

Manuscript Number: APEN-D-17-02135R1

Title: Torrefaction of a solid recovered fuel (SRF) to improve the fuel properties for gasification processes.

Article Type: Research Paper

Keywords: SRF; torrefaction; gasification; syngas; tar; contaminants.

Corresponding Author: Dr. César Berrueco, Ph.D

Corresponding Author's Institution: IREC-Catalonia Institute for Energy Research

First Author: Javier Recari

Order of Authors: Javier Recari; César Berrueco, Ph.D; Neus Puy, PhD; Santiago Alier; Jordi Bartrolí, PhD; Xavier Farriol, PhD

Abstract: This work studies the torrefaction of a solid recovered fuel (SRF) and its effect on the fuel properties for gasification. The SRF (namely FL) was torrefied at two temperatures (290 °C and 320 °C) in a pilot auger reactor (capacity of up to 100 kg/h) and evaluated as a gasification feedstock. This evaluation included the characterization of the obtained torrefied materials (FL290 and FL320) and several gasification tests in a bench-scale fluidized bed reactor. These tests were performed with different gasification agents (air and oxygen/steam) and bed materials (sand, dolomite and olivine) at similar experimental conditions (T=850 °C and ER ~0.3). The evaluation of the gasification performance was presented in terms of product yields and gas composition together with the release of contaminants. Tar species (polycyclic aromatic hydrocarbons) and minor contaminants (H₂S, HCl, HCN and NH₃) were analysed by gas chromatography and ion-selective potentiometry, respectively. Additionally, the calculation of the process efficiency (gasification and its combination with torrefaction) based on the energy content of the producer gas and a preliminary cost analysis that evaluate the main benefits and drawbacks of the torrefaction process are included.. The results indicated that the torrefaction process improved the SRF gasification parameters (lower tar, higher H₂/CO ratio, carbon conversion, etc.) and strongly affected the presence of HCl in the producer gas. However, the preliminary cost analysis advised the combination of both technologies only under certain gasification conditions.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

**Torrefaction of a solid recovered fuel (SRF) to improve the fuel properties for
gasification processes.**

J. Recari^a, C. Berrueco^{b*}, N. Puy^{c,d}, S. Alier^d, J. Bartrolí^c, X. Farriol^a

^aDepartament d'Enginyeria Química. Universitat Rovira i Virgili. Av. Països
Catalans, 26. Tarragona, 43007 Spain

^bCatalonia Institute for Energy Research, IREC. C/ Marcel·lí Domingo, 2. Tarragona,
43007 Spain

^cDepartment of Chemistry. Universitat Autònoma de Barcelona. Edifici Cn- Campus
UAB, 08193 Bellaterra (Cerdanyola del Vallès), Barcelona, Spain.

^dEnergies Tèrmiques Bàsiques SL. C/ Maó 22, 2-1, 08022 Barcelona, Spain.

*Corresponding author. Telephone: +34 977 297 921 Fax: +34 977 202 444. e-mail:
cesar.berrueco@gmail.com

ABSTRACT

This work studies the torrefaction of a solid recovered fuel (SRF) and its effect on the fuel properties for gasification. The SRF (namely FL) was torrefied at two temperatures (290 °C and 320 °C) in a pilot auger reactor (capacity of up to 100 kg/h) and evaluated as a gasification feedstock. This evaluation included the characterization of the obtained torrefied materials (FL290 and FL320) and several gasification tests in a bench-scale fluidized bed reactor. These tests were performed with different gasification agents (air and oxygen/steam) and bed materials (sand, dolomite and olivine) at similar experimental conditions (T=850 °C and ER ~0.3). The evaluation of the gasification performance was presented in terms of product yields and gas composition together with the release of contaminants. Tar species (polycyclic aromatic hydrocarbons) and minor contaminants (H₂S, HCl, HCN and NH₃) were analysed by gas chromatography and ion-selective potentiometry, respectively. Additionally, the calculation of the process efficiency (gasification and its combination with torrefaction) based on the energy content of the producer gas and a preliminary cost analysis that evaluate the main benefits and drawbacks of the torrefaction process are included. The results indicated that the torrefaction process improved the SRF gasification parameters (lower tar, higher H₂/CO ratio, carbon conversion, etc.) and strongly affected the presence of HCl in the producer gas. However, the preliminary cost analysis advised the combination of both technologies only under certain gasification conditions.

Keywords: SRF, torrefaction, gasification, syngas, tar, contaminants.

1. INTRODUCTION

Municipal solid waste (MSW) is not only one of the main by-products of human society, but also a potential energy source that has attracted increasing attention over the years [1]. Among various waste-to-energy technologies, gasification is recognized as a promising method [1,2]. Gasification is usually defined as a partial oxidation of the fuel, which is treated in substoichiometric conditions, leading to the production of a syngas and a series of by-products. The potential benefits of gasification over traditional combustion of solid wastes are mainly related to the advantages of handling (and burning) a gas versus a solid waste [2]. In addition, gasification presents a high level of efficiency and the produced syngas can be used in different application, such as generation of electricity, fuels and chemicals.

At present, biomass is acting as the primary renewable source for gasification [3,4]. However, municipal solid waste (MSW) and related fractions (i.e. Solid Recovered Fuels, SRFs) have the potential to become an interesting alternative [5]. The high availability of waste and its continuous generation assures an almost inexhaustible source for thermal conversion routes as a way for energy recovery. However, waste gasification has still to overcome some problems related to gas quality and the release of contaminants. In this scenario, one possible route, scarcely explored with SRFs, is the use of thermal pretreatments such as torrefaction. These pretreatments have potential to improve the properties of biomass and SRFs making them better feedstocks for conversion into fuels and chemicals [6–9].

Biomass torrefaction involves heating the feedstock at temperatures between 200-300 °C in inert atmosphere, resulting in a hydrophobic product with less moisture, which prevents the biomass from decomposing, and higher energy density for subsequent thermochemical applications [6,10,11].

Considering the energy efficiency, the overall efficiency of a process that combines torrefaction and gasification has been reported to improve or to be slightly lower than the direct biomass gasification [10,12], depending on the process configuration. Several strategies can be adopted, such as include the heat integration of the torrefaction and gasification processes [13] or reinject the volatiles produced in the torrefaction step downstream the gasification unit [12]. Biomass torrefaction also presents positive effects on the gasification process from an operational point of view [6]. Various studies have reported lower storage and transportation costs, together

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

with increasing syngas yields and lower tar levels and acid contents [6,8,14,15] when comparing gasification of torrefied and original biomasses.

Nevertheless, the mentioned advantages of torrefaction may differ for a highly heterogeneous material as waste, composed by different sorts of residues: plastic, paper, cardboard, food waste, glass, etc. As observed with biomass, it is important to explore this route with waste fractions as it can lead to a more homogenous material and attenuate the release of pollutants during the energy valorization of the torrefied materials.

Few investigations have addressed waste torrefaction, such waste from food, kitchen and agricultural waste [11,16–21]. Yuan et al. [19] studied the properties of MSW samples torrefied at various temperatures (250-450 °C). They concluded that in the temperature range of 250-350 °C the calorific values were higher and chlorine contents decreased in the torrefied MSW. Another work by Poudel et al. [16] investigated the effects of torrefaction temperature and time on food waste, concluding that 290-330 °C was the optimum torrefaction region due to a high energy yield (> 90%) and high heating value (which increased > 10%). Manatura et al. [21] presented an exergetic evaluation of the gasification process of torrefied rice husk, an agricultural waste. The reported results depicted the contradictory effects of torrefaction on the gasification efficiency. On the one hand the increase of chemical energy (exergy) of syngas due to lower O/C and H/C in the torrefied material led to higher exergy efficiencies. On the other hand, the release of volatiles during torrefaction, more pronounced at higher torrefaction temperatures, provoked a decrease in overall efficiency. The authors reported that this adverse effect became dominant at a torrefaction temperature of 350 °C, whereas a torrefaction temperature close to 250 °C improved the biomass properties and resulted in enhanced gasification performance and energy efficiency. In contrast to gasification of torrefied biomass or torrefied agricultural waste, there is no published data of torrefied MSW as gasification feedstock.

This work studies the torrefaction of a solid recovered fuel (SRF) and its effect on the fuel properties as gasification feedstock. The evaluated SRF was a fluff material (referred as FL) with high moisture (> 8%) and chlorine content (0.6%). In order to upgrade its properties as fuel, the FL sample was torrefied at two temperatures (290 and 320 °C) in a pilot auger reactor. The assessment of the torrefied materials as gasification feedstock was carried out through the materials characterization and a

1 series of gasification tests. Gasification experiments were carried out in a laboratory
2 scale fluidized bed reactor at fixed operation conditions (gasification temperature of
3 850 °C and equivalence ratio of 0.3) but varying the fluidizing agent (air or a mixture
4 of oxygen/steam) and the bed material (sand, dolomite or olivine). The evaluation of
5 the influence of torrefaction on the gasification performance was one of the key
6 aspects of the work, focusing on the evolution of main compounds (H₂, CO, CO₂,
7 CH₄...) and minor contaminants (tar, H₂S, HCl, HCN and NH₃) in the producer gas.
8
9
10
11
12
13

14 **2. EXPERIMENTAL**

15 **2.1. SRF sample preparation and characterization**

16 The studied SRF was a fluff material (namely FL) provided by a local waste
17 management company. FL was obtained from a mechanical process of mixed
18 domestic waste streams, composed by diverse fractions of paper, biomass and
19 polymers (post-consumer plastics and textiles). More details about this fuel can be
20 found elsewhere [22,23]. This SRF was subjected to a torrefaction pretreatment (see
21 section 2.2) in order to obtain two torrefied batches (referred as FL290 and FL320) to
22 be used as gasification feedstock. The parent SRF was grounded and sieved to a
23 particle size of 8 mm for the torrefaction process and then all samples were milled to
24 1 mm for characterization and gasification purposes. A list of the main techniques and
25 equipments used is shown as follows:
26
27
28
29
30
31
32
33
34
35
36

- 37 • Proximate analysis in a LECO Thermogravimetric (TGA 701), according to
38 EN-15402:2011 and EN-15403:2011 standard methods.
- 39 • Ultimate analysis in a LECO TruSpec CHN-S analyser following the EN-
40 15407:2011.
- 41 • Heating value conducted in a LECO calorimeter (AC-600) according to the
42 EN- 15400:2011 standard method.
- 43 • Halogens (Cl, F and Br) content analysed by ionic chromatography (Dionex
44 ICS-1100) following the EN- 15408:2011 standard method.
- 45 • Ash composition determined in Spectro Arcos 165 spectrophotometer after
46 ash samples digestion in a microwave system (Berghof Speedwave 4),
47 according to the EN-15410:2006 and EN-15411:2006 standard methods.
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2 Table 1 presents the characterization results. Each analysis was performed by
3 triplicate with uncertainties estimated at a 95% probability level.
4

5 **2.2. Torrefaction process**

6

7
8 The FL sample was torrefied at two final temperatures (290 and 320 °C) using a
9 pilot auger reactor. The torrefaction and pyrolysis pilot plant comprises six main
10 parts: the feeding system, a drying reactor, the torrefaction reactor, a cooling screw,
11 the vessel for solids collection and the condensing system (see Figure 1). The drying
12 and torrefaction reactors, together with the cooling screw, consisted in a horizontal
13 pipe (i.d.:160 mm) with a screw conveyor that allowed a precise control of residence
14 time of the different stages (varying the conveyor rotation speed). The drying and
15 torrefaction reactors were temperature controlled using electrical heating elements
16 whereas the last conveyor was cooled using a water jacket. Drying and cooling
17 conveyors had a length of 3000 mm and the torrefaction reactor was 4000 mm long.
18 The reactor, capable of operating at temperature of up to 600 °C, had a capacity up to
19 100 kg/h of biomass and/or wastes in size range of 1-10 mm.
20

21
22 The SRF was fed into the feeding system, moved along the drying reactor and
23 followed to the torrefaction reactor where the conversion took place. The solid
24 fraction was collected after exiting through a cooling screw. The gas fraction was led
25 to the cyclone to remove particles and followed to a condenser, where the
26 condensable gas was collected as liquid fraction.
27

28
29 In order to ensure inert conditions and remove the volatiles, each part of the reactor
30 was purged with a nitrogen flow of about 8 NL/min. Feeder and screws were driven
31 by individual motors allowing for basically independent setting of mass flow (feeder
32 setting) and residence time (screw setting). Notice that the material was transferred
33 between conveyors using rotary valves.
34

35
36 The process was carried out continuously, with a total mass flow rate of about 13
37 kg/h, and a torrefaction residence time of about 15 min in all the cases. A drying
38 temperature of 125 °C was applied, whereas the final torrefaction temperature varied
39 from 290 to 320 °C for the different tests. Apart from the temperature control system,
40 temperature profiles along the different conveyors were measured and recorded using
41 several thermocouples.
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

2.3. Gasification setup and procedure

The fluidized bed gasifier (PID ENG&Tech, Spain) consisted in a Hastelloy X reactor (450 mm long and 23.8 mm internal diameter) externally heated by an electrical furnace. The experimental rig was equipped with a control system (gas flow, feeding system, temperature and pressure) and was able to operate up to 900 °C and 20 bar.

