 7 mg and the particle size was kept in the 50-100 μm range. Samples were heated from ambient to 900 ºC using a heating rate of 40 ºC/min followed by 5 min at 900 ºC under an Ar flow of 100 mL/min. Once the gasification temperature was reached, the corresponding vol.% of gasifying agent (CO_2) was injected into the Ar flow (before the entrance to the furnace) during 30 minutes until the end of the gasification process.

The experimental error for the weight loss and temperature measurements was ± 0.5% and ± 2 ºC, respectively.

The analysis of the gas produced during gasification process was conducted in a mass spectrometer (Thermostar-GSD 320/quadrupole mass analyser; PFEIFFER VACUUM).

2.3. Characterization techniques of manure biomass.

Chars obtained from manure samples were characterized by elemental analysis, TGA, bomb calorimetry and atomic emission spectroscopy inductively coupled plasma (ICP-AES).

The ultimate analysis was used to measure the carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulfur (S) content of a sample. This analysis was performed in an elemental analyzer following the standard UNE-EN 15104:2011and was expressed as a mass percentage of each element in dry basis.

Moisture, ash, fixed carbon and volatile matter content of the samples were obtained by proximate analysis according to ASTM D 3172-73(84) standard [14]. These are the four most important chemical characteristics in any type of fuel. The equipment used to perform the proximate analysis was a thermogravimetric analyzer (TGA / DSC Model 1 METTLER TOLEDO STAR^{e} System).

The heat of combustion was determined using a Parr 1356 bomb calorimeter according to UNE 164001:2005 EX at constant volume and a reference temperature of 25 ºC. The energy equivalent was determined with a standard reference sample of benzoic acid. This way, a known mass amount of the sample was introduced in a gelatin capsule and combusted under an oxygen atmosphere.

A VARIAN LIBERTY RL sequential ICP-AES elemental analysis was used to obtain the weight percentage of metallic elements in the char coming from the manure samples. Table 1 shows the characterization of char samples described in this section.

Table 1. Ultimate and Proximate analyses, HHV and mineral content of char samples (Pre, Dig R and SW).

	*Ultimate Analysis (wt. %)					Proximate Analysis (wt. %)				Bomb calorimeter
Samples	**C**	**H**	**N**	**S**	**O^{diff}**	**Moisture**	**Ash**	**Volatile matter**	**Fixed carbon ^{diff}**	**HHV (MJ/kg)**
Char Pre	40.19	0.57	0.22	0.16	2.01	2.85	56.85	10.33	33.55	16.3
Char Dig R	39.10	0.76	0.53	0.18	0.15	3.96	59.28	13.86	31.74	14.3
Char SW	60.50	0.70	1.00	0.52	3.86	2.12	33.42	10.75	55.83	20.7

	Mineral content and Cl^-, CN^- content (ppm)												
	Al	**Ca**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Na**	**Ni**	**P**	**Si**	**Cl^-**	**CN^-**
Char Pre	5864	28322	-	-	8696	8793	9744	11377	-	25818	9961	-	-
Char Dig R	3954	36060	-	-	6425	12695	14735	14290	-	29266	9492	-	-
Char SW	1097	25015	-	33	6489	9788	9873	5380	-	22715	6280	-	-

***daf:** dry ash free; **O^{diff}:** obtained by difference of C, H, N, S and Ash; **Fixed carbon ^{diff}:** calculated from the difference of Moisture, Ash and Volatile matter.

2.4. Char reactivity

Char reactivity is an important parameter in the evaluation of gasification processes. Several definitions were used to evaluate it although the more extended one is based on the definition of the overall rate (R_i) as follows (Equation 2.1) [15-18]:

$$R_i = -{}^{1}/_{w_i} \cdot {}^{dw_i}/_{dt} = {}^{1}/_{1-x_i} \cdot {}^{dx_i}/_{dt} \quad (2.1)$$

where x_i and w_i are the conversion and weight of char at any time, respectively.

The reactivity depends on the temperature and gas composition and varies with the conversion degree [16, 19]. Thus, a representative value of the reactivity must be presented in order to make reliable comparisons. In this work, the reactivity at 50 % of char conversion was considered to be representative (R_{50}) [15, 18, 19].

The gasification rate (r_i) is also used to describe the gasification reaction and was calculated by Equation 2.2 [20]:

$$r_i = \frac{dx_i}{dt} \quad (2.2)$$

2.5. Life cycle assessment (LCA) methodology

LCA methodology presented in this study was used to estimate and compare gas emissions, energy and economic impacts of the gasification process of manure samples. In this work, the LCA of the gasification process of dairy manure samples (Pre and Dig R) was performed. Two scenarios were considered: gasification of char Pre and gasification of char Dig R (scenarios 1 and 2, respectively). The system boundaries and the two scenarios considered are shown in Figure 1. The design basis for the gasification process was undertaken. In this sense, the whole process presented three main stages: pre-treatment of biomass (dried and crushed), reaction and reconditioning

of products. The gasification process was carried out in a gasifier, leading to the decomposition of manure into two streams: ashes and gas. Ashes can be revalued as additives for cement or building materials. Gas stream was fed into a turbine where it was expanded. The energy was produced by the alternator, which was connected to the network through a parallel power plant park. In LCA studies, the functional unit (FU) quantifies the function of the product system and provides a reference unit [21]. In this work, the FU of the LCA was a production basis of 10,000 tons/year of dried manure. Gas emissions and particularly greenhouse gases (GHG) released during the thermochemical process were analyzed by means of TGA-MS. The gasification process was simulated using a flowsheet simulator (Aspen Plus® 8.4 licensed by Aspen Technology, Inc.), which can be used to calculate the main energy and material streams associated with the gasification of manure samples. In this work, the Aspen Plus® simulator was used to obtain the inputs/outputs of the energy balance. The anaerobic digester was not simulated. In this case, the data used in the economic study (production of biogas by anaerobic digestion) was extracted from real experiments carried out in Canada.

