HYDROPHOBICITY BEHAVIOUR AND FIBRES DISTRIBUTION OF TWO DIFFERENT WOODY BIOMASSES TORREFIED AT DIFFERENT CONDITIONS

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ABSTRACT: This study investigates both the hydrophobicity behaviour of two types of biomasses and the evolution of their fibres content when thermally treated at different torrefaction degrees. The two woody biomasses have been chosen from softwood as *spruce (picea abies)* and annual grass lignocellulosic hardwood as *reeds*. Selected samples of the indicated biomasses were torrefied at different reaction time and temperature values, ranging from 250°C to 310°C, on a small batch reactor utilizing a direct flux of nitrogen as thermal carrier. Before treatment all samples were dried in a convection oven at 103 C° for 24 h. The Mass Yield Ratio (MYR) is the parameter utilized to define the torrefaction degree and, for this investigation, torrefied samples present a MYR of 90%, 80% and 70% for *spruce* and 80%, 70% and 60% for *reeds*. The hydrophobicity was determined in terms of EMC (Equilibrium Moisture Content) at a constant temperature of 25°C and Relative Humidity (RH) ranging from 24% to 75%. The fibres content, lignin, cellulose and hemicellulose, was determined for both raw and torrefied samples according to the so called Van Soest method.
Regarding the hydrophobic behaviour, for both the biomasses, it can be observed that up to a MYR at 80%, the moisture absorption reduces progressively from raw to torrefied samples. Regarding the fibres content analysis, it is confirmed that as torrefaction becomes stronger in terms of MYR, a near-complete breakdown of hemicellulose is observed.

Keywords: torrefaction, fibres, moisture, mass yield ratio.

1 INTRODUCTION

In these last years torrefaction process [1,2] has encountered a growing attention inside the scientific community. During this process raw biomass is heated in an oxygen-free atmosphere and modifies into a solid biofuel product that, from a process point of view, has superior handling, co-firing [3,4] and milling capability [5], improved fluidization properties [6] and, if pyrolysed, allows to improve the quality of the obtained bio-oil [7]. Biomass presents a complex composition, mainly comprised of hemicellulose, cellulose, lignin, extractives (fatty acids, tannins, resins) and ash.

Torrefaction alters the composition and the biomass structure due to thermochemical degradations of the hydrophilic polysaccharides and hydroxyl radicals, causing also an increment in the energy per unit mass, an improvement in bio-resistance, a reduction in the hydroscopicity and a carbon-like appearance [8]. Additional benefits of torrefied biomass include reductions in CO_2 emissions when compared to coal [9] combustion. Besides the volatilization of highly oxygenated species, the released volatiles mainly composed of phenolic compounds, acetic and lactic acid and methanol [8] produce a fuel with a consistent energy yield as output. For a full-scale review on torrefaction pre-treatment, reference is made to Van der Stelt et al. [10].

This experimental study aims at proposing a deep analysis of the evolution of the biomass fibres and compounds occurring during torrefaction process. At the same time the effects of torrefaction on the hydrophobicity behaviour of the selected biomasses are monitored and evaluated.

In particular the possibility of correlating the evolution of the fibres content with the Mass Yield Ratio (MYR) is investigated. From this point of view the role of this parameter as key parameter of the process is enhanced. The moisture content of the same torrefied samples, calculated in terms of EMC (Equilibrium Moisture Content), is therefore determined and correlated with the corresponding MYR values.

Looking at the results pertaining to fibres investigations, they can be particularly useful to improve and extend the existing biomass torrefaction models by including information on fibres degradation. Considering the results on hydrophobicity behaviour, this study confirms the enhanced hydrophobic capability of torrefied biomass and contributes to improve the actual data base for this property till now not well investigated and not yet consolidated.

2 MATERIAL PREPARATION

For this investigation a dedicated equipment has been built. It consists of a vertical stainless steel tube of 200 mm in length and 56 mm in diameter. To heat the biomass bed, a direct convective heating approach has been adopted. A nitrogen flow flushes the biomass bed at a rate of 40±0,20 $l \cdot min^{-1}$ (STP) and the inert conditions are controlled by the continuous detection of the oxygen concentration monitored by an electrochemical sensor.