The experiments were conducted at a gasification temperature of 850 °C and atmospheric pressure. Two gasification agents were tested (air and oxygen/steam) maintaining an equivalence ratio (ER) around 0.3 and employing three bed materials. ER is defined as the moles of oxygen available for gasification divided by the total moles of oxygen required for stoichiometric combustion. The selection of the conditions for the gasification process was based in our previous works of SRF gasification, evaluating the effect of the gasification parameters on the process performance, and the usual conditions in commercial fluidized bed gasifiers [23]. The temperature level (850 °C) was selected to promote steam reforming and steam gasification reactions (specially under O₂/H₂O conditions).

The operation flows, 795 NmL/min of air and ~200 NmL/min of O₂ and 0.4 mL/min of H₂O_(l) in the case of air and oxygen/steam experiments respectively, provided a fluidizing gas velocity five to six times the minimum fluidization velocity (U_{mf}), corresponding to gas residence time in the reactor of between 2-3 s.

The tested bed materials included quartz sand (J.T.Baker), dolomite (Productos Dolomíticos de Málaga S.A.) and olivine (Sibelco Hispania); all sieved to particle size range of 150-200 µm and calcined in a furnace at 900 °C for 4 hours. The sample (FL290 or FL320) was placed in the hopper and introduced continuously into the reactor through a screw feeder at rates from 0.40 to 0.47 g/min.

The producer gas was cleaned prior to gas analysis by passing through a hot filter to remove particulates and a condenser system (Peltier and ice tar trap) to collect liquids and tar products. A Tedlar[®] gas bag was used to collect a fraction of the gas for the minor contaminants assessment whereas the rest was analysed in an on-line micro gas chromatograph. Overall mass and carbon balances of conducted tests closed higher than 95 %. Further details of the experimental setup and procedure can be found in previous studies [15,22,23].

2.4. Gas, tar and minor contaminants analyses

Syngas composition (H_2 , O_2 , N_2 , CO , CO_2 , CH_4 and hydrocarbons up to C_5) was analysed using a micro GC (Agilent 490) whereas the determination of contaminants (tar compounds and minor contaminants) followed different techniques. The quantification of polyaromatic hydrocarbons of the tar samples was carried out in a Hewlett Packard 6850 GC-FID (gas chromatograph with a flame ionization detector). The column configuration and methodology is described in a previous work [24].

Minor contaminants (HCl , H_2S , HCN and NH_3) were quantified by potentiometry through ion-selective electrodes (ISEs, Metrohm). For the assessment of these inorganic traces, a fraction of the gas was collected in a Tedlar[®] gas bag and afterwards it was pumped into a series of impingers filled with solutions to retain specific ions (Cl^- , S_2^{2-} , CN^- , and NH_4^+). The aqueous solutions were analysed by ISEs. Additionally, in steam gasification experiments the condenser liquids were also analysed. All solutions were conditioned (adjusting ionic strength and pH) prior the ion determination on a 905 Titrando (Metrohm). A detailed procedure was described elsewhere [22,23].

3. RESULTS AND DISCUSSION

3.1 Characterization of raw and torrefied samples

Table 1 gathers the characterization results of the raw FL and torrefied samples (FL290 and FL320), together with the mass yield of the torrefaction process under the studied conditions.

The parent material (FL) contained a moisture level of 8.4%, which predictably enough, decreased after torrefaction at 290 and 320 °C up to ~1%. As well, during torrefaction there was a change in volatiles levels with an initial increase at 290 °C from 72% to 74% followed by a decrease at 320 °C (71%). This variation in dry basis corresponded to a loss of volatiles from 79% for raw FL to 75% and 72% for FL290 and FL320, respectively. The content of ashes remained ca. 15%, observing a slight and steady augment as torrefaction level increased. Fixed carbon content rose from 5.8% to 10.4-11.6% with the increase of torrefaction temperature. This increment of fixed carbon can also be related to the increase of carbon content in the sample. The ultimate analysis reflects that C content raised 1.25 times up to 57.6% for FL290. On

1 the other hand, the loss of moisture and some oxygenated volatiles provoked a steep
2 decrease of oxygen, ranging between 19.3-22.3% for the torrefied samples versus the
3 31.7% of FL. H scarcely decreased from 7.5% to 7.0% and 6.6% for FL290 and
4 FL320, respectively. The content of minor components also changed with
5 torrefaction. N rose by 14-22% with the torrefaction severity, however Cl decreased
6 from 0.6% to < 0.5%. Regarding the percentage of S, this parameter slightly oscillated
7 around 0.3% in both torrefied samples. The calorific content improved only in the
8 torrefied sample at 290 °C, i.e. the sample with higher carbon content and less
9 moisture. Apparently, higher temperatures provoked a substantial loss of volatiles and
10 a consequent increase of ash content, affecting the calorific content of the sample.
11 Regarding ash composition, the major compounds detected were aluminium, calcium,
12 phosphorous and silicon. In general, the compounds concentration seemed to increase
13 with the torrefaction temperature but taking into account the levels of ashes, some
14 elements were preferentially released during the torrefaction pretreatment (i.e.
15 calcium, lead, etc.) whereas others slightly increased (i.e. silicon, potassium, etc.).
16
17
18
19
20
21
22
23
24
25
26
27
28

29 **3.2 Gasification test**

30 **3.2.1 Product Yields**

31 Table 2 presents the product yields of the gasification experiments in terms of gas,
32 tar and char. The sum of the yields is above 100% as the oxygen introduced with the
33 gasification agent (air and oxygen/steam) reacts with the feedstock to form
34 compounds as CO and CO₂ during gasification.
35
36
37
38
39

40 Considering the results from air gasification tests with sand, both torrefied
41 feedstocks showed similar gas yields ranging from 96.9%-110.8% but slightly lower
42 gas levels for the material torrefied at the highest temperature. FL320 also yielded
43 lower tar and higher char than FL290, which is consistent with the proximate analysis
44 results (lower volatiles and higher fixed carbon content). The use of dolomite as bed
45 material exhibited a positive effect on the gasification performance. There was a
46 significant reduction of all tar yields (2 times lower than with sand) due to the
47 promotion of tar cracking and polymerization reactions, leading to a slight increase of
48 gas and char yields.
49
50
51
52
53
54
55

56 The use of O₂/H₂O as gasification agent resulted in an increase of gas yields
57 ranging between 127.9-138.7% whereas tar results were similar to those obtained with
58 air and dolomite (~ 3%). The presence of oxygen and steam in the gasification media
59
60
61
62
63
64
65

1 promoted a general decrease of char due to char combustion and steam gasification
2 reactions. In addition, the replacement of sand with catalyst (dolomite or olivine) in
3 the bed also improved the gasification (gas yields above 130% and the lowest tar and
4 char yields). Comparing the catalytic activity of both dolomite and olivine, dolomite
5 decreased significantly tar yield, however olivine reported similar tar yields as those
6 obtained with sand as bed material. This lower efficiency of olivine for tar depletion,
7 in comparison to dolomite, was recently reported in a previous work [25]. In that
8 paper the effect of both catalysts was studied under oxygen/steam gasification of two
9 SRFs.
10
11
12
13
14
15
16
17

18 **3.2.2 Gas composition**

19 This section discusses the evolution of the gas composition produced from
20 gasification of two torrefied SRFs (FL290 and FL320) at a gasification temperature of
21 850 °C and ER ~0.3. Sand or catalyst (dolomite, olivine) were used as bed material
22 and air or oxygen/steam as gasification agent. Figures 2 and 3 plot the main
23 components of the producer gas with different gasification mediums (air and
24 oxygen/steam, respectively).
25
26
27
28
29
30

31 Both feedstocks produced a similar gas composition (Fig. 2), under air gasification
32 conditions and sand as bed material. However, the most torrefied fuel presented a
33 slightly better gas quality, with higher volumetric composition (% vol.) of H₂ than the
34 obtained with FL290 (8.5% for FL320 and 7.9% for FL290). On the other hand, the
35 concentration of CO with FL290 was 9.3% compared to the 8.5% of FL320. These
36 variations in the main gas compounds resulted in the H₂/CO and CO/CO₂ ratios
37 displayed in Table 3. H₂/CO ratios were 0.85 for FL290 and 0.99 for FL320 whereas
38 CO/CO₂ ratios were 0.80 and 0.69, respectively. The reported H₂/CO increase with
39 torrefaction level is consistent with the results presented in previous studies of
40 gasification of torrefied biomass [8,26,27]. This effect can be related to the reduction
41 of oxygenated volatiles during the torrefaction process (that would rapidly evolve
42 towards CO), and the formation of a slightly less reactive char, declining the effect of
43 char steam reforming towards CO and H₂. Additionally, in the case of SRFs, the
44 reactions of pyrolysis of polymers are also relevant, leading to the formation of H₂ as
45 final product [28].
46
47
48
49
50
51
52
53
54
55
56
57

58 Other evaluated parameters were carbon conversion and gas heating value (Table
59 3). The higher levels of hydrocarbons (CH₄, C₂H₄, C₂H₆...) present in the gas
60
61
62
63
64
65

1 produced from FL320 gasification resulted not only in a higher gas calorific value in
2 contrast to FL290 (~5 versus ~4 MJ/Nm³, respectively) but also in a higher carbon
3 conversion (69.1 and 66.5%, respectively). The substitution of sand by dolomite
4 resulted in different trends in the gas compositions but a similar response on the
5 overall gasification performance. Both fuels exhibited a drop of H₂/CO ratio (to
6 values close to 0.7) and an increase of CO/CO₂ mainly due to the rise of CO
7 concentration (to a greater extent for FL320). The presence of calcined dolomite
8 might have promoted char gasification reactions (Boudouard and water gas) leading
9 to an increase of CO [29]. As well hydrocarbons (CH₄, C₂H₄, C₂H₆ and higher)
10 presented a marked decrease attributed to the enhancement of cracking reactions.
11 Despite the reduction of olefins with high heating value, the gas LHV remained
12 almost constant and carbon conversion increased by 5%.