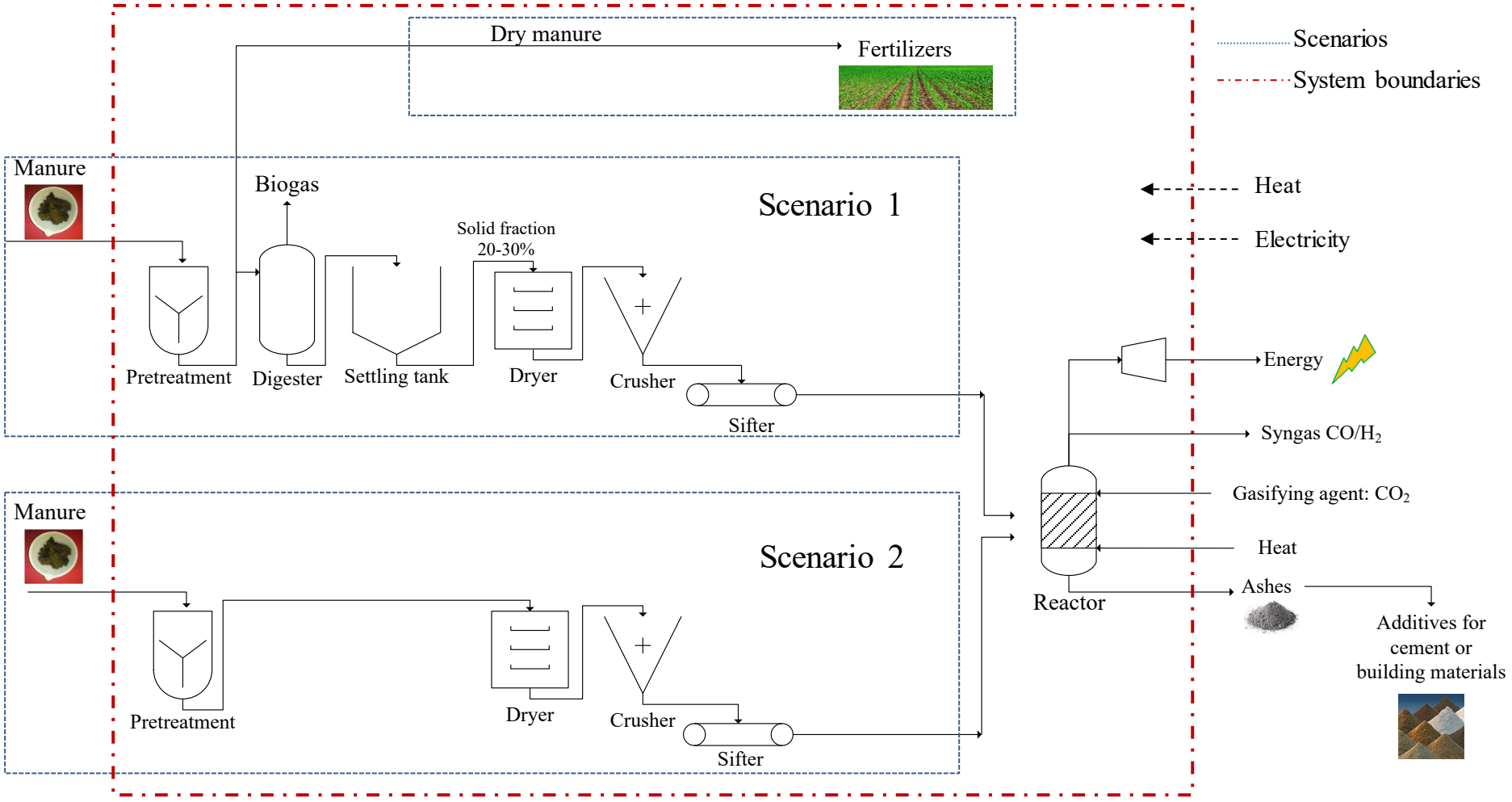


Figure 1. System boundaries and scenarios considered in LCA study.

188 Finally, an economic evaluation of the two scenarios considered was performed. Cost of
189 the main equipment was obtained from suppliers whereas the total fixed capital was
190 calculated from the major equipment cost, multiplying the corresponding Lang factors
191 according to the nature of the item. The total production cost was calculated as the sum
192 of the depreciation (it includes the amortization of the fixed capital and also the property
193 tax) plus the direct production costs (raw materials and utilities whose consumption was
194 calculated from the power of the process). Labor includes the manpower necessary for
195 the correct operation of the process and the general costs of supervision and
196 management. Other costs could be calculated by factors previously defined [22].
197 Net Price Value (NPV), the Internal Rate of Return (IRR) and the Payback are the
198 techno-economic parameters used for analyzing the economic viability of the
199 investment and the project.

200 # 3. RESULTS

201 ## 3.1. Influence of CO_2 concentration on the gasification process.

202 Char Pre was selected to assess the effect of the gasifying agent concentration. The
203 gasifying atmosphere consisted of a mixture of Ar/CO_2. Different experiments were
204 carried out by varying the vol.% CO_2 from 15 to 90. TG and DTG profiles for the
205 gasification of char Pre with different vol.% CO_2 are shown in Figure SS1. The
206 gasification temperature was 900 ºC at a heating rate of 40 ºC/min.

207 As it can be seen in Figure SS1a, the gasification of the char started as soon as the
208 gasifying agent reached the surface of the char. The higher the vol.% CO_2, the higher
209 the maximum weight loss was. In addition, the time at which the maximum weight loss
210 took place decreased when increasing concentrations of CO_2 (Figure 2b).

211 R_{50} values and times to achieve the 50 and 99 % of char conversion (X_{50} and X_{99},
212 respectively) are summarized in Table 2. R_{50} values increased with increasing vol.%
213 CO_2, clearly indicating that the reactivity of the sample increased with the CO_2
214 concentration in the gasifying atmosphere [23].

