7. Reeds as a renewable energy source: Insight into possible conversion pathways

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7.1 Introduction

This chapter deals with the possible use of reed for energy production, with particular regard to innovative thermochemical conversion processes as pyrolysis, gasification and – among upgrading pathways – torrefaction. After introducing the role of wetland biomasses, these energy conversion processes are described in the first section, explaining also their possible role as alternatives to direct combustion of biomass. Different scenarios of the complete reed-to-energy chain are here presented. Beside physical and chemical characteristics of a feedstock, a crucial issue to be considered in assessing the reed suitability for energy production is the feedstock thermal behaviour. For this purpose, a detailed thermal analysis of reed has been performed through combined analytical techniques and the results are presented in the second section of this chapter. The third section is devoted to the investigation of different conversion scenarios of reed, through modelling analysis supported by experimental tests of torrefaction and pyrolysis carried out in a laboratory bench-scale apparatus. The results described in this chapter allow a general assessment of reed as energy source, and they have been used for the techno-economic evaluation of a case study in Wuliangsuhai Lake region, presented in Chapter 8.

7.2 Biomass as a source of energy and the role of wetland biomasses

In the last years, the interest on renewable energy sources has been on the rise. On the one side, the energy demand is constantly growing, in strict

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Cirella, G. T. & Zerbe, S. (Eds.). (2014). *Sustainable water management and wetland restoration strategies in Northern China.* bu,press. https://doi.org/10.13124/9788860461094

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connection to the global population rising and the expansion of developing countries' economies (Nelson 2011). This aspect, combined with the depletion of fossil fuels, caused in the last few years a considerable increasing on the global energy markets of the prices for fossil fuel energy. On the other side, industrialised societies are more and more aware of impacts of fossil fuel utilisation on the environment and on the human health, making the search for environmental and socially acceptable alternatives increasingly important (Kaltschmitt et al. 2007). Respect to other renewable sources such as wind or solar energy, biomass has the main advantage that, if well managed, can ensure a constant supply of energy, being its availability not dependent on meteorological conditions. This is an essential aspect in the vision of an integrated exploitation of different renewable sources.

Beside woody biomass, perennial grasses have gained widespread appeal for energy production, opening new renewable energy scenarios (Strezov et al. 2008). Perennial grasses are now being used as solid fuel in co-fired coal power plants as well as targeted as a choice feedstock for such advanced biofuels as cellulosic ethanol. Furthermore, perennial grasses can also be pressed into pellets, briquettes, and cubes and used as a heating fuel to replace or complement fuels made from wood fibre. Grasses can grow on marginal lands suited for continuous row crop production or in open rural land currently not in agricultural production. They usually have a high productivity and once established, require far fewer inputs in comparison to annual crops in terms of fertiliser and pesticides needs.

In addition to terrestrial grass plants, also the emergent aquatic macrophytes can play an important role as local energy source in places where they are naturally present in great amounts. Wetland plants have a high macro-nutrients accumulation capability because of their generally fast growth and high biomass production (Bragato et al. 2006; Frick et al. 2011). As a consequence, their utilisation for energy production could have, as additional advantage, the disposal of such kind of elements from the ecosystem. In the present research, these considerations have been in particular applied to the emergent aquatic macrophyte *Phragmites australis*, known as common reed. Common reed is one of the most common plants living in wet ecosystems (Bonanno & Lo Giudice 2010; Dienst et al. 2004; Ostendorp 1999). Among other grass plants, common reed is considered to be a promising source of renewable energy, being a perennial fast-growing plant able to produce an interesting amount of dry biomass (3–15 t/ha) and being its provision relatively cheap (Lee 2011).

P. australis can withstand extreme environmental conditions, including the presence of toxic contaminants such as heavy metals (Baldantoni et al. 2004; Quan et al. 2007; Ye et al. 1997; Bonanno & Lo Giudice 2010) and there are many cases in which, as other wetland plants, it is utilised for the removal of pollutants, including metals. Concerning the phytoremediation of metals, there are generally two possible approaches, i.e. (1) "phytostabilization", where the plants are used to immobilise metals and store them belowground in roots and/or soil, in contrast to (2) "phytoextraction" in which hyper-accumulators may be used to remove metals from the soil and concentrate them in aboveground tissues (see Chapter 6). These latter plants must be, in turn, harvested and disposed of to prevent recycling of accumulated metals when the plants decompose (Weis & Weis 2004). Metal translocation into the shoots appears to be very restricted in *P. australis* so that harvesting plants will not be an effective source of metal removal in a wetland system.