13
14
15
16
17
18
19
20
21
22 Fig. 3 shows the results of gas composition of the experiments performed with
23 oxygen/steam as gasification agent. Compared to Fig. 2, the concentration of the main
24 gas compounds increased due to the absence of N₂ from air in the producer gas. In air
25 gasification experiments, N₂ accounted for about 60% of the volumetric composition
26 meanwhile in O₂/H₂O tests, it was lower than 10%. This percentage of nitrogen stem
27 from a small inlet of N₂ (50 NmL/min) in the hopper to facilitate the continuous
28 feeding. Furthermore, the use of pure oxygen and steam enhanced the production of
29 H₂ associated to steam reforming, water gas and shift reactions [30]. In comparison to
30 air gasification results, H₂/CO ratio rose above 2.0, CO/CO₂ ratio ranged between 0.2-
31 0.4 and LHV levels were doubled. The obtained results were also useful to assess the
32 effect of varying the bed material (sand or catalyst). In general, the combination of
33 catalyst and steam reinforced tar cracking and steam tar reforming reactions, which
34 consumed the heaviest hydrocarbons to produce lighter hydrocarbons such as C₂ and
35 CH₄. Hydrogen and carbon monoxide rose and CO₂ concentration diminished when
36 dolomite was used as bed material. The small changes observed in CO and CO₂
37 percentages in the case of FL290, might be linked to a slight higher equivalence ratio
38 (i.e. larger degree of oxidation) in this test. Among all evaluated conditions,
39 gasification of FL320 with dolomite led to the most satisfactory conditions. H₂/CO
40 ratio was around 2.8, the gas calorific value reached a value about 11.0 MJ/Nm³ and
41 carbon conversion was close to 85%. These results corroborated the positive effect of
42 combining torrefaction and gasification using dolomite as bed material. The effect of
43 an additional bed material was tested using olivine, a common bed material in
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 biomass gasification processes. The use of calcined olivine as bed material hardly
2 raised H₂ and CO concentrations nor barely reduced tar content in comparison to sand
3 tests. The values of gas LHV and carbon conversion were in between the results
4 obtained with sand and dolomite.
5
6

7 Summarizing, the producer gas from FL320 presented higher calorific content and
8 lower tar levels than FL290 both with air and oxygen/steam as gasification agents.
9 These results were enhanced with the use of catalyst, especially with dolomite.
10
11

12 **3.2.3 Tar characterization**

13 **3.2.3.1 Tar content**

14 Tar content results (Table 3) are in agreement with the evolution of the discussed
15 tar yields. In air gasification experiments with sand as bed material, tar concentration
16 in the dry producer gas ranged between 25-30 g/Nm³, however it experienced a
17 drastic decrease of 50 % with dolomite in the bed. The obtained values under these
18 conditions (around 13 g/Nm³) are similar to other air gasification tests with SRFs
19 [22,23,31–33] and closer to those obtained in biomass gasification [34,35]. Even
20 though when comparing air experiments to those with O₂/H₂O could seem that the
21 implementation of O₂/H₂O as gasification agent barely reduced tar content, in this
22 case it is convenient to express the content in N₂ free basis (note that N₂ represents
23 about 60% of gas composition in air experiments). As an example of N₂ diluting
24 effect, the tar content of the syngas obtained with FL320 decreased from 34 g/Nm³
25 (with dolomite and air) to 11.3 g/Nm³ (dolomite and O₂/H₂O) when expressed in N₂
26 free basis. Besides, among the two torrefied SRFs, the syngas produced with FL320
27 showed the lowest tar concentration (10.9 g/Nm³ or 11.3 g/Nm³ inert free basis).
28
29

30 Additionally, olivine was tested as bed material only for FL320 gasification under
31 oxygen/steam conditions. However, in line with a previous work [25], olivine just
32 decreased tar content by 9% in comparison with sand (from 24.4 to 22.2 g/Nm³).
33 Therefore, tar and gas composition results reinforced the argument that dolomite
34 might be a suitable catalyst for this type of fuels and gasification conditions.
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53

54 **3.2.3.2 GC-FID analysis**

55 The characterization of tar samples was carried out in a GC with flame ionization
56 detector (GC-FID) to determine the presence of polynuclear aromatic hydrocarbons
57 (PAHs). A standard of 16 PAHs (EPA 610 PAH Mix) was used for the identification
58
59
60
61
62
63
64
65

1
2 of these hydrocarbons. Three additional compounds (1- and 2-methyl-naphthalene, and
3 biphenyl) were also identified and quantified [25].

4 Fig. 4 compares the total amount of tar and PAHs produced by 100 g dry FL
5 (torrefied at 290 and 320 °C) during gasification experiments under different
6 gasification agents and bed materials. As previously commented, tar yields were
7 higher when air was used as gasification agent in comparison with oxygen/steam
8 experiments. This fact may be attributed to a higher extent of tar cracking reactions
9 with steam and the higher reactivity of oxygen. Similarly to the results observed for
10 torrefied biomass [8,15], a greater degree of torrefaction in FL samples showed lower
11 tar production. Therefore, torrefaction level favoured tar depletion. Despite the
12 observed decrease on tar yield, PAH compounds represented on average the 65% of
13 total tar for both torrefied materials. When dolomite was used as bed material, tar
14 yields decreased by 50% and PAHs yields by 60%.

15
16 Fig. 5 and 6 plot the yield of the studied PAHs on tars obtained from air and
17 oxygen/steam gasification experiments, respectively. In all cases, naphthalene,
18 acenaphthylene and phenanthrene were the three main PAH compounds, and among
19 them naphthalene was the dominant aromatic compound. The increase of the
20 torrefaction level led to a clear decrease of naphthalene together with a reduction, to a
21 lesser degree, of the other PAH species, for both studied gasification agents.

22
23 The substitution of bed material from sand to dolomite also presented a positive
24 effect on tar depletion. There was a substantial decrease of tar compounds with this
25 catalyst; practically all tar species halved their yield. These trends were similar for
26 both gasification agents, although dolomite seemed more active for tar cracking under
27 steam rather than under air gasification conditions [36]. An additional test to evaluate
28 the effect of another mineral catalyst (calcined olivine) with FL320 was performed.
29 The use of olivine reduced PAHs but could not reach the levels obtained with
30 dolomite, in particular with the main PAHs compounds (naphthalene, acenaphthylene
31 and phenanthrene). This lower efficiency of olivine on tar cracking was also reported
32 in other works with waste-derived fuels and biomass [25,37] under similar
33 gasification conditions. It is also worth mentioning that in that previous study [25],
34 oxygen/steam gasification of raw FL produced larger amounts of tars ($> 60 \text{ g/Nm}^3$)
35 than the torrefied feedstocks ($< 30 \text{ g/Nm}^3$).

3.2.4 Minor contaminants

This section presents the evolution of the concentration of minor contaminants in the producer gas from gasification experiments with torrefied FL (FL290 and FL320), two gasification agents (air and oxygen/steam) and different bed materials (sand, dolomite or olivine) Additionally, previous results obtained with the parent FL [23,25], have been included to facilitate the discussion. The studied minor contaminants determined through ISEs were hydrogen chloride (HCl), hydrogen sulphide (H₂S), hydrogen cyanide (HCN) and ammonia (NH₃).

3.2.4.1 Air gasification experiments

Fig. 7 displays the minor contaminants concentration produced in air gasification of FL [23], FL290 and FL320 tests with two bed materials (sand and dolomite). In contrast to previous air gasification experiments with raw FL under similar conditions (T=850 °C and ER 0.3) [23] there was a steep diminishment on HCl release after the torrefaction pretreatment, especially at 290 °C (< 50 mg/Nm³). This fact indicates a relevant positive effect of torrefaction (discussed in more detail in the next section).

Comparing both torrefied fuels, HCN and H₂S were the dominant minor contaminants released in the gas. The gasification experiments performed with FL320 showed higher concentration of all contaminants even when dolomite was used as bed material. This fact can be connected to the higher level of tar cracking for the most torrefied material. The heteroatoms (S and N) contained in the tar compounds could evolve towards HCN, NH₃ or H₂S, when tar cracking is more severe [23].

The influence of dolomite on contaminants release was more relevant in some cases depending on the level of torrefaction, but in general the reduction of contaminants followed equivalent trends. HCN levels decreased from ca. 1350 mg/Nm³ to 450 mg/Nm³ on FL290 gasification, whilst the decrease with FL320 was much less remarkable (from 1635 to 1510 mg/Nm³). The presence of metals like Fe and alkaline earth metals (Mg) in dolomite may catalyse N-fuel conversion ending up with lower HCN concentration [22,23].

The emissions of HCl with FL320 was higher than with FL290, this can be related to the larger amount of aluminium (Al) and silicon (Si) in ashes from FL320. The mentioned compounds may react with alkali chlorides (i.e. KCl) to form HCl [38]. In addition, it should be noted that the concentration of elemental chlorine (in mass percentage) was slightly higher in this feedstock.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

In addition, use of dolomite seemed to slightly favour the production of ammonia. NH_3 was hardly produced ($< 1 \text{ mg/Nm}^3$) in the experiments performed with sand but increased on those with dolomite (3 and 55 mg/Nm^3 for FL290 and FL320, respectively). This effect might be related to the decrease of HCN, as dolomite may favour the release of the fuel-N, forming preferentially NH_3 [39] instead of HCN. Moreover, this study shows an important increase of H_2S in the gas from torrefied samples in comparison to the original feedstock where hydrogen sulphide was scarcely detected. The mechanisms of release of sulphur species are complex and can be influenced by many factors, for instance by the presence of inorganic sulphates or other elements in the fuel ash [40,41]. The release of H_2S has been reported to be highly dependent on the affinity between potassium and sulphur, however the competition with Cl and Si at temperatures above 700 °C may prevent the formation of K_2S in solid phase and therefore favour H_2S release [40]. The lower levels of the Ca/Si ratio of the torrefied samples in comparison to the parent SRF may partially explain the observed results. Other plausible explanation is the evolution of the chlorine derived from the dechlorination of PVC. Part of the released Cl could have reacted with the Ca and K of the fuel ash, making these compounds unavailable for sulphur, leading to the release of H_2S . Another fact that supports the hypothesis of the reaction of the released Cl during torrefaction with the SRF ash compounds, is the drop in HCl concentration when dolomite is used as bed material, due to the larger amounts of Ca and Mg available in the dolomite bed. This reduction was about 36-40% for both torrefied materials. The utilization of dolomite reduced H_2S concentration by 30% for both FL290 and FL320 (final values of 405 and 580 mg/Nm^3 , respectively). The results of H_2S diminishment are similar to those presented by Pinto et al. [32], and can be related to the presence of Ca available in the bed, which favours the formation of CaS that would probably remain in the ashes [22,23].

3.2.4.2 Oxygen/steam gasification experiments

Fig. 8 plots the contaminants concentration produced in oxygen/steam gasification of raw FL and torrefied samples at equivalent experimental conditions ($T=850 \text{ }^\circ\text{C}$, ER 0.3). In this case an additional bed material (olivine) was tested with the FL320 sample. The contaminants released in higher level were HCN and NH_3 for both

1 torrefied samples. Contaminants concentration increased with tar cracking, especially
2 increasing NH₃ and decreasing HCN concentration.

3
4 Concerning the experiments with sand, HCN was the major contaminant released
5 with concentration values around 2200 mg/Nm³ for FL290 and the double for FL320.
6 As observed in air gasification experiments (Fig. 7), the replacement of sand with
7 dolomite produced a reduction of hydrogen cyanide together with a rise of ammonia
8 more marked in the FL290 sample. In fact, that increase of NH₃ (2860 mg/Nm³)
9 surpassed the levels of HCN (1470 mg HCN/Nm³). These results may confirm that
10 the presence of steam together with dolomite clearly have promoted the conversion of
11 the fuel-N to NH₃. In particular, the important decrease of tar could provoke the
12 release of part of the nitrogen present in the tar compounds as ammonia. This trend
13 was also observed in a previous work [25] regarding the oxygen/steam gasification of
14 the parent fuel FL (results included in Fig.8). In that study the concentration of NH₃
15 increased with dolomite for two different SRFs. On the other hand, H₂S content was
16 reduced by 75-95% ranging between 40-140 mg/Nm³. In fact, the most remarkable
17 difference was the low formation of HCl detected for the tests performed with
18 torrefied FL compared to the data obtained with the parent FL (HCl levels > 5000
19 mg/Nm³). As commented in the air gasification section, this fact manifests the
20 positive effect of torrefaction, reducing the release of chlorine in the gas phase to a
21 range of 90-230 mg/Nm³. This reduction seemed to be in contradiction with the slight
22 decrease of chlorine content in the torrefied samples, in comparison to the parent fuel.
23 However, the results pointed out that most of the chlorine released as HCl in the
24 producer gas in the experiments with the FL sample stem from some polymers (in the
25 polymer formulation or as additives) and would be released during the torrefaction
26 process. On the other hand, inorganic chlorine present in salts would remain as ashes
27 under the gasification conditions [42,43]. Therefore, although the reduction of
28 chlorine between FL and torrefied samples is limited, the effect of the torrefaction
29 process on HCl release is key. Lower levels of HCl in the producer gas would reduce
30 the risk of corrosion, affecting not only to the design of the syngas conditioning
31 process, but the materials selection for the gasification and syngas cleaning sections.
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53

54 Gasification of FL320 led generally to higher concentrations of minor
55 contaminants than FL290 experiments. One possible explanation for this result is
56 related to the higher level of tar cracking (lower level of tar yields) during the
57 gasification of FL320. The tar produced during MSW derived fuels gasification can
58
59
60
61
62
63
64
65

1 contain N and S compounds, that would evolve towards H₂S, NH₃ and/or HCN during
 2 tar cracking reactions, increasing the release of these contaminants. Apart from the
 3 use of dolomite, another catalyst (olivine) was tested with the most torrefied FL.
 4 According to our previous study [25], olivine reduced nitrogenous contaminants in a
 5 higher extent than dolomite. In this study olivine also resulted in a diminishment of
 6 HCN concentration compared to the utilization of sand as bed material, and similar
 7 ammonia levels. On the other hand, HCl diminished (to 113 mg/Nm³) and H₂S
 8 slightly increased (to 99 mg/Nm³). Usually the decrease of hydrogen chloride led to
 9 an increase of hydrogen sulphide due to the interaction of ash constituents (mainly K),
 10 under oxygen/steam gasification conditions [13].