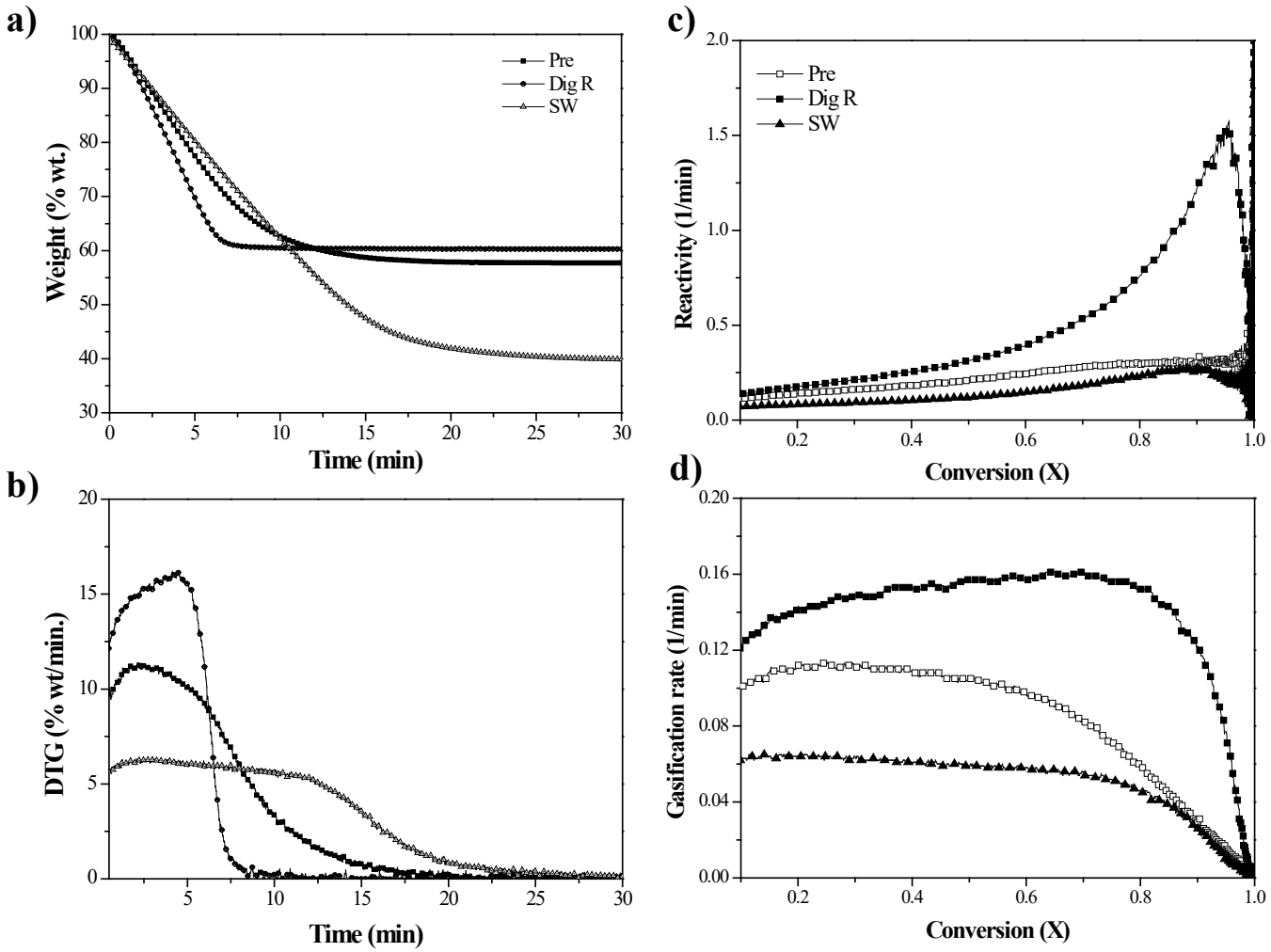
215 **Table 2.** Gasification characteristics of the char Pre under different vol.% CO_2.

CO_2 concentration (vol.%)	X_{99} (min)	X_{50} (min)	R_{50} (1/min)
15	23.02	9.50	0.21
25	19.05	8.93	0.25
40	16.58	8.03	0.34
90	11.58	7.38	0.41

216

217 ### 3.2. Char reactivity.

218 Figure 2 shows both the weight loss profiles versus time in the CO_2 gasification of the
219 char Pre, char Dig R and char SW at a temperature of 900 ºC and the reactivity and
220 gasification rate versus conversion for these three samples. The vol.% CO_2 selected for
221 these experiments was 15%. Although the best choice seemed to be a concentration of
222 90 vol.% CO_2, due to the higher reactivity of the char, a value 15 vol.% was selected for
223 being the typical CO_2 concentration present in flue gas streams [24], which usually are
224 by-products of some industries that can be used for the gasification of biomass char to
225 obtain H_2, CO and some C_2 hydrocarbons.



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227 **Figure 2.** CO_2 gasification of the different char samples: a) TG, b) DTG, c) Reactivity and d) Gasification rate.

228 R_{50} values and times to achieve the 50 and 99% of char conversion (X_{50} and X_{99},
229 respectively) are summarized in Table 3.

230 **Table 3.** Gasification characteristics of the char Pre, char Dig R and char SW at 900 ºC.

231

Biomass sample	X_{99} (min)	X_{50} (min)	R_{50} (1/min)
Char Pre	22.7	9.48	0.21
Char Dig R	13.0	8.23	0.31
Char SW	26.8	7.85	0.12

232

233

234 As it can be observed in Figure 2a, the gasification of the char started as soon as the
235 gasifying agent reached the surface of the char. According to the parameters of Table 3,
236 the reactivity of the different chars was ranked as follows: char Dig R > char Pre > char
237 SW. The amount of ashes that remain after the process was of 60, 57 and 39 wt. %,
238 respectively. According to Di Blasi et al. (2009), the char gasification process ideally
239 takes place at a constant rate, which slowly decreases as the char is being gasified [16].
240 Several deviations from the ideal behavior could be observed in the DTG profiles of
241 manure samples. Char Dig R showed a continuous increase up to time values of 4.5 min
242 followed by a sudden drop. On the other hand, the char Pre DTG profile obtained the
243 maximum rate at low times (2.5 min) with a decrease of the rate afterwards. Char SW
244 showed the DTG maximum at a similar time than that observed with char Pre.
245 However, the decrease of the rate showed an almost flat profile until gasification times
246 of 11.5 min. From this time the rate started to decrease.

