CHARACTERISATION OF THE CHAR OBTAINED FROM BIOMASS GASIFICATION IN A SPOUTED BED REACTOR

Filippo Marchelli[1]*, Cristina Moliner[2], Massimo Curti[3], Giorgio Rovero[3], Marco Baratieri[1], Barbara Bosio[2], Elisabetta Arato[2]
1 Free University of Bozen-Bolzano, Faculty of Sciences and Technology, Piazza Università 5, 39100 Bolzano (Italy)
2 University of Genova, Department of Civil, Chemical and Enviromental Engineering, Via Opera Pia 15, 16145 Genova (Italy)
3 Polytechnic of Torino, Department of Applied Science and Technology, C.so Duca degli Abruzzi 24, 10129 Torino, Italy
*corresponding author: filippo.marchelli@natec.unibz.it

ABSTRACT: There is a need to find ways of employing the solid residue of biomass gasification, char, to enhance the economic and environmental advantages of the process. The possible ways depend on the properties of char, which in turn depend on the conditions in which it is produced. For this study, gasification experiments were performed in a spouted bed gasification pilot plant, using wood pellets and apple pruning residues as feedstock. The char was then collected and characterised, in order to find its composition, ash content, heating value and specific surface area. The results highlight strong differences in the properties of the obtained char, depending on which material is obtained from and in which operating conditions; these properties are not dissimilar from what other studies report. The specific surface areas do not suggest the direct use of this char as activated carbon, but a further activation step or its use as a catalyst support might be possible ways for its valorisation.
Keywords: gasification, char, spouted bed reactor, agricultural residues, syngas.

1 INTRODUCTION

Finding alternatives to traditional fossil fuels is one of the major challenges being faced nowadays. Different actions are being studied in order to overcome this problem without reducing the standards of living. Most of the focus is placed on technologies to exploit renewable sources of energy.

Among the mentioned renewable sources, biomass has gathered a lot of attention, becoming the most used feedstock after fossil fuels [1], and several processes have been developed to convert it, optimised in accordance to its properties.

The main advantage of all processes involving energy production from biomass is the generation of renewable energy. Moreover, if the considered material is a waste, a second advantage arises from its conversion into energy. This avoids the environmental and economic impacts which its disposal would cause (for example, in a landfill), and further valorises an initially considered waste stream. For example, agricultural activities produce an estimated amount of 32.7 Mtoe/year of residues in EU countries [2]. This amount is mostly disposed in landfills, incinerated or abandoned on fields, causing severe impacts on human health and the environment.

Thermochemical processes are suitable for the conversion of lignocellulosic biomass, of which agricultural residues mostly consist of [3]. They take place within short timescales and can exploit all of the fractions of biomass.

Gasification is one of them, and it represents a practical compromise between combustion and pyrolysis. It takes place at high temperature (800 to 1000 °C), with solids being put in contact with an amount of oxygen lower than that necessary for stoichiometrically oxidising all of the biomass.

Gasification is especially effective when biomass is fed [1] and it has been proved to be the most efficient way to obtain energy from vegetal solids [4]. The prevailing product is syngas, a gaseous mixture rich in H_2 and CO, employable for generating energy or chemical compounds [5].

Several types of reactors can be chosen as the ‘gasifier’; their properties affect how biomass and the gasifying agent get in contact, how heat is supplied, and the residence time of the solids.

Fluidised bed reactors are particularly advantageous for the gasification of biomass, because of their high energy and mass transfer rates, which enable the obtainment of good carbon conversion, flexibility and ease of scale-up, mainly due to the fact that drying, pyrolysis, reduction and combustion phenomena happen simultaneously in all of the reactor volume [6].