21 **3.3. Overall efficiency. Torrefaction combined with gasification**

22 The overall efficiency of the process (torrefaction and gasification) was determined as
 23 the energy content (calculated as LHV) in the producer gas in relation to energy
 24 content of the raw feedstock [25] (Eq. 1). Fig. 9 displays a diagram that explains the
 25 mass and energy balances of the overall process. Notice that efficiency is evaluated at
 26 25 °C and does not take into account the sensible heat of the gas at the gasifier exit.

$$32 \eta_{LHV}(\%) = 100 \left(\frac{LHV_{producer\ gas} [MW]}{LHV_{raw\ feedstock} [MW]} \right) \quad Eq. 1$$

33 The efficiency values (η_{LHV}) displayed in Table 4 varied in the range of 42 to 44% for
 34 air gasification experiments. There was a slight decrease of the overall efficiency with
 35 the level of torrefaction. This reduction could be attributed to the loss of volatiles
 36 (from plastic fractions of FL) during torrefaction, causing a smaller gas production.
 37 However the efficiency results were close for both torrefaction levels. Under
 38 oxygen/steam conditions η_{LHV} increased up to a range of 45-55%. The lower
 39 formation of tar and the steady increase of carbon conversion and gas LHV could
 40 explain this fact. The efficiencies at these conditions also decreased with the
 41 torrefaction severity but for the combination of FL320 with dolomite. This experiment
 42 led to higher gas LHV than the obtained with FL290, probably linked to lower degree
 43 of oxidation (i.e. lower equivalence ratio). Additionally, η_{LHV} values for experiments
 44 with the parent material (FL) were calculated using data from a previous work [23].
 45 The obtained results varied in the range of 47-55% for air gasification tests, slightly

1 higher values than those obtained with the torrefied samples. Tests with oxygen/steam
2 resulted in higher efficiencies (49-65%), especially when using dolomite as bed
3 material (with an efficiency peak of 65%).
4

5 In order to evaluate the gasifier performance, the cold gas efficiency (CGE) of the
6 gasification process has been included in Table 4. CGE is calculated according to the
7 energy in the gas (as LHV) in relation to the energy of feedstock introduced in the
8 gasifier (Eq. 2).
9
10
11
12

$$13 \quad CGE_{LHV}(\%) = 100 \left(\frac{LHV_{producer\ gas} [MW]}{LHV_{gasifier\ feedstock} [MW]} \right) \quad Eq. 2$$

14
15
16
17
18
19

20 CGE results ranged between 42-52% for air and between 45-67% for
21 oxygen/steam experiments of torrefied materials. In general, CGE values with the
22 FL320 material led to higher efficiencies due to the lower LHV of the feedstock
23 compared to FL290. This fact could be related to the loss of hydrocarbons from the
24 partial pyrolysis of polymers during torrefaction at 320 °C. As commented for air
25 experiments, the use of catalyst increased the producer gas LHV and hence cold gas
26 efficiency. Contrasting these results with calculated CGE for experiments with FL
27 [25], they followed similar trends to air experiments. Note that part of energy present
28 in the volatiles of the torrefaction process could be reintroduced in the process and
29 therefore improve the overall efficiency.
30
31
32
33
34
35
36
37
38
39

40 **3.4. Preliminary cost evaluation of SRF gasification using torrefaction as** 41 **pretreatment.** 42

43 The results presented in the previous section indicated that the use of torrefaction
44 led to a slight reduction in overall process efficiency for all the evaluated cases.
45 Nevertheless, this assessment does not take into account other benefits associated with
46 the use of torrefaction.
47
48
49
50

51 The high levels of HCl in the syngas is one of the main drawbacks when evaluating
52 SRF gasification. This issue could be considerably overcome using torrefaction,
53 particularly if the level of chlorine was reduced to that of conventional biomass. In
54 addition, other positive effects include the reduction of all the considered minor
55 contaminants, depletion of tar release, and other benefits related to feedstock handling
56
57
58
59
60
61
62
63
64
65

1 (grindability, hydrophobicity, more stable product, higher energy density, higher
2 material density, etc.).

3
4 In an attempt to include these additional parameters in the equation, this section
5 evaluates the performance of the combination of SRF torrefaction and gasification
6 using a preliminary cost analysis, stabilising the cost difference between the evaluated
7 case (at a particular torrefaction temperature, gasification agent and bed material) and
8 the correspondent basis case (direct gasification of FL using the same gasification
9 agent and bed material).
10

11
12 The parameters that were evaluated to determine the cost difference included: cost
13 of torrefaction, cost of tar cleaning, cost of minor contaminants cleaning, cost
14 reduction due to heat integration, and reduction of process revenues due to the
15 decrease of global efficiency. This procedure allowed a preliminary evaluation of the
16 main advantages (i.e. reduction of contaminants) associated with the combination of
17 torrefaction and gasification processes, and the drawbacks associated with the cost
18 increase and the overall process efficiency.
19

20
21 The cost evaluation related to the higher or lower presence of tar and minor
22 contaminants was carried out using as reference the studies of [44,45]. Regarding the
23 tar cleaning, the investment cost was considered constant for all the cases, and the
24 only variation considered was the change in the operating cost. The cost increment
25 was directly proportional to the basis operational cost of 10.1 €/tonne_{feedstock} [45] for a
26 syngas with a tar content of about 11 g/Nm³, taking into account the tar content in
27 each evaluated case. A similar approach was used to evaluate the cost change due to
28 the emission level of minor contaminants (HCl, H₂S, HCN and NH₃). The additional
29 gas cleaning for gases obtained from non-woody biomasses was evaluated as 30
30 €/tonne_{feedstock} [44]. About half of this cost corresponds to the investment cost, and
31 was kept constant in all the cases. On the other hand, a direct proportion was applied
32 to evaluate the operational cost, assigning an operational cost of 15 €/tonne_{feedstock} for
33 the cleaning of a gas containing a concentration of all the considered contaminants of
34 about 6000 mg/Nm³.
35
36

37
38 The assessment of the torrefaction cost was based in the study of Shah et al. [46].
39 This study allows the calculation of torrefaction cost, including the influence of
40 different parameters, such as initial feedstock moisture content, torrefaction
41 temperature, plant operating window and initial capital investment. The analysis of
42 this study led to an estimation of torrefaction cost of about 19 ± 3 €/tonne_{feedstock} and
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 23 ± 3 €/tonne_{feedstock} for the torrefaction at 290 and 320 °C, respectively. An initial
2 moisture in the range of 5-10% and a plant operating window of 10 months/year were
3 used. In addition, a plausible reduction of torrefaction cost was considered, given that
4 a heat integration between gasification and torrefaction could be applied. This
5 reduction was estimated in a 30 % of the total torrefaction cost.
6
7

8
9 Finally, the changes in overall process efficiency were evaluated considering the
10 variation of energy produced (as syngas). The cost evaluation was carried out
11 considering that the syngas was converted to electricity (with an estimated efficiency
12 of 70%) and consequently a reduction in overall process efficiency would provoke a
13 reduction in the revenues for electricity sale (at a price of 50 €/MWh). The revenue
14 difference was calculated using the difference between the overall efficiency of each
15 case and the efficiency of the correspondent basis case (Table 4). This value was
16 multiplied by the LHV of the SRF sample, the electric efficiency and the electrical
17 price.
18
19

20 The results of the cost evaluation are presented in Fig. 10 and 11. Two main
21 conclusions can be extracted from the obtained results. First, the use of SRF
22 torrefaction when the feedstock is treated via air gasification leads to an increase in
23 the process cost that would not recommend the use of torrefaction. The main cost both
24 for FL290 and FL320 using sand as bed material corresponded to the increment of
25 cost due to the torrefaction process, and the relative low variation in tar or minor
26 contaminants cleaning cost. When dolomite was used as bed material, the main cost
27 for the torrefied samples corresponded to the reduction of revenues due to the
28 decrease of the global efficiency.
29
30

31 On the other hand, the evaluation of O₂/H₂O gasification showed a promising cost
32 reduction for all the evaluated cases, but particularly when a torrefaction temperature
33 of 290 °C was applied using sand as bed material, and for the FL320 sample and
34 dolomite as bed material. These results are mainly connected with the lower tar and
35 minor contaminants produced under these conditions, leading to a more pronounced
36 cost reduction, together with a lower variation in the product revenue due to the
37 reduction of global process efficiency. Again, when dolomite was used as bed
38 material, the main cost for the torrefied samples corresponded to the reduction of
39 revenues due to the decrease of the global efficiency.
40
41

42 Although the obtained results present torrefaction as a promising pretreatment for
43 SRF in some particular conditions, these are preliminary results and only evaluate the
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 cost difference among each condition and its basis case. A complete techno-economic
2 study should be performed in order to determine the total cost of the process under the
3 different conditions, assessing for instance the additional costs related to the use of
4 different bed materials, the oxygen separation, etc.
5
6

7 In addition, the global efficiency of the process could be improved by applying
8 some strategies, such as the reintroduction in the gasification of the volatiles produced
9 in the torrefaction step [12], leading to a slight reduction in the cost due to the
10 reduction of the revenues.
11
12
13

14 **4. CONCLUSIONS**

15
16 This paper studies the torrefaction of a solid recovered fuel (SRF) and its influence
17 on the fuel properties for gasification purposes.
18
19

20 The torrefaction pretreatment in the range of 290-320 °C improved the gasification
21 performance of the SRF (lower tar, higher H₂/CO ratio, carbon conversion, etc.) at
22 expense of increasing the release of some minor contaminants (H₂S and NH₃),
23 particularly when using air as gasification agent. However, a relevant fact is that HCl
24 concentration was greatly reduced from > 5000 mg/Nm³ for oxygen/steam
25 gasification of raw FL to values below 250 mg/Nm³ for torrefied feedstocks, showing
26 an additional benefit of torrefaction for this type of feedstock.
27
28

29 The results of process global efficiency indicate that the torrefaction process could
30 provide a series of relevant benefits without a significant reduction in overall
31 efficiency. Nevertheless, the preliminary cost evaluation showed that the combination
32 of torrefaction of SRF materials and gasification is more adequate for processes of
33 gasification using O₂/H₂O rather than for air gasification conditions.
34
35

36 In addition, a series of strategies, such as an energy integration between both
37 processes (not feasible at lab-scale), or the use of the produced volatiles during
38 torrefaction, could result in a more efficient SRF gasification using torrefaction as
39 pretreatment, from an energetic and operational point of view.
40
41
42
43
44
45
46
47
48
49
50
51
52
53

54 **ACKNOWLEDGEMENTS**

55 This research was supported by the European Regional Development Funds
56 (ERDF, “FEDER Programa de Competitivitat de Catalunya 2007-2013”) and the
57 Spanish Government (project MAT2014-52416-P). C. Berrueco is grateful to the
58
59
60
61
62
63
64
65

1 Spanish Ministry of Economy and Competitivity for funding his Ramon y Cajal
2 contract (RYC-2011-09202). N. Puy appreciates the funding through the Torres
3 Quevedo subprogram from the Spanish Ministry of Economy and Competitivity
4 (PTQ-12-05545). J. Recari expresses his gratitude to the Universitat Rovira i Virgili
5 for funding his PhD contract.
6
7
8
9