This direct heating approach jointly with the high gas flow rate allows to achieve a high heat flux between the gas flow and the biomass particles so enhancing the homogeneity and the reproducibility of the tests. The temperatures monitoring is performed by using *k* type thermocouples fixed at suitable positions inside the equipment and symmetrically buried inside the bed and located at a half radius distance from the reactor centre.

For a deep description of the configuration design adopted for the reactor and the details regarding the equipments of the experimental plant, reference is made to a recent publication of the Authors [11].

For this work, two types of biomass have been selected on account of their intrinsic chemical, physical and structural differences: common reeds (*Arundo donax*) and spruce (*Picea abies*).
For the raw samples of the indicated biomasses, the ultimate and the chemical components analysis are indicated on the following Table I.

Table I: Ultimate and chemical components analysis of the two raw biomass species.

Species	Ultimate analysis wt%[db]				
	C	**H**	**N**	**S**	**O**
spruce	47.66	6.32	0.14	0.11	45.49
reeds	44.43	5.92	0.47	0.10	44.71
	Fibres content and compounds wt%[db]				
	Hemicel	**Cellul.**	**Lignin[b]**	**Extr.**	**Ash**
spruce	16.63	52.32	26,29	4.08	0.28
reeds	33.21	48.11	13.71	0.60	4.37

[db]: dry basis; [b]: lignin + degraded components.

Reeds belong to an annual grass lignocellulosic *hardwood* type while spruce to a *softwood* kind. Making reference to their structural form, grasses have a rigid outer ring connected to softer pith consisting of thin cell walls normally presenting a hollow cylindrical shell configuration. On the contrary, softwood present a uniform microscopic structure largely due to the abundance of a single cell type, the so-called tracheids.

The biomass structure is emerged as an important parameter both on chemical deconstruction and thermal treatment of lignocellulosic biomass [12]. Looking specifically at the effects induced by torrefaction treatment, Prins et al. [13] have verified that deciduous and coniferous wood present a different behaviour due to the difference in xylan content of the hemicellulose. The final form of the spruce samples utilized for this experimental study have been made available from local sawmills and originates from a preliminary selection of the wood as coming from a shredder. To guarantee a dimensional uniformity, they were preliminary sieved by a vibrating screensand and the final specimens carefully selected in terms of defect and bark free and without knots. The resulting final size of the spruce samples set inside the following ranges: 10-30 mm in length/width and 6-10 mm in thickness. As to reeds, they have been cut in specimens of 10 mm in length to ensure longitudinal matching, while their mean diameter sets in the range of 2 to 3 mm. These last samples appear therefore as empty cylinders having a mean surface thickness lower then 1 mm. Regarding preparation, the proposed selection represents a compromise to guarantee on one hand the uniformity of the specimens, on the other to maintain a dimensional distribution of the specimens consistent with that of the biomass normally available to feed real torrefaction plant. It is to point out that the results carried out in this work are expected to give significant information for real plants working conditions and design. Usually, for real plant, biomass is supplied in different size and shapes excluding, at the moment, a severe dimensional particles selection. Before beginning the torrefaction tests, all the raw samples have been maintained under laboratory conditions and then dried in a convection oven at 105 °C (± 3°C) for 24 h. This procedure is required to define the reference state of the oven-dry untreated biomass for all the proposed elaborations. Before use, samples were finally stored in desiccators containing silica gel. This drying procedure has been applied for each of the torrefied samples too.

The oven-dry mass of the samples has been measured to the nearest 10^{-4} gr. with a digital balance.

3 EXPERIMENTAL TORREFACTION PROCEDURE

Each biomass sample refers to a multiple amount particles of biomass corresponding to 45 gr. for spruce and, due to lower density, to 17 gr. for reeds. The adopted approach do not consider the monitoring of the biomass core temperature. The *torrefaction temperature* declared throughout this work refers therefore to the mean value detected by four thermocouples buried inside the biomass bed and equally distributed in order to guarantee and control the uniformity of the tests. The torrefaction is considered to begin when the mean value of the indicated thermocouples temperature sets above 200°C.

This conforms to the accepted assertion that when temperature reaches the limit of 200°C, torrefaction starts off due to the beginning of hemicellulose degradation[10,11]. The *torrefaction time* is taken into account from this instant and stops when the temperature of the biomass bed is cooled down below 200°C. The torrefaction process is mainly characterized by the *Mass Yield Ratio (*MYR). This parameter identifies the mass loss during the process and is defined as follows:

MYR= mass of torrefied biomass / mass of raw biomass

This quantity is usually expressed on a dry basis (db) and so is done in this work. In this work the MYR values range from light to severe torrefaction conditions. For spruce, four torrefaction temperatures have been chosen: 265°C, 280°C, 295°C, 310°C and three MYR conversion values approximately from 90% to 70%, have been fixed. For reeds, the selected temperatures correspond to: 250°C, 270°C, 290°C, 310°C and the MYR conversion degree is included in the range from 80% to 60%.