From an ecotoxicological perspective, it could also be argued that the transfer of metals into shoot biomass is an undesirable property, as metals so accumulated could pass into the food chain via herbivores and detritus feeders (Ye et al. 1997). However, *P. australis* show a high N and P concentration in tissues and may have greater potential to remove nutrients from eutrophicated wetlands. Phosphate is easily concentrated in the belowground tissues, while nitrate concentration is higher in leaf and stalk. Harvesting the aboveground tissues could take most of the nitrate out of the sediment (Tian et al. 2009).

Focusing on common reed, in the international literature few experiences can be found concerning its utilisation for energy production. One of the first studies on reed utilisation for energy purposes dates back to the 1980s in Sweden, in particular for the application of reeds in direct combustion (Graneli 1984). Nevertheless, in the following years, even if this species has been widely studied for its phytodepuration potential (Weis & Weis 2004; Bonanno & Lo Giudice 2010; Baldantoni et al. 2004; Quan et al. 2007; Ye et al. 1997), few experiences can be found in international literature concerning the energy utilisation of *P. australis*. In fact, the low bulk density (20–60 kg m^{-3}) of reed makes it unattractive for long distant transportation and increases handling and storage costs.

Only in the last years, the interest on this topic rose again, mainly in Europe (Kuhlman et al. 2013). Most investigations deal with the combustion of reed (Barz et al. 2006; Kask et al. 2007; Kitzler et al. 2012; Komulainen et al. 2008; Kronbergs & Kronbergs 2011), some with biogas production (Hansson & Fredriksson 2004; Komulainen et al. 2008). Besides this, a promising but not yet completely characterised application of common reeds seems its thermochemical conversion through pyrolysis (Sutcu 2008; Zhao et al. 2011; Park et al. 2012) or gasification (Kitzler et al. 2011; Yang et al. 2012; Link et al. 2013), in the perspective of converting the biomass into liquid or gaseous fuels that can be used in a more efficient way respect to the direct combustion of a solid fuel. Sutcu, in 2007, carried out some experiments about pyrolysis of common reeds in a tubular fixed-bed system, achieving the maximum oil yield at 550 °C pyrolysis temperature, a heating rate of 25 °C/min and a sweeping gas flow rate of 100 ml/min (Sutcu 2008). The feedstock ultimate and proximate analyses are in good agreement with the result of Lange (2006) and the comments followed by Barz et al. (2006). They indicate three points: (1) compared to other biomass fuels, the relative high LHV indicates the reed as a promising energy source; (2) the nitrogen content is very low so that no problems concerning nitrogen oxide emissions were expected; (3) the higher contents of chloride, sulphur and ash might cause problems regarding emissions and process management if the reed is used in conventional combustion technologies.

7.3 Thermochemical conversion of biomass

Biomass can be converted into energy by means of different methods, as shown in Figure 1. Focusing only on thermochemical conversion processes, the easiest application is represented by direct combustion in a furnace, after simple mechanical pre-treatments (e.g., chopping, pressing, briquetting). The released heat can be then used for steam generation and energy (heat and electricity) production. Nevertheless, traditional combustion of solid heterogeneous fuels is affected by several environmental impacts such as the release of particulate matter and unburned hydrocarbons that can be somehow mitigated through the adoption of expensive clean-up stages downstream the process.

As an alternative, pyrolysis and gasification processes can be used in order to convert the biomass into gaseous (i.e. producer gas) or liquid fuels that can be used in a more efficient way. For example, cleaner combustion technologies (i.e. premixed burners) can be used, as well as high-efficiency internal combustion engines (e.g. alternative engines, gas turbines).

7.3.1 Processes: Torrefaction, pyrolysis and gasification

Many of the problems in biomass gasification are related to the properties of the fuel. Biomass is thermally unstable and has a low energy density and, as a consequence, its gasification leads to tar formation and low energy products. For this reason, in the last few years biomass torrefaction process has gained a renewed attention on the biomass-to-energy production chain. This thermal pre-treatment is a sort of slow pyrolysis process carried out at low temperature (max. 280–300 °C) that makes better physical and thermochemical properties of biomass (Bergman & Kiel 2005; Arias et al. 2008; Bridgeman et al. 2008), such as grindability, uniformity, hydrophobicity and heating value – and can be a suitable pre-treatment to improve the gasification/pyrolysis of the feedstock (Prins et al. 2006).