10 REFERENCES

- 11
12
13
14
15 [1] Zhang Q, Wu Y, Dor L, Yang W, Blasiak W. A thermodynamic analysis of
16 solid waste gasification in the Plasma Gasification Melting process. *Appl*
17 *Energy* 2013;112:405–13. doi:10.1016/j.apenergy.2013.03.054.
18
19 [2] Arena U. Process and technological aspects of municipal solid waste
20 gasification. A review. *Waste Manag* 2012;32:625–39.
21 doi:http://dx.doi.org/10.1016/j.wasman.2011.09.025.
22
23 [3] Alimuddin Z, Zainal B, Lahijani P, Mohammadi M, Rahman A. Gasification of
24 lignocellulosic biomass in fluidized beds for renewable energy development : A
25 review. *Renew Sustain Energy Rev* 2010;14:2852–62.
26 doi:10.1016/j.rser.2010.07.026.
27
28 [4] Ahmad AA, Zawawi NA, Kasim FH, Inayat A, Khasri A. Assessing the
29 gasification performance of biomass: A review on biomass gasification process
30 conditions, optimization and economic evaluation. *Renew Sustain Energy Rev*
31 2016;53:1333–47. doi:10.1016/j.rser.2015.09.030.
32
33 [5] Arena U. Gasification: An alternative solution for waste treatment with energy
34 recovery. *Waste Manag* 2011;31:405–6. doi:10.1016/j.wasman.2010.12.006.
35
36 [6] Sarkar M, Kumar A, Tumuluru JS, Patil KN, Bellmer DD. Gasification
37 performance of switchgrass pretreated with torrefaction and densification. *Appl*
38 *Energy* 2014;127:194–201. doi:10.1016/j.apenergy.2014.04.027.
39
40 [7] Arnsfeld S, Senk D, Gudenau HW. The qualification of torrefied wooden
41 biomass and agricultural wastes products for gasification processes. *J Anal*
42 *Appl Pyrolysis* 2014;107:133–41. doi:10.1016/j.jaap.2014.02.013.
43
44 [8] Dudyński M, van Dyk JC, Kwiatkowski K, Sosnowska M. Biomass
45 gasification: Influence of torrefaction on syngas production and tar formation.
46 *Fuel Process Technol* 2015;131:203–12. doi:10.1016/j.fuproc.2014.11.018.
47
48 [9] Chew JJ, Doshi V. Recent advances in biomass pretreatment–Torrefaction
49 fundamentals and technology. *Renew Sustain Energy Rev* 2011;15:4212–22.
50 doi:http://dx.doi.org/10.1016/j.rser.2011.09.017.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [10] Huang Y-F, Cheng P-H, Chiueh P-T, Lo S-L. Leucaena biochar produced by microwave torrefaction: Fuel properties and energy efficiency. *Appl Energy* 2017. doi:10.1016/j.apenergy.2017.03.007.
- [11] Chen WH, Lu KM, Tsai CM. An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction. *Appl Energy* 2012;100:318–25. doi:10.1016/j.apenergy.2012.05.056.
- [12] Prins MJ, Ptasiński KJ, Janssen FJJG. More efficient biomass gasification via torrefaction. *Energy* 2006;31:3458–70. doi:10.1016/j.energy.2006.03.008.
- [13] Kirsanovs V, Zandeckis A. Investigation of Biomass Gasification Process with Torrefaction Using Equilibrium Model. *Energy Procedia* 2015;72:329–36. doi:10.1016/j.egypro.2015.06.048.
- [14] Chen W-H, Peng J, Bi XT. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew Sustain Energy Rev* 2015;44:847–66. doi:10.1016/j.rser.2014.12.039.
- [15] Berrueco C, Recari J, Güell BM, Alamo G Del. Pressurized gasification of torrefied woody biomass in a lab scale fluidized bed. *Energy* 2014;70:68–78. doi:10.1016/j.energy.2014.03.087.
- [16] Poudel J, Ohm T-I, Oh SC. A study on torrefaction of food waste. *Fuel* 2015;140:275–81. doi:10.1016/j.fuel.2014.09.120.
- [17] Benavente V, Fullana A. Torrefaction of olive mill waste. *Biomass and Bioenergy* 2015;73:186–94. doi:10.1016/j.biombioe.2014.12.020.
- [18] Liu S, Qiao Y, Lu Z, Gui B, Wei M, Yu Y, et al. Release and Transformation of Sodium in Kitchen Waste during Torrefaction. *Energy & Fuels* 2014;28:1911–7. doi:10.1021/ef500066b.
- [19] Yuan H, Wang Y, Kobayashi N, Zhao D, Xing S. Study of Fuel Properties of Torrefied Municipal Solid Waste. *Energy & Fuels* 2015:150728062838002. doi:10.1021/ef502277u.
- [20] Ahmed II, Gupta AK. Pyrolysis and gasification of food waste: Syngas characteristics and char gasification kinetics. *Appl Energy* 2010;87:101–8. doi:10.1016/j.apenergy.2009.08.032.
- [21] Manatura K, Lu J-H, Wu K-T, Hsu H-T. Exergy analysis on torrefied rice husk pellet in Fluidized Bed gasification. *Appl Therm Eng* 2016;111:1016–24. doi:10.1016/j.applthermaleng.2016.09.135.
- [22] Berrueco C, Recari J, Abelló S, Farriol X, Montané D. Experimental investigation of solid recovered fuel (SRF) gasification: Effect of temperature and equivalence ratio on process performance and release of minor contaminants. *Energy & Fuels* 2015:151009130829006.

doi:10.1021/acs.energyfuels.5b02032.

- 1
2 [23] Recari J, Berrueco C, Abelló S, Montané D, Farriol X. Gasification of two
3 solid recovered fuels (SRFs) in a lab-scale fluidized bed reactor: Influence of
4 experimental conditions on process performance and release of HCl, H₂S,
5 HCN and NH₃. *Fuel Process Technol* 2016;142:107–14.
6 doi:10.1016/j.fuproc.2015.10.006.
7
8 [24] Berrueco C, Montané D, Matas Güell B, del Alamo G. Effect of temperature
9 and dolomite on tar formation during gasification of torrefied biomass in a
10 pressurized fluidized bed. *Energy* 2014;66:849–59.
11 doi:10.1016/j.energy.2013.12.035.
12
13 [25] Recari J, Berrueco C, Abelló S, Montané D, Farriol X. Effect of bed material
14 on oxygen/steam gasification of two solid recovered fuels (SRFs) in a bench-
15 scale fluidized bed reactor. *Energy & Fuels* 2017. doi:Submitted to
16 journal/Unpublished results.
17
18 [26] Woytiuk K, Campbell W, Gerspacher R, Evitts RW, Phoenix A. The effect of
19 torrefaction on syngas quality metrics from fluidized bed gasification of SRC
20 willow. *Renew Energy* 2017;101:409–16. doi:10.1016/j.renene.2016.08.071.
21
22 [27] Couhert C, Salvador S, Commandré JM. Impact of torrefaction on syngas
23 production from wood. *Fuel* 2009;88:2286–90. doi:10.1016/j.fuel.2009.05.003.
24
25 [28] Mastral JF, Berrueco C, Ceamanos J. Pyrolysis of high-density polyethylene in
26 free-fall reactors in series. *Energy and Fuels* 2006;20:1365–71.
27 doi:10.1021/ef060007n.
28
29 [29] He M, Hu Z, Xiao B, Li J, Guo X, Luo S, et al. Hydrogen-rich gas from
30 catalytic steam gasification of municipal solid waste (MSW): Influence of
31 catalyst and temperature on yield and product composition. *Int J Hydrogen*
32 *Energy* 2009;34:195–203. doi:10.1016/j.ijhydene.2008.09.070.
33
34 [30] Hwang IH, Kobayashi J, Kawamoto K. Characterization of products obtained
35 from pyrolysis and steam gasification of wood waste, RDF, and RPF. *Waste*
36 *Manag* 2014;34:402–10. doi:10.1016/j.wasman.2013.10.009.
37
38 [31] Dunnu G, Panopoulos KD, Karellas S, Maier J, Toulidou S, Koufodimos G, et
39 al. The solid recovered fuel Stabilat®: Characteristics and fluidised bed
40 gasification tests. *Fuel* 2012;93:273–83. doi:10.1016/j.fuel.2011.08.061.
41
42 [32] Pinto F, André RN, Carolino C, Miranda M, Abelha P, Direito D, et al.
43 Gasification improvement of a poor quality solid recovered fuel (SRF). Effect
44 of using natural minerals and biomass wastes blends. *Fuel* 2014;117:1034–44.
45 doi:10.1016/j.fuel.2013.10.015.
46
47 [33] Arena U, Di Gregorio F. Gasification of a solid recovered fuel in a pilot scale
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- fluidized bed reactor. *Fuel* 2014;117:528–36. doi:10.1016/j.fuel.2013.09.044.
- [34] Miccio F, Piriou B, Ruoppolo G, Chirone R. Biomass gasification in a catalytic fluidized reactor with beds of different materials. *Chem Eng J* 2009;154:369–74. doi:10.1016/j.cej.2009.04.002.
- [35] Campoy M, Gómez-Barea A, Ollero P, Nilsson S. Gasification of wastes in a pilot fluidized bed gasifier. *Fuel Process Technol* 2014;121:63–9. doi:10.1016/j.fuproc.2013.12.019.
- [36] Abdoulmoumine N, Adhikari S, Kulkarni A, Chattanathan S. A review on biomass gasification syngas cleanup. *Appl Energy* 2015;155:294–307. doi:10.1016/j.apenergy.2015.05.095.
- [37] Devi L, Ptasinski KJ, Janssen FJJG, Van Paasen SVB, Bergman PC a, Kiel JH a. Catalytic decomposition of biomass tars: Use of dolomite and untreated olivine. *Renew Energy* 2005;30:565–87. doi:10.1016/j.renene.2004.07.014.
- [38] Chen H, Chen X, Qiao Z, Liu H. Release and transformation behavior of Cl during pyrolysis of torrefied rice straw. *Fuel* 2016;183:145–54. doi:10.1016/j.fuel.2016.06.031.
- [39] Jeremiáš M, Pohorelý M, Bode P, Skoblia S, Beňo Z, Svoboda K. Ammonia yield from gasification of biomass and coal in fluidized bed reactor. *Fuel* 2014;117:917–25. doi:10.1016/j.fuel.2013.10.009.
- [40] Tchapda AH, Pisupati S V. A review of thermal co-conversion of coal and biomass/waste. *Energies* 2014;7:1098–148. doi:10.3390/en7031098.
- [41] Bläsing M, Zini M, Müller M. Influence of feedstock on the release of potassium, sodium, chlorine, sulfur, and phosphorus species during gasification of wood and biomass shells. *Energy and Fuels* 2013;27:1439–45. doi:10.1021/ef302093r.
- [42] Montané D, Abelló S, Farriol X, Berruoco C. Volatilization characteristics of solid recovered fuels (SRFs). *Fuel Process Technol* 2013;113:90–6. doi:10.1016/j.fuproc.2013.03.026.
- [43] Ma W, Hoffmann G, Schirmer M, Chen G, Rotter VS. Chlorine characterization and thermal behavior in MSW and RDF. *J Hazard Mater* 2010;178:489–98. doi:10.1016/j.jhazmat.2010.01.108.
- [44] Van Paasen, S.V.B; Cieplik, M.K; Phokawat NP. Gasification of Non-woody Biomass. *Economic and Technical Perspectives of Chlorine and Sulphur Removal from Product Gas*. 2006.
- [45] Boerrigter H, van Paasen SVB, Bergman PC a, Könemann JW, Emmen R, Wijnands A. “Olga” Tar Removal Technology. 2005.

[46] Shah A, Darr MJ, Medic D, Anex RP, Khanal S, Maski D. Techno-economic analysis of a production-scale torrefaction system for cellulosic biomass upgrading. *Biofuels, Bioprod Biorefining* 2012;6:45–57. doi:10.1002/bbb.336.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

TABLES

Table 1. Characterization and torrefaction yields of studied samples (as received basis).

		FL	FL290	FL320
Torrefaction yield (g/100g SRF fed)		100	90.9	83.5
Proximate Analysis (wt.%)	Moisture	8.39±0.41	0.91±0.14	1.12±0.10
	Volatiles	72.58±0.86	74.10±0.67	71.47±0.05
	Fixed carbon	5.78±0.44	10.42±0.28	11.55±0.24
	Ash	13.24±1.01	14.57±0.33	15.86±0.17
Ultimate Analysis (wt.%)	C	46.03±0.54	57.55±0.90	53.68±0.53
	H	7.49±0.02	7.07±0.15	6.55±0.07
	O (by difference)	31.71±0.55	19.31±0.92	22.28±0.54
	N	0.66±0.06	0.75±0.06	0.85±0.01
	S	0.26±0.01	0.31±0.02	0.27±0.02
	F	<0.02	<0.02	<0.02
	Cl	0.59±0.06	0.42±0.04	0.49±0.04
LHV (MJ kg⁻¹)		23.29±0.22	25.44±0.38	23.06±0.18
Ash composition (mg kg⁻¹_{fuel ar})	Aluminium as Al₂O₃	30754±584	30802 ± 556	33659 ± 1226
	Calcium as CaO	39541±539	40107 ± 1214	43436 ± 2041
	Chrome as Cr	143±20	205 ± 23	192 ± 8
	Iron as Fe₂O₃	4094±214	4586 ± 102	7699 ± 443
	Lead as Pb	642±17	520 ± 23	733 ± 21
	Magnesium as MgO	4319±573	4667 ± 122	4947 ± 236
	Manganese as MnO	241±8	275 ± 5	277 ± 8
	Nickel as Ni	87±7	120 ± 11	119 ± 2
	Phosphorus as P₂O₅	13385±541	13709 ± 583	15272 ± 554
	Potassium as K₂O	2162±126	2498 ± 272	2708 ± 44
	Silicon as SiO₂	20262±837	24780 ± 620	25585 ± 128
	Sodium as Na₂O	4104±183	4299 ± 72	4750 ± 70
Titanium as TiO₂	2436±357	3347 ± 211	3637 ± 170	
	Vanadium as V	<50	<50	<50
	Zinc as Zn	631±80	669 ± 21	670 ± 23

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

Table 2. Product yields of torrefied SRFs gasification experiments. (T= 850 °C and Steam/SRF ~ 1).