Table II: Torrefaction settings for S1 to S7 spruce and R1 to R8 reeds samples.

Term	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	
Temp. (°C)	265	280	280	295	310	295	310	
Time(min.)	49	20	76	30	17	92	36	
MYR^t	90	90	80	80	80	70	70	
MYR^{exp}	89.3	89.	79.4	80.2	79.1	68.4	69.0	
Term	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
Temp. (°C)	250	270	290	270	290	310	290	310
Time(min.)	90	27	13	120	43	13.5	90	28
MYR^t	80	80	80	70	70	70	60	60
MYR^{exp}	81.6	81	80.5	71.1	71.6	71.9	62.4	62.3

[t]: target MYR; [exp]: experimental

The indicated Table II reports for both spruce and reeds samples the corresponding values of time and temperature parameters corresponding to the experimental test conditions.

The corresponding MYR value achieved during experimental test is indicated as MYR^{exp} (*experimental*), while the target value, assumed as an indicative value for comparison, is reported as MYR^t (*target*). For spruce the seven resulting samples are named from S1 to S7, ranging from light to severe torrefaction conditions.

The same Table II reports the results for reeds. In this case eight samples have been considered and named

from R1 to R8. For both the species, the reference state is assumed to be defined by the analysis and conditions indicated on the previous Table I.

4 EXPERIMENTAL TESTS

4.1 Fibres content determination

The amount of lignin, cellulose and hemicellulose have been determined for both raw and torrefied samples according to the Van Soest method [14]. This procedure consists in measuring the NDF, ADF and ADL fractions of biomass. Synthetically the NDF (Neutral Detergent Fibre) represents the insoluble fraction of the sample determined by boiling the sample in a detergent solution with a pH of 7.0. The obtained soluble fraction contains sugars, pectins, lipids, protein, non-protein nitrogen, soluble carbohydrates, starch, while the remaining NDF portion contains cellulose, hemicellulose, lignin, silica, and any heat-damaged protein. By boiling this fraction in an acid detergent solution, the soluble portion, containing hemicellulose, is separated from the insoluble ADF (Acid Detergent Fibre) fraction that contains cellulose and lignin.

This residual part is further treated in a strong acid solution (sulphuric acid at 72%) that allows to obtain a soluble fraction containing the cellulose and a final insoluble fraction ADL (Acid Detergent Lignin) whose main component is lignin. This procedure has been performed at least twice for each sample by utilizing a fiber extraction FIWE6 apparatus (Velp Scientifica, Italy).

4.2 Equilibrium Moisture Content (EMC) determination

Before beginning the torrefaction tests, the moisture content of the biomass samples was determined in triplicate according to AOAC standard method 930.15 [15]. This procedure is required to define the reference state of the oven-dry raw biomass samples for all the proposed elaborations. Before use, samples were finally stored in desiccators containing silica gel.

The oven-dry mass of the samples has been measured to the nearest 10^{-4} gr. with a digital balance. For all the samples, the EMC has been measured in a controlled climate chamber for 72h (Thermotron Chamber Model S1-0) at a constant temperature of 25°C and Relative Humidity (RH) ranging from 24% to 75%, conforming therefore to a recent procedure proposed by Lam et al. [16]. The EMC measurement, triplicated for reproducibility test, was determined as follows:

$$EMC = \frac{ms_e - ms_d}{ms_d}$$

where ms_e and ms_d are the mass of the sample at the selected RH equilibrium state and at dry conditions respectively. It is to point out that there is not yet a consolidated procedure to test the hydrophobic behaviour of torrefied biomass. Reference can be made to recent published works [17].