247 Char conversion is a heterogeneous process in which the chemical reactions take place
248 over the surface of the material [16]. The reactivity of the samples depends on three
249 main characteristics: the sample chemical structure, the porosity and the inorganic
250 components [16]. The concentration of the gasifying agent also plays an important role
251 in the process. In this regard, the concentration of the reactive gas was maintained

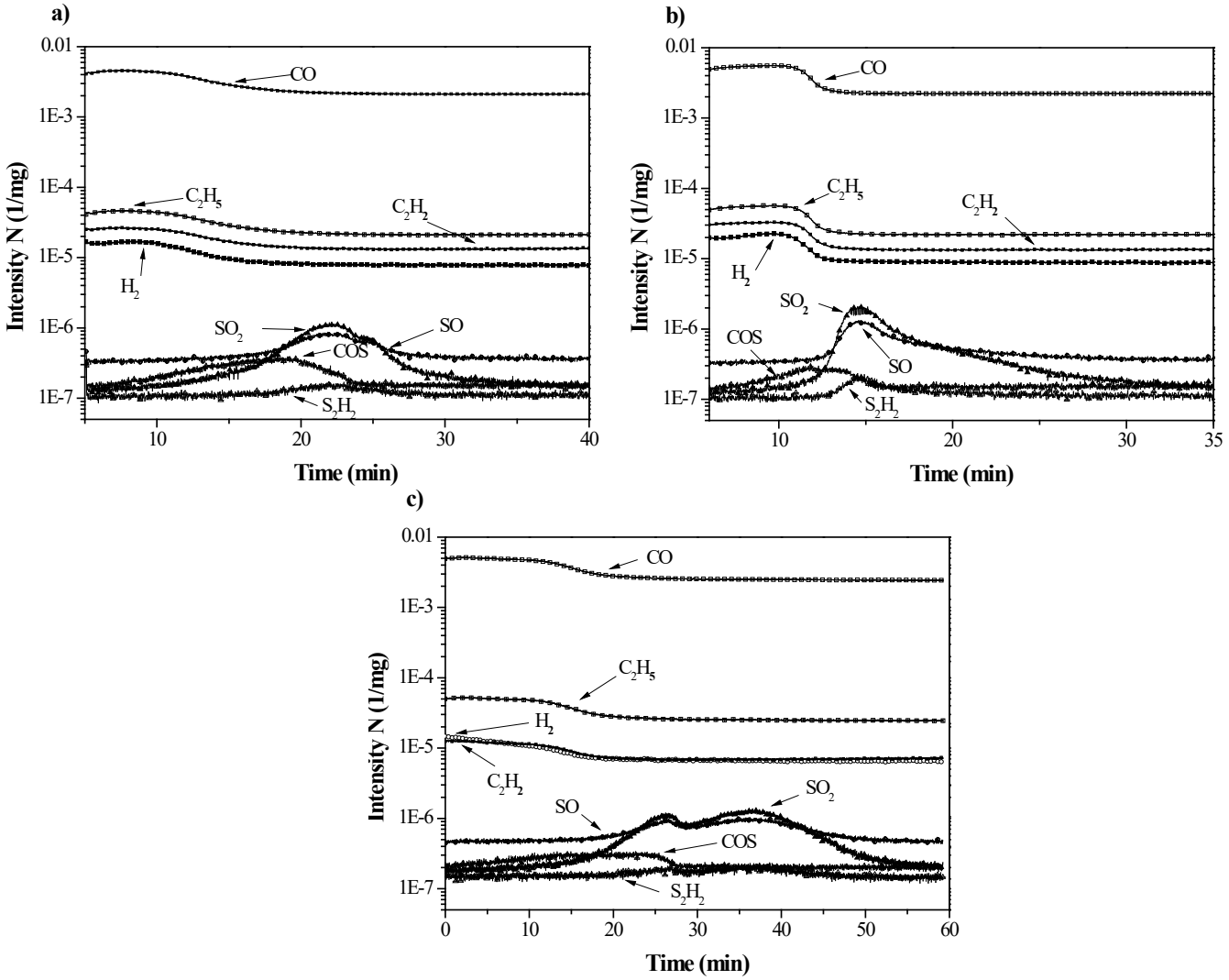
constant for all experiments. Therefore, the sample reactivity was only attributed to the surface area and the catalytic activity of indigenous inorganic matter in the biomass [16]. In order to evaluate the influence of the char structure in the process, nitrogen adsorption/desorption isotherms were performed. Table SS1 shows the BET surface area and the micropore volume for the char samples studied. The highest surface area (47.6 m^2/g) corresponded to the most reactive sample (Dig R) which was in agreement with the trend observed previously for R_{50}, X_{50} and X_{99} parameters. Consequently, their gasification took place at higher rates [25]. However, this fact does not seem to completely explain the gasification behavior of the samples under study, as it does not provide information about the differences found in the gasification profiles. In this regard, indigenous inorganic matter present in the biomass composition had an important role during the gasification process due to their catalytic nature and the different shapes of the gasification rates profiles that are commonly attributed to them [25-27].

In order to evaluate the catalytic effect of inorganic matter, typical reactivity and gasification rates versus conversion profiles were plotted in Figure 2c and 2d. It can be observed that the reactivity profiles showed a sudden rise at high conversion values, which is usually found in biomass chars or alkali catalyzed carbons [5, 25, 28]. The increase in the reactivity was associated with the fact that the carbon material was consumed during the gasification process. Therefore, the metal to carbon ratio increased and the catalytic effect was strengthened [29, 30]. As expected, the higher the ash content (Table 1) of the sample (Dig R > Pre > SW), the more prominent the increase of the samples reactivity at high conversion values was [29, 30]. Concerning the gasification rates profiles, SW showed a flat profile which is usually related to a low catalytic activity as found for other biomass chars in previous studies [5]. On the other

277 hand, char Dig R showed an increase of the reactivity, obtaining the maximum value at
278 a conversion around 0.75 whereas for char Pre it showed at lower values (X= 0.22).