SRF	Gasification agent	ER	Bed material	Yield (g/100 g dry SRF)		
				Gas	Tar	Char*
FL290	Air	0.29	Sand	104.5±0.8	7.9±0.3	3.9±0.1
FL290	Air	0.31	Dolomite	110.8±0.8	3.5±0.1	5.3±0.2
FL320	Air	0.29	Sand	96.9±0.7	5.7±0.2	6.4±0.2
FL320	Air	0.29	Dolomite	99.5±0.7	3.0±0.1	7.2±0.2
FL290	O ₂ /H ₂ O	0.32	Sand	132.6±1.3	3.3±0.7	3.7±0.6
FL290	O ₂ /H ₂ O	0.32	Dolomite	138.7±1.4	2.0±0.4	2.5±0.4
FL320	O ₂ /H ₂ O	0.30	Sand	127.9±1.0	3.1±0.6	5.9±1.0
FL320	O ₂ /H ₂ O	0.31	Dolomite	133.5±1.0	1.5±0.3	4.2±0.7
FL320	O ₂ /H ₂ O	0.31	Olivine	130.3±1.0	2.9±0.6	1.0±0.2

* Residual char given in ash free basis. Ash content ~ 14.70 g/100g dry FL290 and ~ 16.04 g/100g dry FL320.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

Table 3. Gasification parameters of experiments. (T= 850 °C and Steam/SRF ~ 1).

SRF	Gasification agent	Bed material	H₂/CO	CO/CO₂	Gas LHV (MJ/Nm³ dry)	Xc	Tar content (g/Nm³ dry)	Tar content (g/Nm³ dry N₂ free)
FL 290	Air	Sand	0.85±0.04	0.80±0.12	4.08±0.10	66.5±1.8	29.61±1.65	89.49±4.98
FL 290	Air	Dolomite	0.72±0.03	0.91±0.14	4.21±0.10	70.8±1.9	13.07±0.73	37.84±2.11
FL 320	Air	Sand	0.99±0.04	0.69±0.11	5.09±0.13	69.0±1.9	24.65±1.37	68.46±3.81
FL 320	Air	Dolomite	0.72±0.03	1.20±0.19	5.14±0.13	71.6±1.9	12.79±0.71	34.01±1.89
FL 290	O ₂ /H ₂ O	Sand	2.60±0.07	0.25±0.03	9.18±0.75	76.0±1.7	26.33±4.27	29.09±4.72
FL 290	O ₂ /H ₂ O	Dolomite	2.57±0.07	0.28±0.03	9.95±0.82	81.8±1.9	14.84±2.41	16.29±2.64
FL 320	O ₂ /H ₂ O	Sand	2.58±0.07	0.29±0.03	9.83±0.81	80.1±1.8	24.36±3.95	26.74±4.34
FL 320	O ₂ /H ₂ O	Dolomite	2.75±0.08	0.37±0.04	10.99±0.90	85.1±1.9	10.88±1.76	11.34±1.84
FL 320	O ₂ /H ₂ O	Olivine	2.33±0.06	0.34±0.04	10.25±0.84	83.1±1.9	22.20±3.60	24.28±3.94

Table 4. Efficiencies of the process (overall efficiency and CGE).

SRF*	Gasification agent	Bed material	η_{LHV}	CGE_{LHV}
FL 290	Air	Sand	42.14±0.52	42.47±0.33
FL 290	Air	Dolomite	44.10±0.55	44.44±0.34
FL 320	Air	Sand	41.73±0.52	50.51±0.39
FL 320	Air	Dolomite	43.23±0.54	52.33±0.41
FL 290	O ₂ /H ₂ O	Sand	45.00±1.23	45.35±0.89
FL 290	O ₂ /H ₂ O	Dolomite	51.62±1.41	52.03±1.02
FL 320	O ₂ /H ₂ O	Sand	44.19±1.21	53.48±1.05
FL 320	O ₂ /H ₂ O	Dolomite	55.22±1.51	66.83±1.31
FL 320	O ₂ /H ₂ O	Olivine	47.41±1.30	57.38±1.12
FL	Air	Sand	47.41±0.39	47.41±0.39
FL	Air	Dolomite	54.88±0.45	54.88±0.45
FL	O ₂ /H ₂ O	Sand	49.24±1.12	49.24±1.12
FL	O ₂ /H ₂ O	Dolomite	64.76±1.48	64.76±1.48
FL	O ₂ /H ₂ O	Olivine	49.93±1.14	49.93±1.14

* Data for FL air experiments from [23] and for FL oxygen/steam experiments from [25].

FIGURE CAPTIONS

1
2 **Fig. 1.** Scheme of torrefaction process.

3
4 **Fig. 2.** Gas composition (dry basis) in air gasification experiments (T= 850 °C, ER
5 ~0.3).
6

7
8 **Fig. 3.** Gas composition (dry basis) in oxygen/steam gasification experiments (T=
9 850 °C, ER ~0.3 and Steam/SRF ~ 1).
10

11 **Fig. 4.** Total tar and PAHs yields in: a) air and b) oxygen/steam gasification
12 experiments. (T=850 °C, ER ~0.3 and Steam/SRF ~ 1).
13
14

15 **Fig. 5.** Tar composition of FL290 and FL320 air gasification experiments (T=850 °C,
16 ER 0.3 and bed materials: sand and dolomite).
17

18 **Fig. 6.** Tar composition of FL290 and FL320 oxygen/steam gasification experiments
19 (T= 850 °C, ER ~0.3, bed materials: sand, dolomite and olivine).
20
21

22 **Fig. 7.** Minor contaminants in air gasification experiments (T=850 C and ER~0.3).
23 Data for FL experiments from [16].
24

25 **Fig. 8.** Minor contaminants in oxygen/steam gasification experiments. (T=850 C,
26 ER~0.3 and Steam/SRF~1). (T=850 C and ER~0.3). Data for FL experiments from
27 [25].
28
29
30

31 **Fig. 9.** Scheme of the mass and energy balances for the combination of torrefaction
32 and gasification.
33
34

35 **Fig. 10.** Preliminary cost evaluation for SRF air gasification experiments.
36

37 **Fig. 11.** Preliminary cost evaluation for SRF oxygen/steam gasification experiments.
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

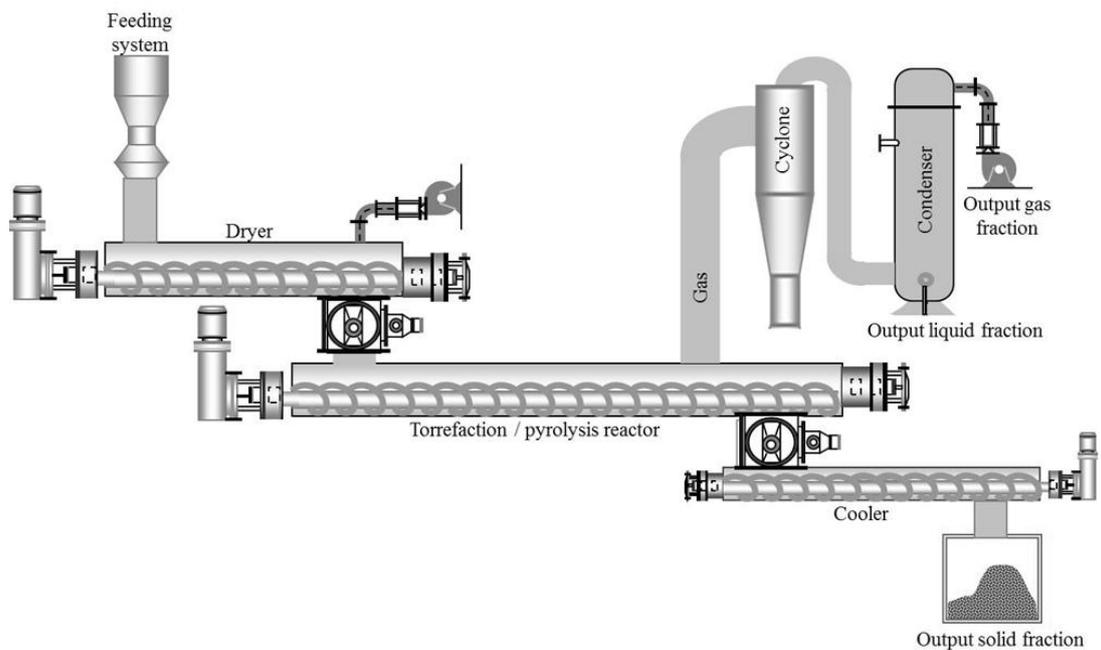


Fig. 1. Scheme of torrefaction process.

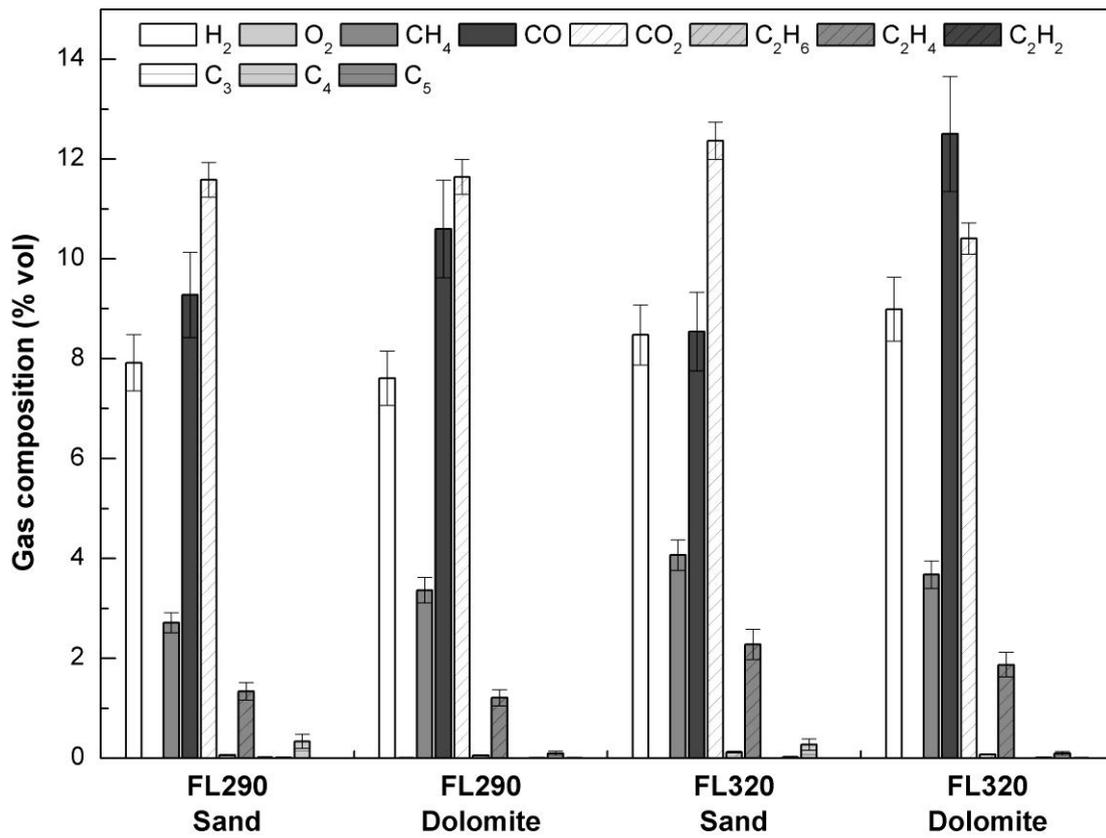


Fig. 2. Gas composition (dry basis) in air gasification experiments ($T= 850\text{ }^{\circ}\text{C}$, $ER \sim 0.3$).