5 RESULTS PRESENTATION AND DISCUSSION

5.1 Mass Yield Ratio (MYR) results

The experimental MYR data reported on Table II refer to the mean value of three replicates for each temperature and time conditions reported on the same Table II. These results make evidence the effects of temperature and time on the obtained torrefaction degree. Considering a couple of samples presenting the same target MYR, for instance *S3* and *S5* (80% target MYR), a temperature increase of 30°C (from 280°C sample *S3* to 310°C sample *S5*) entails a reduction of 59 min. (from 76 to 17 min.). This means that an increment of 10.7% in temperature reflects on a reduction of 77.6% on torrefaction time. For the *reeds* samples *R4* and *R5* (target value of 70%) a positive variation of temperature of 7.4% (from 270°C to 290°C) entails a reduction in time of 64,2% (from 120 to 43 min.). As deeply analysed by the Authors on their recent published paper [11], this peculiarity of the torrefaction process can significantly impact on both the design procedure of the torrefaction reactor and the selection of the most suitable working time and temperature conditions in view of the optimization of the process.

5.2 Fibres content results

The results of the fibres analysis are reported on the following Table III for both torrefied spruce and reeds samples. This Table indicates also the amount of extractives as a global value comprehensive of several compounds like fatty acids, tannins, resins etc.

Table III: fibres content for spruce (S1-S7) and reeds (R1-R8) torrefied samples and corresponding extractives amount. Values expressed as dry mass fraction (w%^{db}).

Term	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	
Hemicel.	11.7	10.4	5.63	5.9	6.5	5.02	5.2	
Cellulose	49.6	50.5	48.3	49.4	47.4	40.7	42.1	
Lignin[b]	32.2	31.8	39.6	38.4	39.4	45.5	47.1	
Extrac.	6.11	6.9	6.1	5.9	6.4	8.3	5.2	
Term	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
Hemicel.	8.9	9,8	9,6	5.5	6,7	6.8	4.6	4.0
Cellulose	45.6	51.7	46.0	35.8	37.0	39.0	27.1	30.5
Lignin[b]	21.0	19.6	20.2	26.7	26.3	29.3	33.6	39.1
Extrac.	15.9	11.6	16.1	23.2	21.3	15.9	25.2	16.9

[b]: total lignin including degraded components.

Making reference to hemicellulose and cellulose, it emerges that the content of these two fibres decreases as the torrefaction becomes stronger in terms of MYR. Synthetically, this is due to thermal degradation of carbohydrate fraction and evaporation of carbon dioxide and water [18,19]. In particular torrefaction involves near-complete breakdown of hemicellulose that reduces, for spruce samples, moving from the raw biomass (Table I) to S7 samples, up to 68%, while for reeds the reduction sets at around 87%. The Acid Detergent Lignin method, applied for the determination of the acid insoluble lignin, makes evidence the increase of this quantity as the severity of torrefaction increases. This is probably due to the formation of condensed acid-insoluble structure inside the thermally degraded product [20]. In particular for hardwood, it has been observed that lignin can be partially soluble in the highly concentrated sulphuric acid so that the total effective

lignin content can be compromised.

On the indicated Table III lignin is reported as "*total lignin*" comprehensive therefore of the degraded compounds. The determination of the lignin content for specimens thermally treated and the selection of the most appropriate methodologies for its measurement are still open questions and widely debated on several papers. For a deep discussion on this issue, reference is made to [21]. A significant note can be deduced from this results: it jumps out that the extractive amount, corresponding to the soluble NDF fraction, is significantly higher for torrefied reeds compared to that of the torrefied spruce.

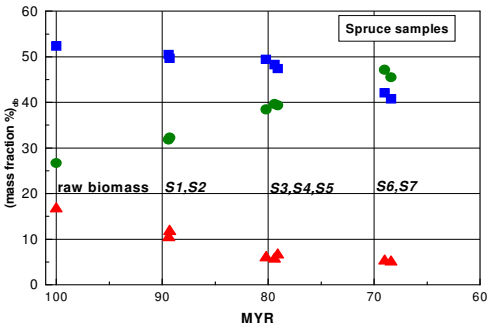

Figure 1: Fibres distribution in terms of mass fraction Vs. MYR for raw and treated spruce samples:
▲: hemicellulose; ● lignin; ■ cellulose.

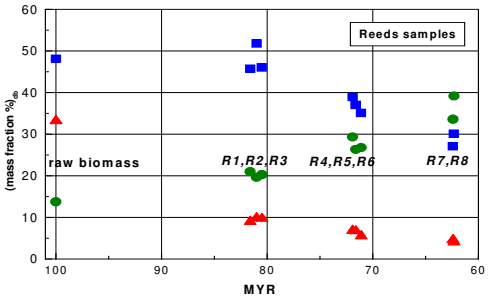

Figure 2: Fibres distribution in terms of mass fraction Vs. MY R for raw and treated reeds samples:
▲: hemicellulose; ● lignin; ■ cellulose.