2 SPOUTED BED REACTORS

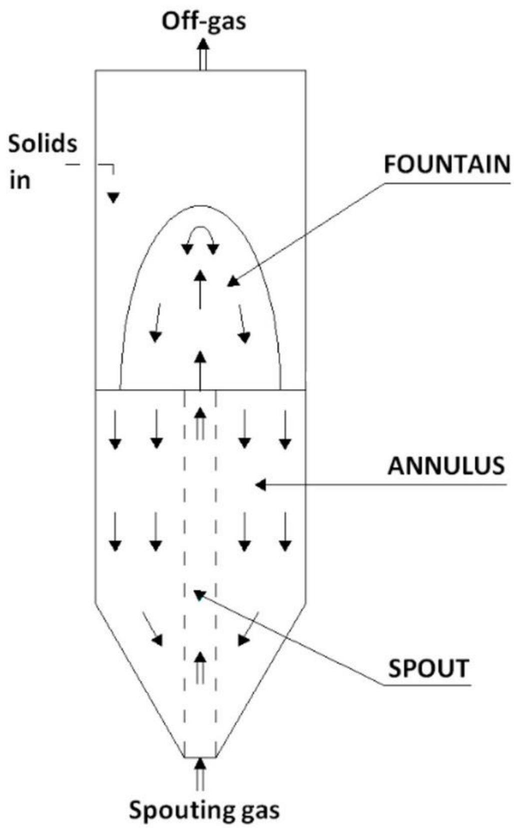

Figure 1: Scheme of a spouted bed reactor

This study focuses on a spouted bed reactor (Fig. 1), which is a kind of fluidised bed reactor. In it, the gas is introduced through a single central orifice. Consequently, it travels through a bed of particles creating a central channel, called *spout*, in which particles are dragged up, leading to the establishment of the *fountain*. Then, particles fall back onto the surface of the bed and reach the *annulus*, a zone where particles are closely packed and travel slowly downwards and radially inwards [7].

The structure of spouted beds enables enhanced mass and energy transfer rates with respect to traditional fluidised beds, making them suitable to handle coarse and irregular particles without problems [8,9], avoiding the need for extensive pre-treatment. This is particularly interesting for biomass gasification, in which solid particles are typically uneven and are drowned in an inert material (usually sand), which has the role of improving the mixing and keeping the required temperature.

Nowadays, spouted bed reactors are the focus of a great number of studies for their use as chemical reactors in a wide variety of processes, including biomass gasification [10–12]. Most of the work has although been performed in lab-scale facilities. A pilot scale 20 kW_{th} unit has been developed, and it yielded promising results [13]; it was employed for this study, with the aim of characterising the solid residue of the process.

3 CHAR VALORISATION

An open challenge in biomass gasification is the valorisation of the solid residue, char. Char usually has a carbon content of 50 to 80 % [14]. Since gasification is aimed at producing syngas, char only represents a small by-product; in fixed bed gasifiers, it can be produced up to an amount of 10 % of the fed material, with usual values in the range between 2 and 5 %. It is a matter of fact that the features of char depend on the operative conditions of the process in which it is produced [16].

As in every process, valorising residues and by-products enhances the conversion and overall environmental and economic sustainability. Its further use as fuel represents an optimisation of the energy efficiency of the whole process, but other applications have been studied, such as natural soil amendment, catalyst for tar removal or cracking, heavy metal adsorbent, activated carbon for filters, and others [15]. A number of studies have also focused on further activation steps, performed through physical or chemical ways, aimed at enhancing its properties [15].

Identifying the best application relies on the knowledge of the char composition and physical structure. To the knowledge of the authors, an extensive study on the char obtained in spouted bed gasifier has not been performed yet.

The aim of this work is helping the closure of this gap, thanks to a characterisation of the char obtained in the spouted bed pilot unit, from different materials and operating conditions.

4 MATERIALS AND METHODS

4.1 Fuel feedstock characterisation

The gasified materials were wood pellets and residues from the pruning of apple trees. The thermo-chemical properties of the latter have already been published in previous works [17].

The following characterisation standards were followed:

- UNI EN ISO 18134-2:2015 (2015) for the determination of moisture;
- UNI EN 14775:2010 (2010) for the determination of ash content;
- UNI EN ISO 16948:2015 (2015) for the elemental analysis, using the VARIO Macro Cube Analyzer;
- UNI EN 14918:2010 (2010) for the calorimetric analysis, using the IKA C 200 bomb calorimeter.

Thermogravimetric analyses were employed to evaluate the amount of volatile matter. All of the analyses were performed in the Laboratories of Bioenergy and Biofuels of the Free University of Bolzano.

The results can be found in Table I.

Table I: Properties of the employed feedstock.