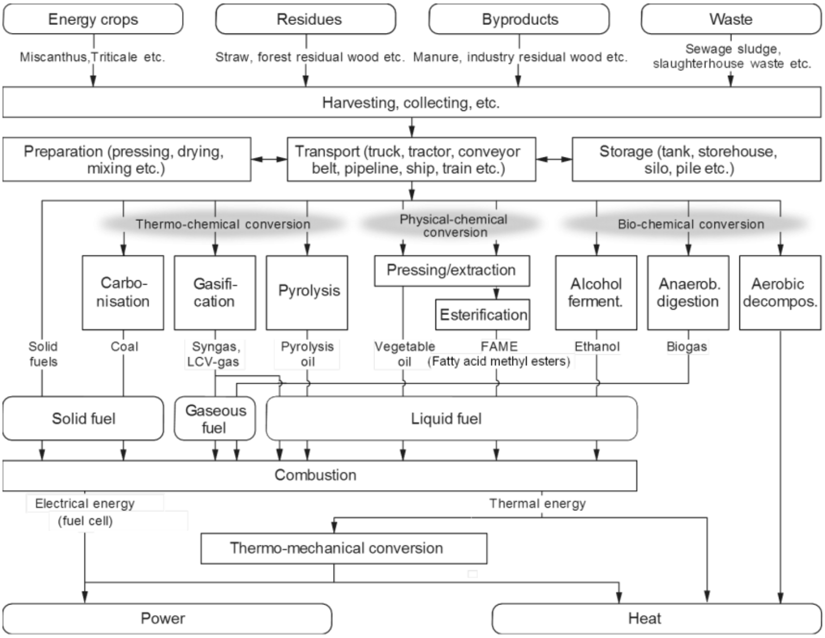


Figure 1 – Schematic representation of different biomass-to-energy pathways (rounded boxes: energy carriers; boxes: conversion processes); adapted from Kaltschmitt et al. (2007).

Pyrolysis is a thermal treatment carried out in absence of oxygen that allows to transform the biomass into liquid (pyrolytic oils and tar), gaseous (synthesis gas or syngas) and solid (char or biochar) products. Tar, a complex mixture of condensable hydrocarbons of high molecular mass, can cause operational problems in downstream processes by blocking gas coolers, filter elements and engine suction channels (Li & Suzuki 2009). Recently, char or biochar starts to be considered, besides as fuel, as a valuable compound useful to increase soil fertility and carbon sequestration in soil (Kwapinski et al. 2010). On the basis of the heating rate, one of the main parameters beside the peak temperature, it is possible to distinguish between “fast” and “slow” pyrolysis. The aim of the former, characterised by high heating rate (up to 1000 °C per second) and peak temperature of about 650 °C, is the maximisation of the liquid product yield. In Table 1 the typical product yields of pyrolysis carried out at different process conditions are reported.

Table 1 – Typical product yields %, (dry wood basis) obtained by different modes of pyrolysis of wood (Bridgwater 2004).

Pyrolysis conditions	Liquid	Char	Gas
Moderate temperature, short residence time	75	12	13
Low temperature, very long residence time	30	35	35
High temperature, long residence times	5	10	85

Pyrolysis could also be seen as the first step in combustion and gasification processes. In fact, if an oxidant agent is introduced, the pyrolysis is followed, respectively, by the total or by the partial oxidation of the primary products (Figure 2). The sub-stoichiometric conditions that characterise the gasification process can be reached through the injection of steam (in the case of "steam gasification"), air or oxygen (in the last two cases the process is generically named "partial oxidation").

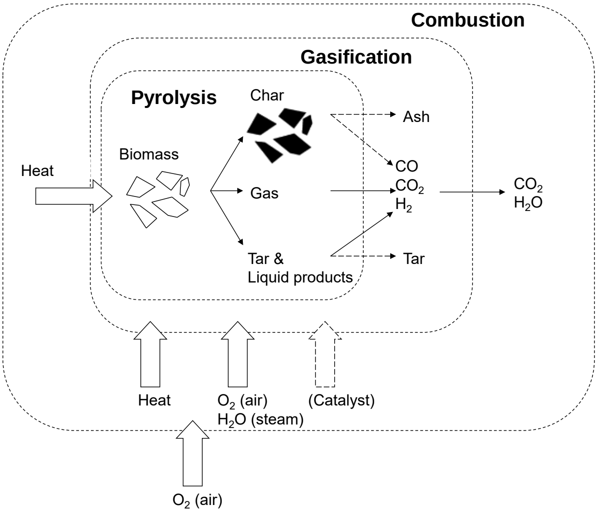


Figure 2 – Schematic representation of pyrolysis as the first step of gasification and combustion; readapted from Knoef (2005).

7.3.2 Overview on biomass conversion technologies in China

Nowadays, China is one of the countries with the most dynamic economies in the world. The energy necessary to ensure this fast economic growth is mostly produced from coal (74 % in 2011, according to the International Energy Agency), which is cheap and easily available. The drawback is the high emission of greenhouse gases. Producing "clean" energy is one of the most challenging tasks for China in the 21st Century.