This is probably due to the different amount of compounds that are made soluble during the working Van Soest method adopted for this analysis.

The results of the fibres evolution is depicted on the previous Figs. 1 and 2, where the fibres content for each torrefied samples is reported in terms of mass fraction (dry basis db), Vs. MYR for spruce and reeds specimens respectively.

Considering the clear trend that emerges from the analysis of the cited Figs. 1 and 2, the emerging correlation between the fibres content and the MYR confirms the role of this parameter as key factor of the process also in terms of fibres content: samples presenting similar MYR conversion (the same target value) present also a similar distribution of the fibres content. During this tests and procedure dedicated to the fibres investigation, this study has pointed out some discrepancies regarding in particular the reliability of the Van Soest Method in measuring the exact amount of fibres when samples have been previously thermally treated.

5.3 Moisture content results

Considering the characteristic of the three fibres with respect to the hydrophobicity, the highest capacity of water adsorption belongs to hemicellulose, followed by cellulose and lignin [22]. Moisture absorption of woody material is due to the presence of hydroxyl groups responsible of forming hydrogen bonds. The removal of these OH groups and the chemical rearrangement of fibres structure during torrefaction [23] enhances the hydrophobic behaviour of the torrefied biomass. The experimental study here proposed aims at verifying the effects of the torrefaction treatment on the hydrophobicity behaviour for the two selected biomasses. Besides, this work offers the opportunity to verify some questionable results, recently published [24], that assert that these effects have limited significant above 250°C.

The following Table IV reports a complete view of the results achieved during this investigation.

Table IV: Experimental EMC (%) for spruce and reeds samples at 25°C and different RH (%) values of the climate chamber.

RH	S1	S2	S3	S4	S5	S6	S7	
24	3.5	3.3	3.2	3.2	3.2	3.3	3.2	
35	6.0	5.9	5.3	5.4	5.4	5.4	5.3	
41	6.2	6.1	5.5	5.6	5.5	5.6	5.5	
49	6.6	6.6	5.8	5.9	5.9	5.9	5.9	
68	8.8	8.6	7.7	7.8	7.7	7.7	7.6	
75	9.4	9.2	8.2	8.4	8.2	8.2	8.1	
RH	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
24	3.4	2.7	2.8	3.5	2.7	2.7	2.9	3.2
35	5.7	5.4	5.5	5.7	5.2	5.3	5.3	5.4
41	5.9	5.6	5.7	5.9	5.4	5.5	5.5	5.6
49	6.3	5.9	6.0	6.2	5.8	5.8	5.9	6.0
68	8.3	8.0	8.2	8.2	7.8	7.8	7.7	7.9
75	9.1	8.8	9.1	8.9	8.8	8.6	8.5	8.7

This Table reports, for both the species, the EMC values reached by the samples at defined RH conditions of the climate chamber, in the range of 24-75%, and at a constant temperature of 25°C. Inside this range and for spruce specimens, it has been preliminary tested that raw biomass increases its water adsorption of 8.2% (from 4.7 to 12.9); a target MYR of 90% (S1) is enough to limit the water adsorption increment to 5.9% (from 3.5 to 9.4, table IV).

If the target MYR conversion is lower then 90% as the case of samples S4 (80%) and S7(70%), the increase limits at 5.2% for S4 and 4.9% for S7, this difference being partially appreciable only at the higher RH values, as highlighted on the following Figure 3.

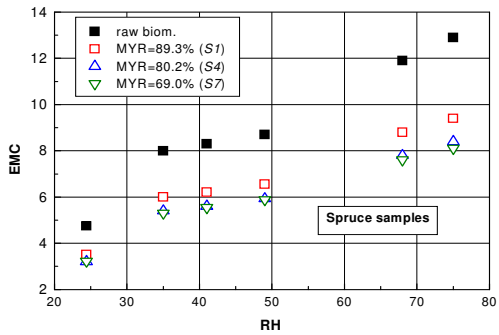

Figure 3: Hydrophobicity behaviour of spruce expressed in terms of EMC Vs. RH for raw biomass and samples presenting an increased torrefaction degree (*S1*, *S4*, *S7*).