279 Figure 3 shows the MS profiles for the gasification process at 900 ºC for char Pre, char
280 Dig R and char SW. The gas product distribution was similar in all cases. Two clear
281 emission zones were detected.
282 Regarding the first one, the main gaseous products of the CO_2 gasification were
283 released as CO, H_2, SO_x and C_1 and C_2 hydrocarbons (C_xH_y). The gas profile of these
284 products followed the same trend than that of the DTG profile showed in Figure 2b. It
285 can be observed that the main product obtained was CO, which is produced by CO_2
286 gasification of the char (C (char) + $CO_2 \leftrightarrow 2CO$). On the other hand, H_2 and
287 hydrocarbons (C_xH_y) were also found in similar proportions. Lower yields of H_2 and
288 C_xH_y were observed for sample SW, which is due to the lower proportion of H_2 in the
289 char. Anyway, these compounds were mainly produced due to the thermal cracking and
290 dehydrogenation of the char ($C_nH_m \leftrightarrow C_{n-x}H_{m-y} + H_2 + CH_4 + C$).
291 The second emission zone was characterized by the production of sulfur compounds
292 such as COS and SO_2. Their evolution patterns were closely related. COS production
293 was attributed to the reaction of CO with elemental sulfur in the char [31]. COS was
294 detected up to gasification times close to those obtained for the full gasification of
295 manure samples. On the other hand, the emission of SO_2 started after COS was
296 detected. This fact might point out that SO_2 was produced by a further oxidation of
297 COS. Furthermore, the maximum peak for SO_2 production took place once the COS
298 yield started decreasing. This confirmed that the production of SO_2 was mainly
299 attributed to gas-phase reactions, explaining that the detection of this compound was
300 performed once the manure chars were fully converted.

Summarizing, the CO_2 gasification of manure chars seemed to have three pathways. Firstly, the main components in the char (C, H and S) were oxidized, which was mainly attributed to an easier exposure to the reactant gas. Secondly, the sulfur reacted with the formed CO to formed COS. Finally, SO_2 was formed in the gas phase.



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306 **Figure 3.** Mass spectra for the CO_2 gasification at 900 ºC of: a) char Pre, b) char Dig R and c) char SW.

3.3. Life cycle assessment

The SWOT matrix concerning the use of manure as fertilizer is shown in Figure 4.

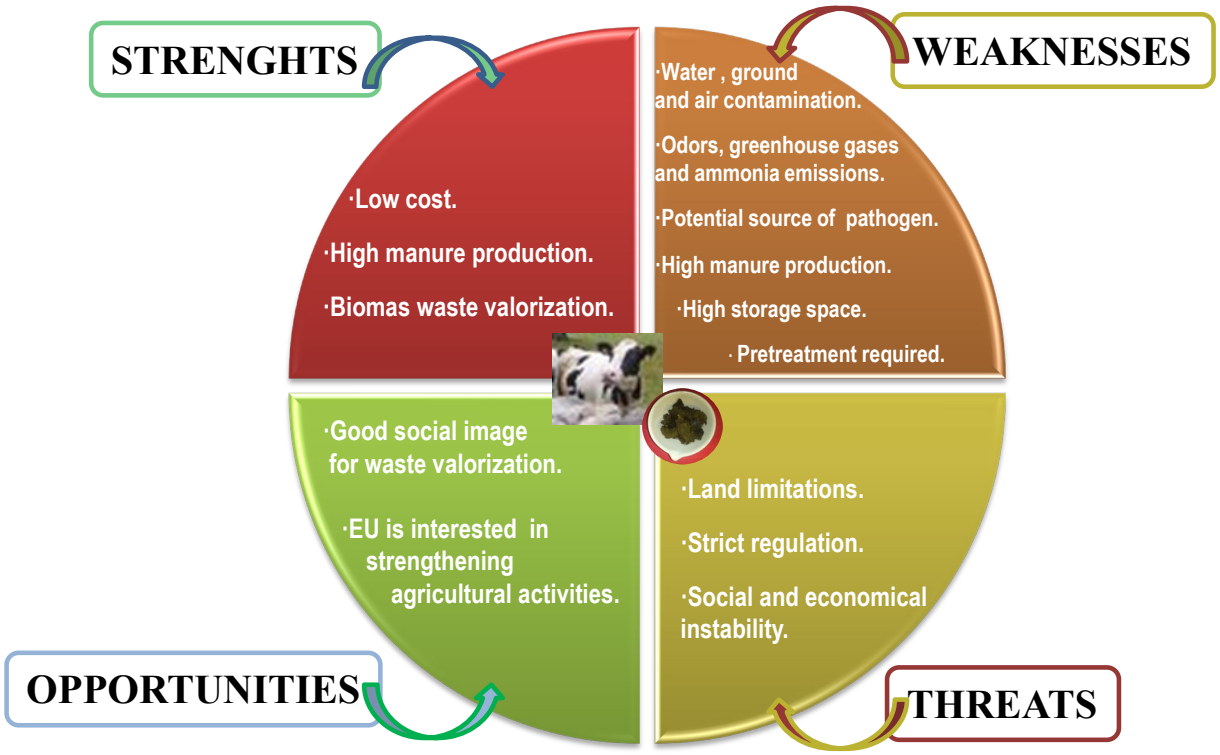

Figure 4. SWOT matrix concerning the use of manure as fertilizer.

SWOT analysis is only a tool to evaluate the strengths, weaknesses, opportunities and threats based on a wide knowledge of the present situation and the future trends of the market [32].

In this case, the SWOT analysis was applied to decide whether the use of manure as fertilizer is the most appropriate use to this type of biomass. According to the SWOT matrix, there are more weaknesses than strengths in the use of manure as fertilizer. As it can be seen, the item “high manure production” was placed in both the strengths and the weaknesses. The high production is a strength since the viewpoint of a continuous raw

320 material but also is a weakness because there is more production than the fertilizer
321 market can assume. Moreover, land limitations are one of the threats.
322 Therefore, by considering manure as a raw material of a gasification process, the
323 strength and the opportunities were the same as in the case of fertilizers and the majority
324 of the weaknesses and the threats (pollution, contamination and the strict regulation)
325 could be solved.

326 **3.3.1. Gas emissions**

327 The integrated peak areas for the main emissions detected by TGA-MS were obtained in
328 order to compare the two scenarios under study. CO, H_2, C_2H_2, C_2H_5, SO and SO_2 were
329 the main gases evolved which were considered in the LCA study. Figure 5 shows the
330 integrated peak areas of MS spectra. It can be seen that CO was the main gas produced
331 during the gasification of both samples. Gasification of char Dig R (scenario 2) yielded
332 a higher amount of gases than that of char Pre. Concerning the individual gases, H_2 and
333 C_2 hydrocarbons production were higher in the case of sample char Dig R. Moreover,
334 the production of SO_x also was higher for this sample.