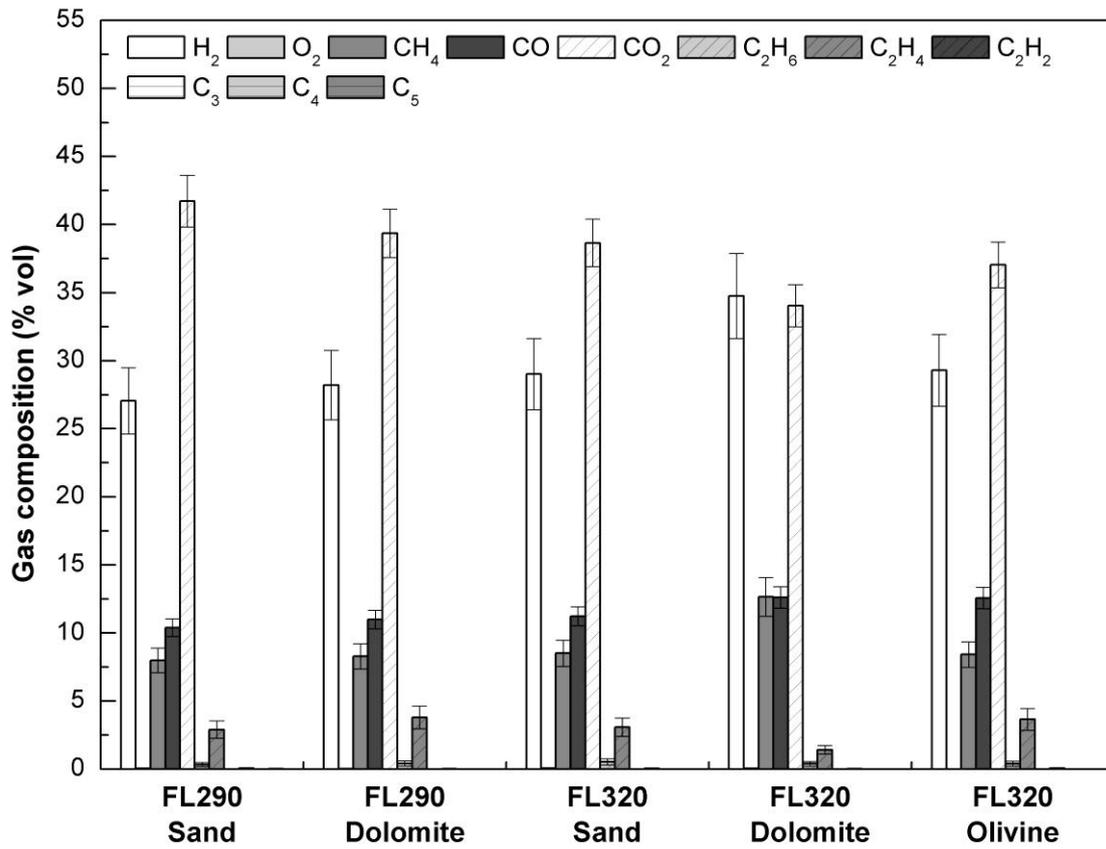


Fig. 3. Gas composition (dry basis) in oxygen/steam gasification experiments ($T=850\text{ }^{\circ}\text{C}$, $\text{ER} \sim 0.3$ and $\text{Steam/SRF} \sim 1$).

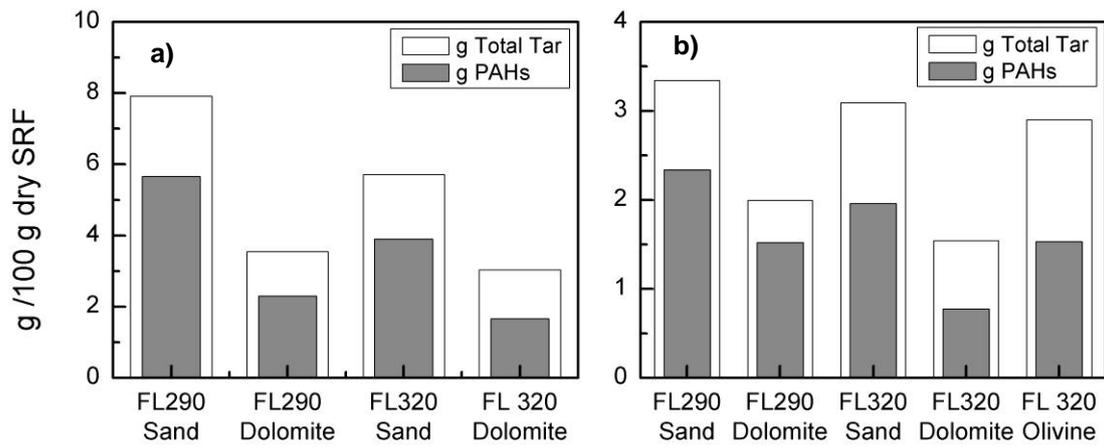


Fig. 4. Total tar and PAHs yields in: a) air and b) oxygen/steam gasification experiments. ($T=850\text{ }^{\circ}\text{C}$, $ER \sim 0.3$ and $Steam/SRF \sim 1$).

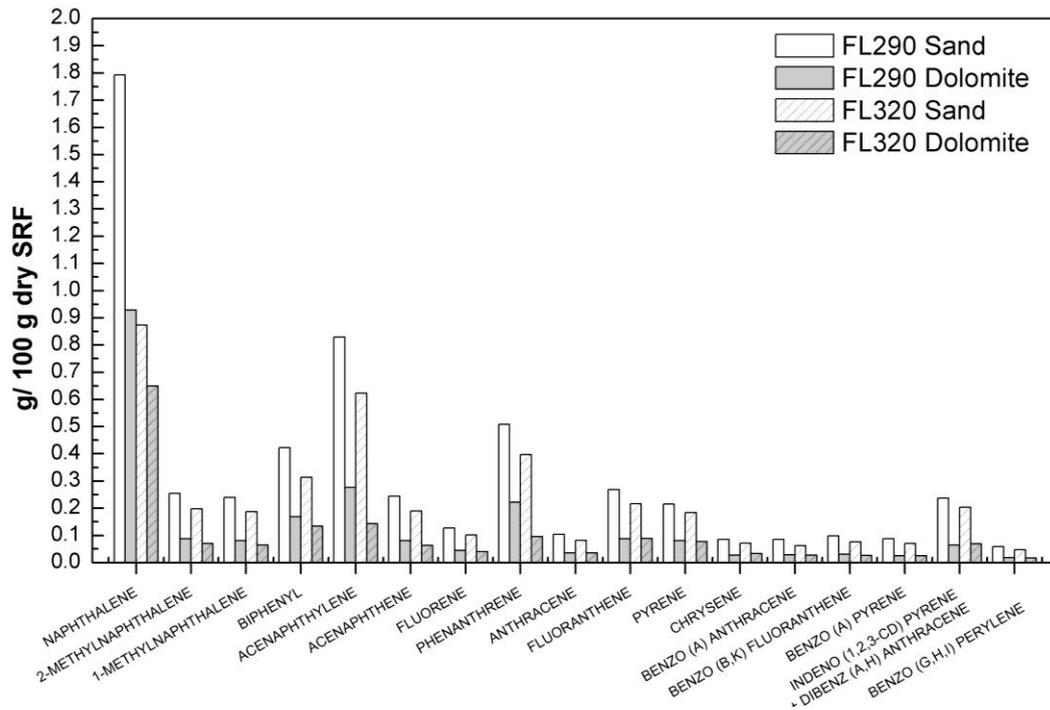


Fig. 5. Tar composition of FL290 and FL320 air gasification experiments (T=850 °C, ER 0.3 and bed materials: sand and dolomite).

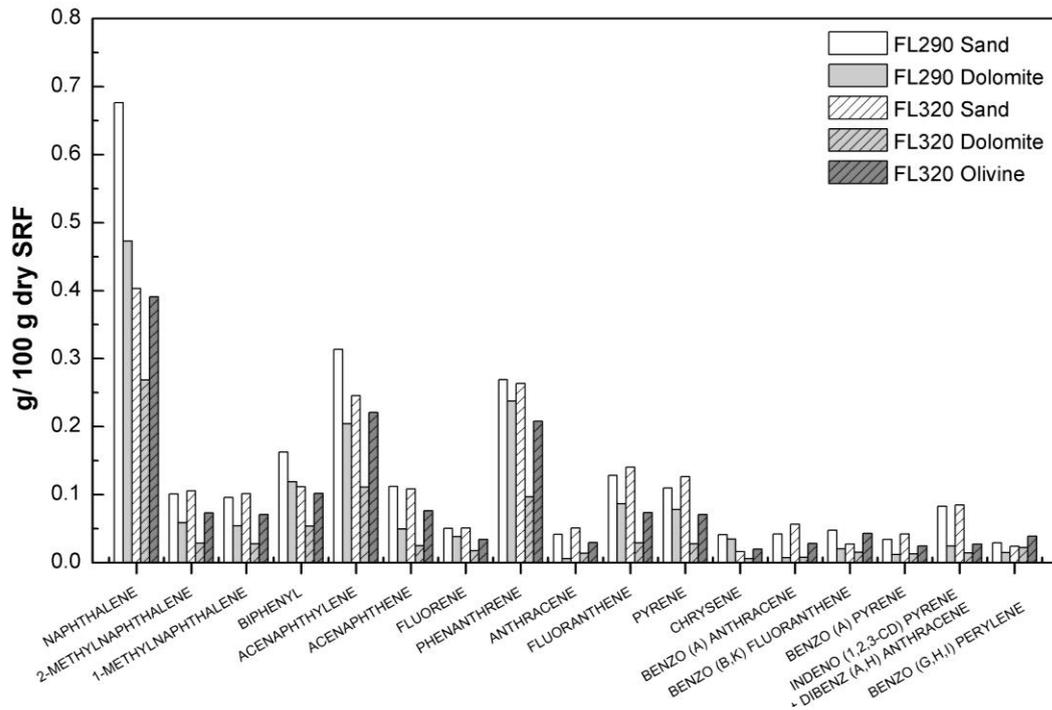


Fig. 6. Tar composition of FL290 and FL320 oxygen/steam gasification experiments (T= 850 °C, ER ~0.3, bed materials: sand, dolomite and olivine).

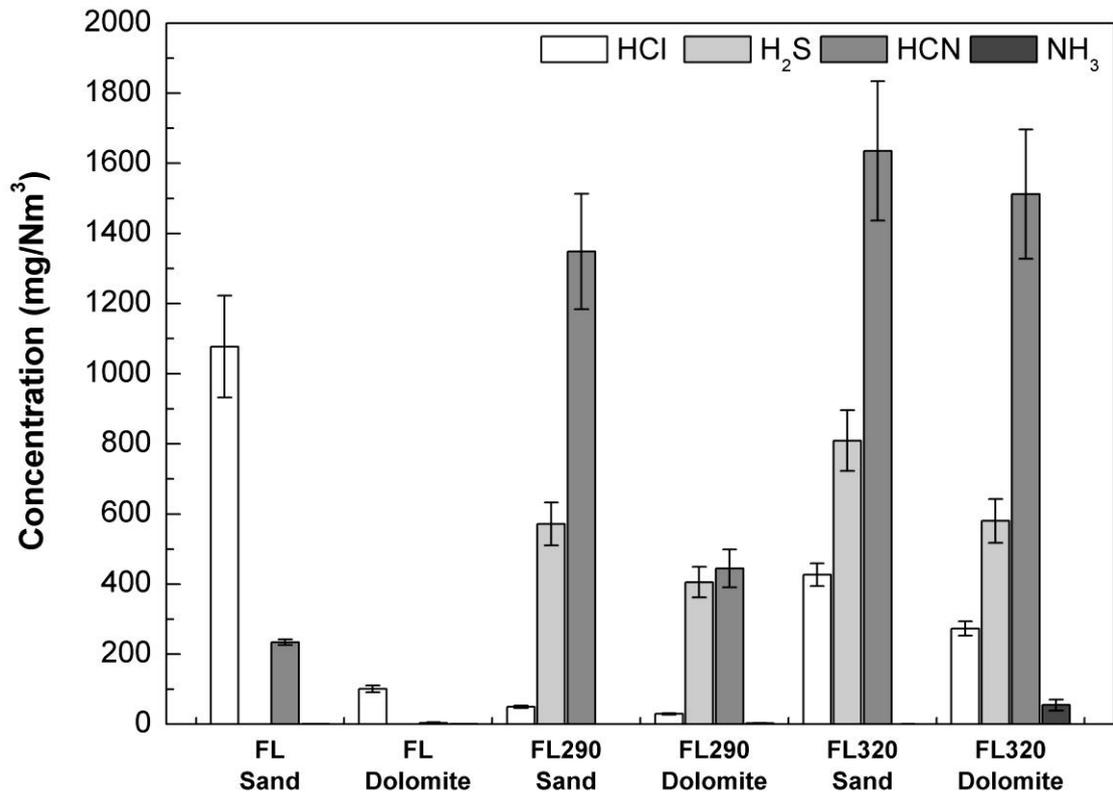


Fig. 7. Minor contaminants in air gasification experiments (T=850 C and ER~0.3).
Data for FL experiments from [16].