Also for this property it is confirmed that samples referred to the same target MYR, as in the case of S3, S4 and S5 (MYR=80%), present also a similar hydrophobicity behaviour trend: this is enhanced on the following Figure 4 for the aforementioned samples S3, S4, and S5.

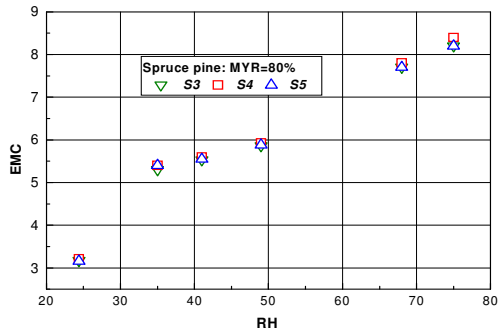

Figure 4: Hydrophobicity behaviour for spruce samples at the same target MYR set at 80%.

This behaviour is confirmed for reeds too. For this type of biomass the results are synthesized on the following Figure 5 where the whole set of data is depicted.

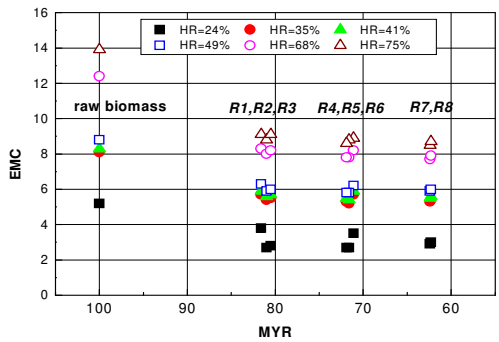

Figure 5: Hydrophobicity behaviour of all the reeds sample in terms of EMC Vs. MYR at the RH values of the climate chamber.

This representation clearly evidences the detail that a MYR conversion set around the 80% can be regarded as the lower limit below which the EMC appears to be slightly dependent from the torrefaction conversion. Making reference to the cited question [24], the limit of 250°C is as well confirmed (all the R samples present a torrefaction temperature higher than 250°C) but this behaviour, from the point of view of this work, can be described in term of the MYR as a more generalized parameter including, for this property too, the effects of the torrefaction.

6 CONCLUSIONS

Competitiveness and quality of solid biomass fuel may be significantly increased by incorporating torrefaction in the production chain. It is well known from literature that torrefied products present a significant hydrophobic behaviour. The biomass storage chain value can then be improved if the raw biomass is preliminary torrefied. This work presents the results of an extended experimental investigation regarding the determination of the fibres and moisture content of two types of biomasses submitted to a torrefaction process from light to severe process conditions. In this investigation two species of biomass have been considered: *spruce* belonging to softwood and *reeds* to hardwood. On a wider classification, spruce pertains to *woody biomass*, while reeds to *non woody biomass.* The Mass Yield Ratio (MYR) can be in particular correlated with the fibres content, confirming therefore the role of this parameter as synthetic parameter of the process, as observed on a recent work of the Authors for thermal properties [11]. For the same samples the EMC has been determined by submitting the samples to different Relative Humidity (RH) values ranging from 24% to 75% and at a constant temperature of 25°C. These tests confirm that the higher is the torrefaction degree (higher MYR) the higher is the hydrophobicity of the samples that significantly reduces from the corresponding trend of the raw biomass. Another important result is that the the MYR value close to 80% can be regarded, for both the investigated biomasses, as the lower limit to set the dependency of the moisture content from the MYR.

As a general synthesis of this experimental study, it emerges that the knowledge of the torrefaction degree of the biomass, expressed in terms of MYR, can gives a direct information on both the fibres distribution and the moisture content of the torrefied biomass. These conclusions could be helpful if exploited to enhance the decision-making strategy to scale-up this process from small pilot plants to industrial torrefaction units.

7 REFERENCES

[1] Chen WH, Kuo PC. A study on torrefaction of various biomass materials and its impacts lignocellulosic structure simulated by a thermogravimetry. Energy 2010; 35: 2580–2586.

[2] Chen WH, Hsu HC, Lu KM, Lee WJ, Lin TC. Thermal pretreatment of wood (Lauan) block torrefaction and its influence on the properties of the biomass. Energy 2011; 36: 3012–3021.