335 On the other hand, the process which higher amount of CO_2 captured was the
336 gasification of char Pre (scenario 1). During the simulation of the gasification by the
337 Aspen Plus® simulator, the gasifying agent flow was adjusted leading to a total
338 consumption of CO_2. Tables 4 and 5 show the different flows used to determine the
339 highest CO_2 flow which can be eliminate during gasification of chars Pre and Dig R,
340 respectively, taking into account that 'CO_2 in' is the CO_2 input (15 vol.% of 'Gasifying
341 agent') and 'CO_2 out' is the CO_2 output of the gasification reactor. This way, the
342 gasification of char Pre (scenario 1) appeared to be the most environmental friendly
343 process since it allowed to capture CO_2 and reduce the SO_x release.

344 **Table 4.** CO_2 flow consumed during gasification for scenario 1.

Gaifying agent flow (kg/h)	CO_2 in (kg/h)	CO_2 out (kg/h)	$CO_{2,in}/CO_{2,out}$
7498	1628	49.8	32.7
7250	1574	27.9	**56.5**
7000	1519	27.0	56.3
6500	1411	25.2	55.9
6000	1302	23.5	55.5

345

346 **Table 5.** CO_2 flow consumed during gasification for scenario 2.

Gaifying agent flow (kg/h)	CO_2 in (kg/h)	CO_2 out (kg/h)	$CO_{2,in}/CO_{2,out}$
6938	1506	49.8	30.3
6500	1411	25.9	**54.5**
6250	1357	25.0	54.3
6000	1302	24.1	54.0
5500	1194	22.4	53.3

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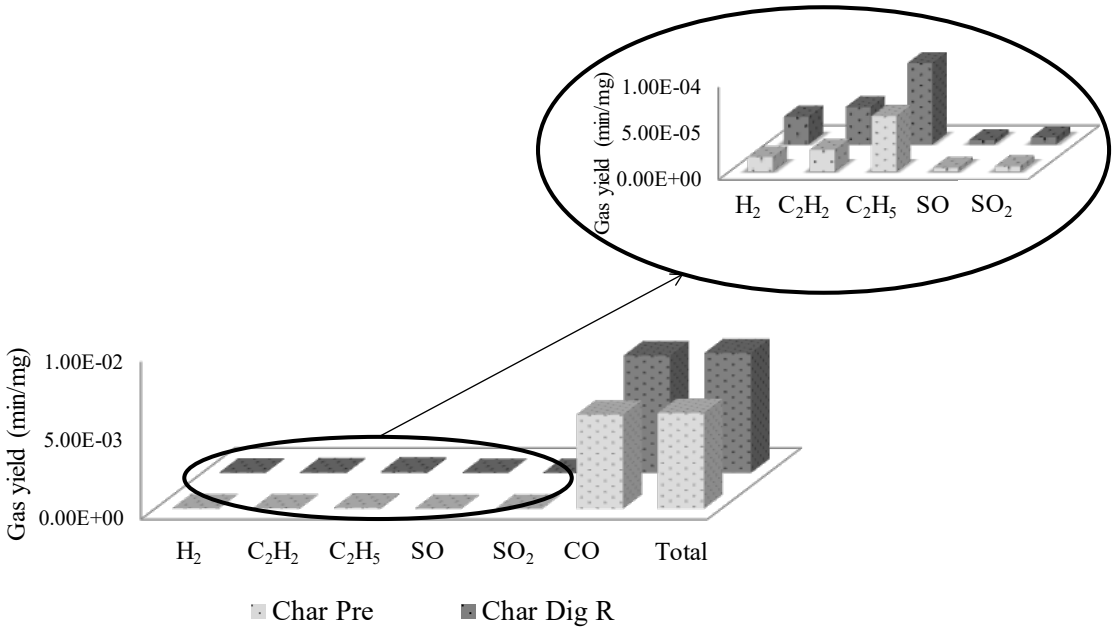

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349 **Figure 5.** Integrated peak areas of the main gas evolved during CO_2 gasification.

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3.3.2. Energy balance

As abovementioned, the gasification process could be divided into three stages. Manure samples need to be pretreated (drying and grinding) before being fed into the gasifier. Therefore, the energy consumption for the manure pretreatment should be considered. All the energy inputs with positive value and energy outputs with negative value for the two scenarios considered are shown in Table 6 and obtained from the Aspen Plus® simulator.

As it can be seen in Table 6, the gasification of both char Pre (scenario 1) and char Dig R (scenario 2) showed a negative net energy balance (more energy was consumed than generated). Anaerobic digestion improved the energy balance but less energy was obtained in the turbine.

According to these results, the gasification of char Dig R was considered the best option from the energetic point of view.

Table 6. Energy inputs and outputs for the studied scenarios.

Scenario	Equipment	Unit	Value
1	*Biomass Pretreatment*		
	Grinding	MJ/h	32
	Production		
	Gasifier	MJ/h	13094
	Cyclon	MJ/h	32
	Turbine	MJ/h	-6264
	Total	MJ/h	6894
2	*Biomass Pretreatment*		
	Grinding	MJ/h	32
	Production		
	Gasifier	MJ/h	11937
	Cyclon	MJ/h	29
	Turbine	MJ/h	-5688
	Total	MJ/h	6310

3.3.3. Economic evaluation

The capital investment was calculated according to the percentage method [22, 33]. A continuous operating time of 8000 h/year was established and the raw material consumption was 1,250 kg/h for the two scenarios studied. Table 7 shows the list of the main equipment and its individual costs. A summary of the percentage method is depicted in Tables SS2 and SS3. It is important to highlight that for both scenarios studied the gas turbine was the most expensive equipment.

394 **Table 7.** Main equipment and their individual cost.

Scenario	Equipment	C_{2014}(€)
1	Pre storage tank	59011
	Ball mill	87424
	Gasifier	70277*
	Cyclone to remove residual particles in the gasificator	15757
	Turbine	663151
	CO_2 vessel storage	376556
	Compressor	44252
2	Pre storage tank	47372
	Ball mill	87424
	Gasifier	70277*
	Cyclone to remove residual particles in the gasificator	15757
	Turbine	602171
	Anaerobic digester	200000
	CO_2 vessel storage	376556
	Compressor	44252

*Stainless steel equipment

395 The stock of raw materials for ten days production was the working capital considered
396 in this economic study. Once the fixed and circulating capital were computed, the
397 overall investment of the process can be obtained. In addition, an inflation rate of 2%
398 was considered. Sales for each scenario are summarized in Table 8. As it can be seen,
399 the energy and ashes sales were higher for scenario 1.