	Wood pellets	Apple pruning
Proximate analysis (wt. %)		
Moisture Content	5.07 ± 0.03	8.13 ± 0.20
Fixed Carbon (dry)	22.44	19.95
Volatile Matter (dry)	77.30	77.18
Ash (dry)	0.26	2.87
Ultimate analysis (wt. % dry)		
C	50.06 ± 0.70	48.88 ± 0.39
H	6.23 ± 0.08	5.71 ± 0.09
O	43.38 ± 0.68	42.15 ± 0.53
N	0.06 ± 0.05	0.26 ± 0.05
S	0.01 ± 0.16	0.13 ± 0.07
Ash	0.26 ± 0.10	2.87 ± 0.11
HHV (MJ/kg) dry	19.47 ± 0.52	18.73 ± 0.63

4.2 Spouted bed pilot plant

The pilot plant (Fig. 2) was already described exhaustively in a work presented in the previous edition of EUBCE [13], so here only the most relevant features are discussed.

The core of the plant is a spouted bed reactor, in which gasification reactions take place. Its dimensions are reported in Table II.

Table II: Dimensions of the spouted bed gasifier.

Dimension	
Side	20 cm
Height	2 m
Base angle	60°
Spouting orifice diameter	21 mm
Base height	50 cm
Feeding point height	70 cm

The fluidising agent is fed from the central orifice of the base; biomass is introduced into the reactor through a system connected to the lateral wall. The produced gases leave the reactor from its top. The pyramidal part of the reactor is always filled with an inert bed of sand, enhancing the mass and heat transfer.

Air is supplied through a blower; it acts as both the fluidising and gasifying agent. A burner is located between the air blower and the reactor, and it is employed to pre-heat the system and modify the oxygen and carbon dioxide inflow; when an adequate temperature is reached, the pre-heating is completed through the combustion of wood pellets.

Figure 2: Main body of the reactor (on the left) and cyclone with the tank (on the right)

Syngas is treated in a cleaning section: first it passes through a cyclone, which captures char and coarse particles originated from sand erosion, and stores them in a tank from which they can be collected. After this, a water scrubber removes the remaining particles and cools down the syngas, in order to analyse or discharge it.

Several thermocouples allow the monitoring of the temperature inside the reactor, while the composition of the syngas is analysed through TFS (Tunable Filter Spectroscopy) and TCD (Thermal Conductivity Detector), with the model ETG 6700 provided by "ETG Risorse e Tecnologie" (Montiglio Monferrato, Italy).

The calorific value of the syngas (in MJ/Nm^3) is calculated with the following correlation [18]:

$$LHV = (0.126 \cdot y_{CO}) + (0.108 \cdot y_{H2}) + (0.358 \cdot y_{CH4})$$

in which y_i is the percentage volume fraction of the i compound (carbon monoxide, hydrogen or methane).

4.3 Residual char characterisation

Char was collected from the cyclone after continuous gasification tests.

Representative samples were selected, weighted and, as for biomass, analysed in order to assess their composition and calorific value, employing the same procedures. Furthermore, the specific surface area, pore size and pore distribution of the char were measured with the BET (Brunauer-Emmet-Teller) method; it employs nitrogen adsorption at 77 K, and was performed with the 3Flex Surface Characterization Analyzer (Fig. 3, Micromeritics Co., USA), in the laboratories of the Free University of Bolzano.

Each analysis was repeated three times and an average was calculated as the final value.

Figure 3: The device for the BET analysis

5 PERFORMED EXPERIMENTS

After preheating the reactor with the aid of the burner, gasification experiments were performed employing one kind of biomass. Steady conditions were reached and kept constant for a maximum of 40 minutes at a time, allowing the production of significant amounts of char.

Different gasification conditions were tested. In particular, the residues of the pruning of apple trees were gasified with Equivalent Ratios (ERs) equal to 0.32 and 0.42; then, the char was collected after the system cooled down. For wood pellets, an analogous approach was followed, with ERs equal to to 0.25 and 0.30.

The ER is defined as:

$$ER = \frac{\dot{m}_{air}}{\dot{m}_{air,st}}$$

in which $\dot{m}_{air}$ is the mass flow of air fed, and $\dot{m}_{air,st}$ is the mass flow of air which should be fed for a complete oxidation of the biomass.

The char was collected from the tank connected to the cyclone, and representative samples were analysed.

6 RESULTS AND DISCUSSION

6.1 Gasification results

After an unsteady phase, constant values of temperature and composition were reached for each operating condition. These data represent a time averaged result, calculated over the stable conditions intervals.