[3] Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on thE grindability and reactivity of woody biomass. Fuel Process Technology 2008; 89: 169–175.

[4] Bergman PCA, Boersma AR, Zwart RWR, Kiel JHA.

Torrefaction for biomass co-firing in existing coal-fired power stations. ECN Biomass 2005.
[5] Li J, Brzdekiewicz A, Yang W, Blasiak W. Co-firing based on biomass torrefaction in a pulverized coal boiler with aim of 100% fuel switching. Applied Energy 2012; 99: 344–354.
[6] Bergman PCA, Boersma AR, Kiel JHA, Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction for entrained-flow gasification of biomass. ECN Project Report ECN-RX-04-046 2004. ECN, Petten, the Netherlands.
[7] Zheng A, Zhao Z, Chang S, Huang Z, Wang X, He F, Li H. Effect of torrefaction on structure and fast pyrolysis behaviour of corncobs. Bioresource Technology 2013; 128: 370–377.
[8] Sklar T. Torrefied wood, a bio-energy option that is ready to go : biomass-digest-specialreport/, 2009. Accessed 12 January 2012.
[9] Childs W. Torrefied biomass: an ideal co-firing solution. Presentation, Integro Earthfuels Inc. 2012. http://www.integrofuels.com/.
[10]Van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinski KJ. Biomass upgrading by torrefaction for the production of biofuels. A review: Biomass and Bioenergy 2011; 35: 3748-3762.
[11]Grigiante M., Antolini D. Mass yield as guide parameter of the torrefaction process. An experimental study of the solid fuel properties referred to two types of biomass. Fuel 2015; 153: 499–509.
[12]Chen WH, Kuo PC. Torrefaction and Co-Torrefaction Characterisation of Hemicellulose, Cellulose and Lignin as well as Torrefaction of Some Basic Constituents in Biomass. Energy 2011; 36: 803–811.
[13]Prins MJ, Ptasinski JKJ, Janssen FJJG. Torrefaction of Wood. Part 2: Analysis of Products.. Journal Analytical Applied Pyrolysis 2006; 77: 35–40.
[14]Goering HK, Van Soest PJ. Forage fiber analyses (apparatus, reagents, procedures, and some applications).Agriculture handbook n°. 379, Agriculture
[15]AOAC method 930.15. Loss on drying (moisture) for feeds (at 135 _C for 2 hours)/dry matter on oven drying for feed (at 135 _C for 2 hours) official methods. Official methods of analysis. 17Th Ed. AOAC International, Gaithersburg, MD; 2000.
[16]Lam PS, Sokhansanj S, Bi XT, Lim CJ, Larsson SH. Drying characteristics and equilibrium moisture content of steam-treated Douglas fir (Pseudotsuga menziesii L.). Bioresources Technology 2012;116: 396–402.
[17]Acharjee TC, Coronella CJ, Vasquez VR. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. Bioresource Technology 2011;102: 4849–54.
[18]Gonzalez-Pena MM, Curling SF, Hale MDC. On the effect of heat on the chemical composition and dimensions of thermally-modified wood. Polymer Degradation Stability 2009;94: 2184-2193.
[19]Telmo C, Lousada J. The explained variation by lignin and extractive contents on higher heating value of wood. Biomass and Bioenergy 2011; 35: 1626-1667.
[20]Yan W, Acharjee TC, Coronella CJ, Vasquez VR. Thermal pretreatment of lignocellulosic biomass. Environmental Progress Sustainable Energy 2009; 28: 435-440.
[21]Parka J, Menga J, Limb KH, Rojasa OJ, Parka S. Transformation of lignocellulosic biomass during torrefaction. Journal of Analytical and Applied Pyrolysis 2013; 100: 199–206. Research Service USDA, Washington (DC), USA, 1970; 20.
[22]Bjork H, Rasmuson A. Moisture equilibrium of wood and bark chips in superheated steam. Fuel 1995; 74: 1887–1890.
[23]Stelte W, Clemons C, Holm JK, Sanadi A, Ahrenfeldt J, Shang L, Henriksen UB. Pelletizing properties of torrefied spruce. Biomass and Bioenergy 2011; 35: 4690-4698.
[24]Medic D, Darr M, Shah A, Rahn S. Effect of torrefaction on water vapour adsorption properties and resistance to microbial degradation of corn stover. Energy Fuel 2012; Doi:10.1021/ef3000449.