400 Manufacturing operation, raw materials, energetic requirement, utilities and plan
401 maintenance are the items considered for calculating the operating costs. The cost of the
402 raw materials was zero as it was considered as a residual biomass. These costs are
403 shown in Tables SS4 and SS5.

404 **Table 8.** Summary of annual sales for each scenario studied.

Scenario	Products	Production year (t/year)//(kWh/year)	Sale price (€/kg)//(€/kWh)	Sales (€/year)
1	Ashes	5403	0.107[(1)]	578145
	Energy	$1.39 \cdot 10^7$	0.220[(2)]	3062400
2	Ashes	5398	0.107	577607
	Energy	1,26·107	0.220	2780800
	Biogas	1140	0.045[(3)]	51300

405 [(1)]Price of char and ash [34]
406 [(2)]Price of energy International Renewable Energy Agency. Available at:
407 http://www.irena.org/DocumentDownloads/Publications/RE_Technologies_Cost_Analysis-
408 BIOMASS.pdf; 2012.
409 [(3)]The price of biogas and fuel gas was assumed to be equal to that of natural gas [35]

410

411 Figure 6 shows the IRR, NPV and the payback period for each scenario. A linear
412 amortization in 15 years was considered for the income statement estimation.

413 Generally, the higher the IRR, the more the project should be undertaken. Payback for
414 char Pre gasification was 9 years whereas for char Dig R was 10 years. Furthermore, the
415 gasification of char Pre was the most economically viable scenario with the highest IRR
416 and NPV (16% and 2.36 million €, respectively).

417 The gasification of char Pre was the most viable scenario from the economic and
418 environmental viewpoint. However, the gasification of char Dig R was the best
419 energetic option.

420

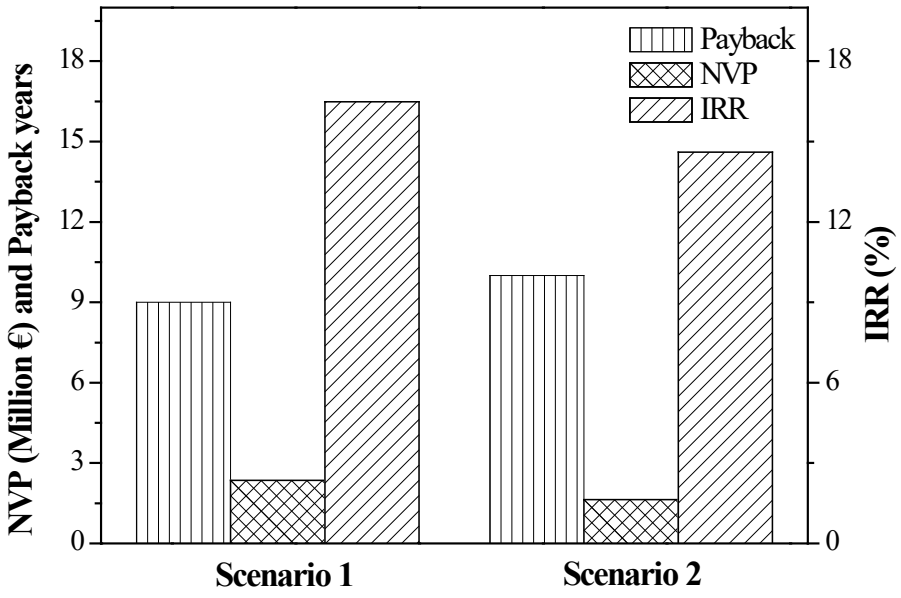

Figure 6. NVP, IRR and Payback for the two scenarios studied.

On the basis of the results obtained, the gasification of manure is a better option against its traditional use as fertilizer since the weaknesses of the latter use is solved.

4. CONCLUSIONS

Concerning the time to achieve the 99% of char conversion, the reactivity of the samples was ranked as follows: char Dig R > char Pre > char SW. The reactivity of the samples mainly depended on the chemical structure, porosity and inorganic components. According to the results obtained, the higher surface area (47.6 m^2/g) corresponded to the most reactive sample (char Dig R). Furthermore, the highest ash content of the samples also corresponded to char Dig R (59.28 %), which corroborated the higher reactivity of this sample at high conversion values. The gas product distribution detected with the TGA-MS technique was similar for all samples. The main gaseous products released during CO_2 gasification process were CO, H_2, SO_x, C_2H_2 and C_2H_5. Concerning the LCA study, the gasification of char Pre was the most viable scenario from the economic and environmental point of view and the gasification of the

char Dig R was the best energetic option. To sum up, the gasification of manure is a better option against its traditional use as fertilizer since the weaknesses of the latter use is solved.

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REFERENCES

[1] Cao JP, Huang X, Zhao XY, Wei XY, Takarada T. Nitrogen transformation during gasification of livestock compost over transition metal and Ca-based catalysts. Fuel 2015; 140: 477-83.

[2] Fernandez-Lopez M, Puig-Gamero M, Lopez-Gonzalez D, Avalos-Ramirez A, Valverde J, Sanchez-Silva L. Life cycle assessment of swine and dairy manure: Pyrolysis and combustion processes. Bioresour Technol 2015; 182: 184-92.

[3] Zarkadas IS, Sofikiti AS, Voudrias EA, Pilidis GA. Thermophilic anaerobic digestion of pasteurised food wastes and dairy cattle manure in batch and large volume laboratory digesters: Focussing on mixing ratios. Renew Energ 2015; 80: 432-40.

[4] Lahijani P, Zainal ZA, Mohamed AR, Mohammadi M. CO2 gasification reactivity of biomass char: Catalytic influence of alkali, alkaline earth and transition metal salts. Bioresour Technol 2013; 144: 288-95.