Table III: Average steady state temperature

Biomass	ER	Temperature [° C]
Wood pellets	0.25	881
	0.30	903
Apple pruning	0.32	881
	0.42	963

From the steady temperature results (Table III), it can be inferred that the overall better properties of wood pellets (ash and moisture content) permit to work at higher temperatures for similar ER, compared to apple pruning residues. However, in both cases, suitable working conditions for the gasification process can be obtained.

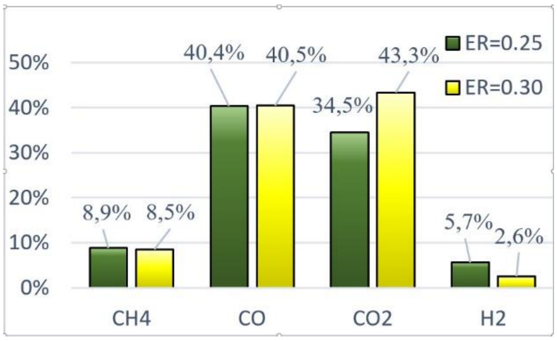

Figure 4: Composition of the syngas (not considering nitrogen) obtained from the gasification wood pellets

Observing the syngas composition results (Fig. 4), as expected, it is evident that working with a lower ER reduces the amount of carbon dioxide and increases that of hydrogen, not affecting significantly the percentages of methane and carbon monoxide.

Working with a lower ER also yields a syngas with higher calorific value: in fact, it is 3.11 MJ/Nm^3 when the ER is 0.25 and 2.65 MJ/Nm^3 when it is 0.30.

6.2 Char characterisation results

The assessment of the properties of char highlighted great differences depending on the employed feedstock, as even a visual observation would suggest (Fig. 5).

As explained in the previous section, both materials were gasified with two different ERs, which were maintained for the same time. Thus, it can be assumed that the properties of char represent an average of what can be obtained in each separate working condition. All the following results are calculated on a dry basis.

Table IV: Elemental composition of the char (dry, wt. %)

	Wood pellets char	Apple pruning char
C	53.64 ± 0.36	18.00 ± 0.04
H	0.22 ± 0.15	0.14 ± 0.15
N	0.19 ± 0.04	0.17 ± 0.01
S	2.01 ± 1.98	0.53 ± 0.06
Ash	45.69 ± 3.08	85.75 ± 0.58

The elemental composition is reported in Table IV. Most notably, the difference in ash is considerable. It may be caused by the different working conditions, even if the fact that the percentage of ash in the feedstock was an order of magnitude higher for apple pruning residues could be relevant. A visual observation suggest that the two ash samples have a different composition (Fig. 6), which could be analysed in further works.

For both cases, ash content is also increased by the products obtained during the start-up procedure, which partly involves the combustion of wood pellets. In proper continuous working conditions, this would not affect the char significantly.

The significant ash content is although a sign that the features of the spouted bed reactor enable the reaching of high carbon conversions.

Figure 5: Char from apple pruning residues (on the left) and from wood pellets (on the right)

Figure 6: Ashes obtained from the apple pruning char (on the left) and from wood pellets (on the right)

High heating values (HHV) are obviously affected by the ash content, being 17.52 MJ/kg for wood pellets char and 4.92 MJ/kg for apple pruning char.

Observing the BET results (Table V), it can be seen that the difference in surface area is significant, and it could be due to the great difference in carbon content of the two studied samples.

Table V: Results of the BET analyses on the char

	Wood pellets char	Apple pruning char
Specific surface area (m^2/g)	103.97	49.45
Pore volume (cm^3/g)	0.138	0.091
Average pore width (nm)	5.18	6.24

Usually, the surface area of char does not exceed 300 m^2/g [19]; observing the results presented in other studies about char as a residue of biomass gasification [20], even from industrial scale plants [21], shows that our results are comparable in several cases. Even some studies aimed at the production of char (trough pyrolysis or carbonisation) feature materials with lower surface area, as reported in the review by Qambrani and colleagues [16].

When comparing these results with literature, it should be pointed out that most studies on char from biomass focus on experiments aimed at its production, through pyrolysis or carbonisation, so the operating conditions are optimised in order to enhance the yield and properties of this product. In particular, high residence times and low heating rates allow to obtain char with better properties. However, Fatehi and Bai [22] argued that the available experimental data are not enough to define what the specific surface area of the char depends on.