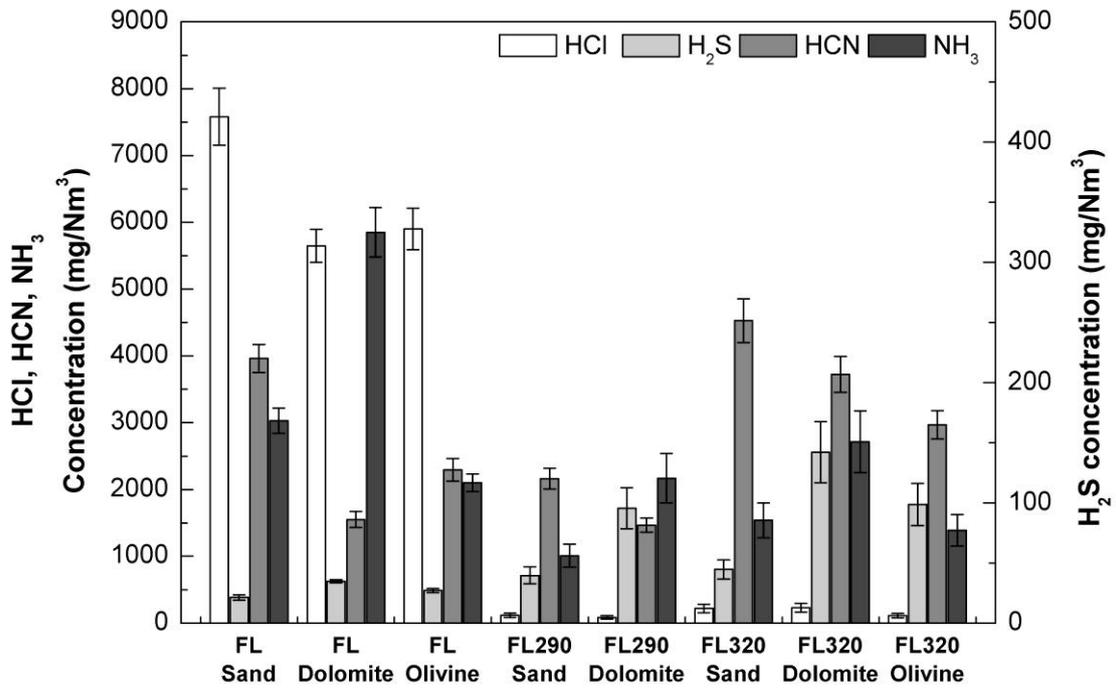


Fig. 8. Minor contaminants in oxygen/steam gasification experiments. (T=850 C, ER~0.3 and Steam/SRF~1). (T=850 C and ER~0.3). Data for FL experiments from [25].

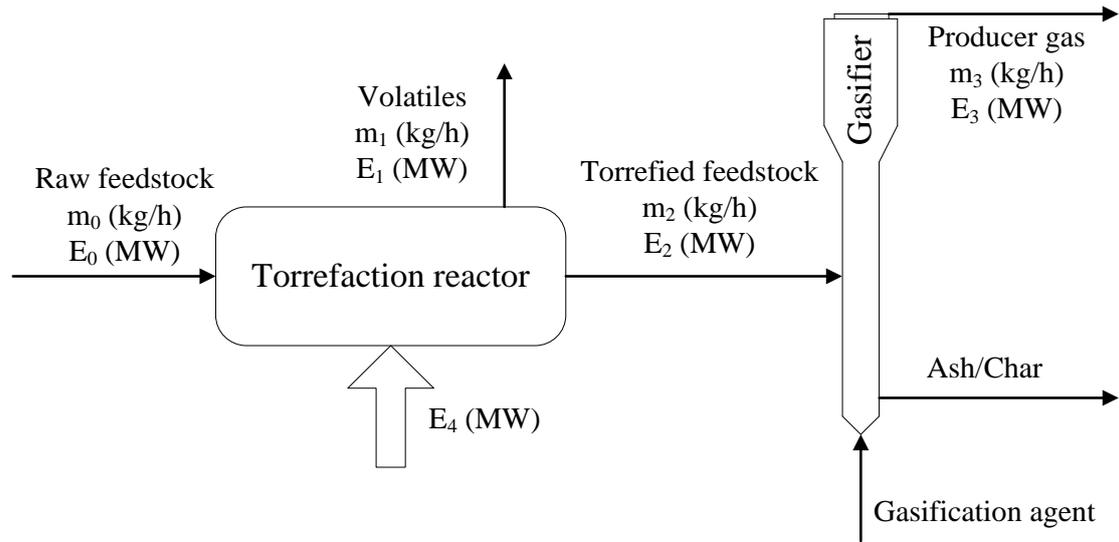


Fig. 9. Scheme of the mass and energy balances for the combination of torrefaction and gasification.

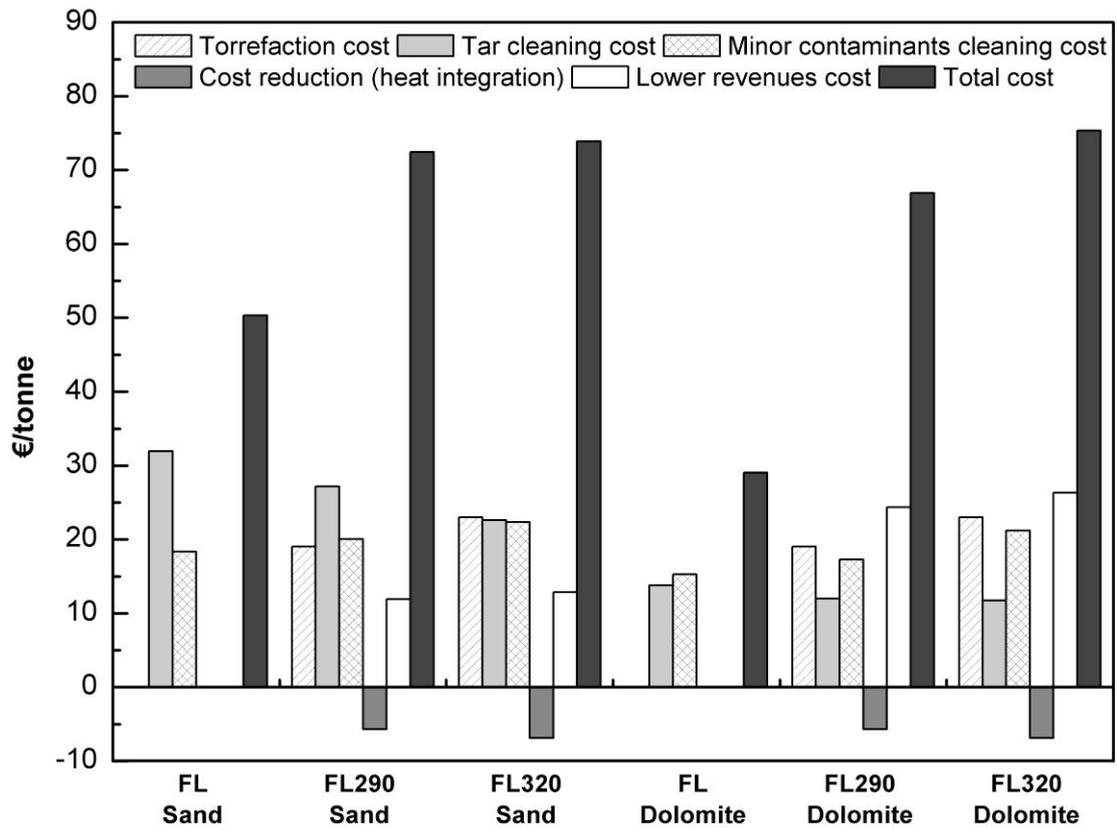


Fig. 10. Preliminary cost evaluation for SRF air gasification experiments.

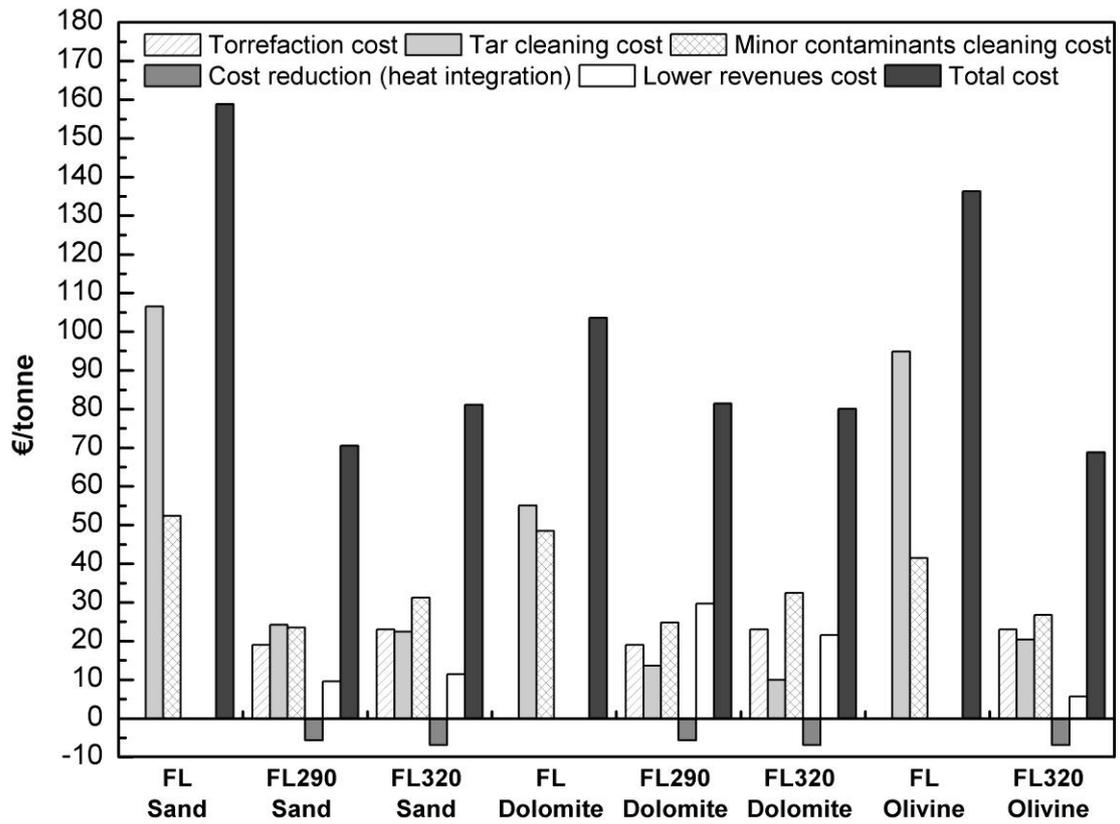


Fig. 11. Preliminary Cost evaluation for SRF oxygen/steam gasification experiments.

May, 19th 2017

Dear Professor Jinyue Yan,

Please find enclosed the revised manuscript entitled “Torrefaction of a solid recovered fuel (SRF) to improve the fuel properties for gasification processes” by J. Recari, C. Berrueco, N. Puy, S. Alier, J. Bartrolí and X. Farriol

The revised version of the manuscript takes into account the comments and suggestions made by the reviewers and journal editors. The following items are also attached:

- The detailed responses to reviewers/editors
- A copy of the revised paper that includes the track changes of the revisions
- The final revised manuscript.

Looking forward to hearing from you.

Best regards,

Dr. C. Berrueco.