460 [5] López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L.
461 Gasification of lignocellulosic biomass char obtained from pyrolysis: Kinetic and
462 evolved gas analyses. Energy 2014; 71: 456-67.
463 [6] Guizani C, Escudero Sanz FJ, Salvador S. The gasification reactivity of high-
464 heating-rate chars in single and mixed atmospheres of H2O and CO2. Fuel 2013; 108:
465 812-23.
466 [7] Valin S, Grateau M, Thiery S, Gauthier G, Defoort F, Melkior T. Influence of
467 atmosphere (N2/CO2/H2O) on wood centimetre-scale particle devolatilisation at 800°C.
468 Fuel 2015; 139: 584-93.
469 [8] Scala F. Fluidized bed gasification of lignite char with CO2 and H2O: A kinetic
470 study. P Combust Inst 2015; 35: 2839-46.
471 [9] Su S, Song Y, Wang Y, Li T, Hu S, Xiang J, et al. Effects of CO2 and heating rate
472 on the characteristics of chars prepared in CO2 and N2 atmospheres. Fuel 2015; 142:
473 243-9.
474 [10] Irfan MF, Usman MR, Kusakabe K. Coal gasification in CO2 atmosphere and its
475 kinetics since 1948: A brief review. Energy 2011; 36: 12-40.
476 [11] Iribarren D, Susmozas A, Dufour J. Life-cycle assessment of Fischer–Tropsch
477 products from biosyngas. Renew Energ 2013; 59: 229-36.
478 [12] Susmozas A, Iribarren D, Dufour J. Life-cycle performance of indirect biomass
479 gasification as a green alternative to steam methane reforming for hydrogen production.
480 Int J Hydrogen Energy 2013; 38: 9961-72.
481 [13] Wu H, Hanna MA, Jones DD. Life cycle assessment of greenhouse gas emissions
482 of feedlot manure management practices: Land application versus gasification. Biomass
483 Bioenergy 2013; 54: 260-6.

484 [14] ASTM D 3172-73(84). Standard method of proximate analysis of coal and coke in
485 gaseous fuel; coal and coke section 5, Annual book of ASTM standard, vol. 05-05;
486 1989. p.299.
487 [15] Mandapati RN, Daggupati S, Mahajani SM, Aghalayam P, Sapru RK, Sharma RK,
488 et al. Experiments and kinetic modeling for CO2 gasification of indian coal chars in the
489 context of underground coal gasification. Ind Eng Chem Res 2012; 51: 15041-52.
490 [16] Di Blasi C. Combustion and gasification rates of lignocellulosic chars. Prog Energ
491 Combust 2009; 35: 121-40.
492 [17] Fermoso J, Arias B, Pevida C, Plaza MG, Rubiera F, Pis JJ. Kinetic models
493 comparison for steam gasification of different nature fuel chars. J Therm Anal Calorim
494 2008; 91: 779-86.
495 [18] Zhang L, Huang J, Fang Y, Wang Y. Gasification reactivity and kinetics of typical
496 Chinese anthracite chars with steam and CO2. Energy Fuels 2006; 20: 1201-10.
497 [19] Gómez-Barea A, Ollero P, Fernández-Baco C. Diffusional effects in CO2
498 gasification experiments with single biomass char particles. 1. Experimental
499 investigation. Energy Fuels 2006; 20: 2202-10.
500 [20] Huang Y, Yin X, Wu C, Wang C, Xie J, Zhou Z, et al. Effects of metal catalysts on
501 CO2 gasification reactivity of biomass char. Biotechnol Adv 2009; 27: 568-72.
502 [21] ISO, 2006. ISO 14040. Environmental management – life cycle assessment –
503 principles and framework International Organization for Standardization, Geneva; 2006.
504 [22] Peters M. Economics for Chemical Engineers. McGraw-Hill Education 2003.
505 [23] Nowicki L, Antecka A, Bedyk T, Stolarek P, Ledakowicz S. The kinetics of
506 gasification of char derived from sewage sludge. J Therm Anal Calorim 2011; 104:
507 693-700.

508 [24] Gil MV, Riaza J, Álvarez L, Pevida C, Pis JJ, Rubiera F. Oxy-fuel combustion
509 kinetics and morphology of coal chars obtained in N2 and CO2 atmospheres in an
510 entrained flow reactor. Appl Energy 2012; 91: 67-74.
511 [25] Duman G, Uddin MA, Yanik J. The effect of char properties on gasification
512 reactivity. Fuel Process Technol 2014; 118: 75-81.
513 [26] Struis RPWJ, Von Scala C, Stucki S, Prins R. Gasification reactivity of charcoal
514 with CO2. Part II: Metal catalysis as a function of conversion. Chem Eng Sci 2002; 57:
515 3593-602.
516 [27] Struis RPWJ, Von Scala C, Stucki S, Prins R. Gasification reactivity of charcoal
517 with CO2. Part I: Conversion and structural phenomena. Chem Eng Sci 2002; 57:
518 3581-92.
519 [28] López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L.
520 Comparison of the steam gasification performance of three species of microalgae by
521 thermogravimetric-mass spectrometric analysis. Fuel 2014; 134: 1-10.
522 [29] Marquez-Montesinos F, Cordero T, Rodríguez-Mirasol J, Rodríguez JJ. CO2 and
523 steam gasification of a grapefruit skin char. Fuel 2002; 81: 423-9.
524 [30] Dupont C, Nocquet T, Da Costa JA, Verne-Tournon C. Kinetic modelling of steam
525 gasification of various woody biomass chars: Influence of inorganic elements.
526 Bioresour Technol 2011; 102: 9743-8.
527 [31] Chen L, Bhattacharya S. Sulfur emission from victorian brown coal under
528 pyrolysis, oxy-fuel combustion and gasification conditions. Environ Sci Technol 2013;
529 47: 1729-34.
530 [32] Russo D, Dassisti M, Lawlor V, Olabi AG. State of the art of biofuels from pure
531 plant oil. Renew Sust Energ Rev 2012; 16: 4056-70.
532 [33] Hillstrom K. Encyclopedia of Small Business: A-I. Gale Group 2002.

533 [34] Woolf D, Lehmann J, Fisher EM, Angenent LT. Biofuels from Pyrolysis in
534 Perspective: Trade-offs between Energy Yields and Soil-Carbon Additions. Environ Sci
535 Technol 2014; 48: 6492-9.
536 [35] Norsker N-H, Barbosa MJ, Vermuë MH, Wijffels RH. Microalgal production — A
537 close look at the economics. Biotechnol Adv 2011; 29: 24-7.