Nevertheless, the specific surface area values are not promising for its application as activated carbon, unless a further activation step is performed. In fact, commercial activated carbons feature surface areas in the range of 500 to 1500 m^2/g [23].

The use as soil amendment cannot be suggested either, since the amount of inorganic and organic contaminants could make it toxic for the living organisms; aromatic hydrocarbons and heavy metals are examples of this [24]. Given the inorganic structure of char, it could be suitable as a support for catalyst, especially for processes aimed at removing tars from syngas [20].

Recirculating the char to the reactor could be profitable, especially for wood pellet char, enhancing the overall carbon conversion. However, the ashes might potentially create sintering and slagging problems, even though the fluid dynamics of the spouted bed are supposed to strongly hinder these phenomena [7]. Regarding apple pruning char, the amount of ashes is preponderant; further analyses might highlight the presence of profitable compounds in these ashes, such as what has been found in rice straw [25].

7 CONCLUSIONS

A spouted bed gasifier pilot plant was used to perform the gasification of wood pellets and apple pruning residues.

The results highlighted that the reactor can work in a steady way in several working conditions, being able to obtain syngas from both materials.

The solid residue of gasification, char, was collected and analysed. It was found that the high ash content of apple pruning residues is transferred to the char, so that it has a double amount of ash compared to wood pellets char. This difference in ash content generates a difference in the High Heating Values, which is low for apple pruning char and medium for wood pellets char.

The BET analysis showed that the surface area is low for apple pruning char and medium for wood pellets char. For both cases, it is comparable to values reported in literature. However, it is too low for a direct use as activated carbon and may benefit from a further activating step.

Other possibilities are recirculating char to the reactor, in order to enhance the carbon conversion, or using it as a support for catalyst.

All of these alternatives should be taken into account: in a complete continuous plant, they would transform a waste, which would need to be disposed with non-negligible costs, into a valuable product.

A more detailed study would be necessary to understand how working conditions exactly affects the properties of char, but it should be considered that char is a relatively small by-product, and the process optimisation should mainly be based on maximising the quality and yield of the syngas.

8 REFERENCES

[1] P. Basu, Biomass Gasification and Pyrolysis, Elsevier, 2010. doi:10.1016/C2009-0-20099-7.

[2] C. Panoutsou, J. Eleftheriadis, A. Nikolaou, Biomass supply in EU27 from 2010 to 2030, Energy Policy. 37 (2009) 5675–5686. doi:10.1016/j.enpol.2009.08.032.

[3] Q. Feng, Y. Lin, Integrated processes of anaerobic digestion and pyrolysis for higher bioenergy recovery from lignocellulosic biomass: A brief review, Renew. Sustain. Energy Rev. (2017). doi:10.1016/j.rser.2017.03.022.

[4] A.A. Ahmad, N.A. Zawawi, F.H. Kasim, A. Inayat, A. Khasri, Assessing the gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation, Renew. Sustain. Energy Rev. 53 (2016) 1333–1347. doi:10.1016/j.rser.2015.09.030.

[5] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: The state of the art overview, J. Energy Chem. 25 (2016) 10–25. doi:10.1016/j.jechem.2015.11.005.

[6] P.A. Salam, S.C. Bhattacharya, A comparative study of charcoal gasification in two types of spouted bed reactors, Energy. 31 (2006) 228–243. doi:10.1016/j.energy.2005.01.004.

[7] N. Epstein, J.R. Grace, Spouted and Spout-Fluid Beds, Cambridge University Press, Cambridge, 2010. doi:10.1017/CBO9780511777936.

[8] C.E. Moliner Estopiñan, Valorisation of Agricultural Residues, Universitat Politècnica de València, 2016. doi:10.4995/Thesis/10251/68495.

[9] A. Sahoo, G.K. Roy, Mixing characteristic of homogeneous binary mixture of regular particles in a gas–solid fluidized bed, Powder Technol. 159 (2005)

150–154. doi:10.1016/j.powtec.2005.08.010.
[10] A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, Steam gasification of biomass in a conical spouted bed reactor with olivine and γ-alumina as primary catalysts, Fuel Process. Technol. 116 (2013) 292–299. doi:10.1016/j.fuproc.2013.07.008.
[11] D. Bernocco, B. Bosio, E. Arato, Feasibility study of a spouted bed gasification plant, Chem. Eng. Res. Des. 91 (2013) 843–855. doi:10.1016/j.cherd.2012.09.012.
[12] G. Lopez, A. Erkiaga, M. Amutio, J. Bilbao, M. Olazar, Effect of polyethylene co-feeding in the steam gasification of biomass in a conical spouted bed reactor, Fuel. 153 (2015) 393–401. doi:10.1016/j.fuel.2015.03.006.
[13] D. Bove, C. Moliner, M. Curti, G. Rovero, M. Baratieri, B. Bosio, E. Arato, G. Garbarino, F. Marchelli, Experimental Studies on the Gasification of the Residues From Prune of Apple Trees, Proceeding 24th Eur. Biomass Conf. Exhib. (2016). doi:10.5071/24thEUBCE2016-2CV.3.18.
[14] S. Vakalis, A. Sotiropoulos, K. Moustakas, D. Malamis, M. Baratieri, Utilisation of biomass gasification by-products for onsite energy production, Waste Manag. Res. 34 (2016) 564–571. doi:10.1177/0734242X16643178.
[15] J.S. Cha, S.H. Park, S.-C. Jung, C. Ryu, J.-K. Jeon, M.-C. Shin, Y.-K. Park, Production and utilization of biochar: A review, J. Ind. Eng. Chem. 40 (2016) 1–15. doi:10.1016/j.jiec.2016.06.002.
[16] N.A. Qambrani, M.M. Rahman, S. Won, S. Shim, C. Ra, Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review, Renew. Sustain. Energy Rev. 79 (2017) 255–273. doi:10.1016/j.rser.2017.05.057.
[17] D. Bove, C. Moliner, M. Baratieri, B. Bosio, E. Arato, Kinetic Characterization of the Residues from the Pruning of Apple Trees for their Use as Energy Vectors, Chem. Eng. Trans. 50 (2016). doi:10.3303/CET1650001.
[18] C. Gai, Y. Dong, Experimental study on non-woody biomass gasification in a downdraft gasifier, Int. J. Hydrogen Energy. 37 (2012) 4935–4944. doi:10.1016/j.ijhydene.2011.12.031.
[19] L. Khezami, A. Ould-Dris, R. Capart, Activated carbon from thermo-compressed wood and other lignocellulosic precursors, BioResources. 2 (2007) 193–209. doi:10.15376/biores.2.2.193-209.
[20] J.J. Hernández, M. Lapuerta, E. Monedero, Characterisation of residual char from biomass gasification: effect of the gasifier operating conditions, J. Clean. Prod. 138 (2016) 83–93. doi:10.1016/j.jclepro.2016.05.120.
[21] J. Ahmad, E. Cordioli, F. Patuzzi, D. Prando, M.J. Castaldi, M. Baratieri, Possible Utilization Pathways of Char from Biomass Thermochemical Conversion: Char as a Catalytic Filtering Medium for Tar Cracking, Eur. Biomass Conf. Exhib. Proc. (2016) 475–479. doi:10.5071/24theubce2016-2bo.2.3.
[22] H. Fatehi, X.-S. Bai, Structural evolution of biomass char and its effect on the gasification rate, Appl. Energy. 185 (2017) 998–1006. doi:10.1016/j.apenergy.2015.12.093.
[23] N.A. Rashidi, S. Yusup, A review on recent technological advancement in the activated carbon production from oil palm wastes, Chem. Eng. J. 314 (2017) 277–290. doi:10.1016/j.cej.2016.11.059.
[24] D. Prando, F. Patuzzi, J. Ahmad, T. Mimmo, M. Baratieri, Environmental Impact of Char from Four Commercial Gasification Systems, 24th Eur. Biomass Conf. Exhib. Proc. (2016) 828–830. doi:10.5071/24thEUBCE2016-2CV.3.9.
[25] C. Moliner, B. Bosio, E. Arato, A. Ribes, Thermal and thermo-oxidative characterisation of rice straw for its use in energy valorisation processes, Fuel. 180 (2016) 71–79. doi:10.1016/j.fuel.2016.04.021.

9 ACKNOWLEDGMENTS

The authors of this work are deeply grateful to Michele Fossati, who provided significant help with the accomplishment of the gasification experiments, and to Vittoria Benedetti, Daniele Basso and Francesco Patuzzi, who offered their precious time to share their knowledge and help the execution of the char analysis.