China tries to tackle this challenges by increasing the share of renewable energies from 8 % in 2013 to 15 % in 2020 (Moch 2013). Whereas wind, photovoltaic and hydropower has been mostly used for electricity production, biomass is often burned in rural areas for heat production (Moch 2013). Latter role is comparable small, only 1 % of the total energy consumption in 2002 (Zhang 2012), and up to now relies mostly on small-scale technology, e.g. stoves for local heat production by combustion or digestion. Nonetheless, biomass resources (agricultural residues, grassland biomass and forest residues) can have a relevant role on substituting coal, being their energy potential equal to almost 30 % of China's energy consumptions (Zhou et al. 2011). According to the China 12th Five-Year Plan for Renewable Energy, the production of biogas in rural areas is intended to increase to 50 million households by 2015 (Moch 2013). Seven billion tonnes (t) of solid waste are produced annually, with a proportion of 60 % biomass waste (EC2 2011). The available amount of crop straw corresponds to 0.82 billion t, but 20 % are burned in the field without being utilised (Zhang 2012).

Up to now in China, in the rural areas, household energy is mainly produced by means of direct coal or biomass combustion (Zhang et al. 2013a) with methods characterised by very low energy efficiencies, e.g. 10 % for the traditional stoves burning crop residues and 7 % for the Kang, a kind of coupled stove and heated bed system in rural northern China (Junfeng et al. 2005; Liu et al. 2008), as shown in Photograph 8a, b. This causes serious indoor air pollution related to respiratory aerosols, SO_2 (in particular when coal is burned) and CO emission (Zhang & Smith 2007).

Because of the high amount of biomass feedstock in China, several research institutes and universities are devoted to research, development, demonstration and application on biomass gasifier (Zhang et al. 2013a). According to the review of technological development of biomass gasification for a variety of applications in China performed by Leung et al. (2004), biomass gasification for the purpose of electrical energy generation is very promising, possessing great potential in research and development in China. The main biomass gasification demonstration projects are summarised in Table 2.

Table 2 – Biomass gasification demonstration projects in China (Zhang et al. 2013a).

Type	Feedstock	Purpose	Capacity	Location
Downdraft	Sawdust	Drying	200 kWt	Beijing
	Crop residues	Cooking	300 kWt	Shangdong
	Wood residues	Cooking	700 kWt	Liaoning
	Crop residues	Cooking	300 kWt	Hunan
	Agricultural residues	Heat and power	200 kWe	Jilin
Bubbling Fluidised Bed	Crop residues	Cooking and heating	300 m^3/h	Henan
	Rice husk	Electricity	400 kWe	Anhui
	Rice husk	Heating	120 MW	Jiangsu
	Rice husk	Gas	160-220 m^3/h	Anhui
Circulating Fluidised Bed	Rice husk, rice and wheat stalk	Electricity	5500 kWe	Jiangsu
	Sawdust, rice husk or straw	Electricity	1000 kWe	Fujian
	Wood powder	Heating	1000 kWt	Guangdong
	Wood powder	Heating	7000 kWt	Jilin
	Crop residues	DME	1000 t/a	Guangdong
	Wood powder	Electricity	1000 kWe	Hainan
	Corn straw	Electricity	600 kWe	Hebei

Figure 3 – Location of the sampling points in Wuliangsuhai Lake (Inner Mongolia, China); digitised background from Landsat satellite images.

7.4 Characterisation of reed as energy source: chemical-physical properties and advanced thermal analysis

Several samples have been collected in Wuliangsuhai Lake wetland area (Figure 3) and subsamples from stems have been characterised by means of elemental and calorimetric analysis. The choice to focalise the analyses only on stems come from the weight distribution in *P. australis,* that – according to

Shi et al. (2010) – is more or less 47 % in roots, 37 % in stems, 15 % in leaves and 1 % in inflorescences.

The samples collected are only of aboveground tissues, therefore these percentages became 70 %, 28 % and 2 % for stems, leaves and inflorescences, respectively. This weight distribution is also confirmed by Li et al. (2013). The moisture content of the collected samples has been determined according to the UNI CEN/TS 14774-2. Stem subsamples were dried at 45 °C for 48 hours and ground with a Retsch Mill MM400. Ash content (UNI EN 14775), elemental composition (UNI EN 15104), sulphur and chlorine content (UNI EN 15289), phosphorus (UNI EN 15290) and Lower Heating Value (UNI EN 14918) have been determined.

Table 3 – Chemical and physical characterisation of *P. australis* stem tissues. IDs refer to the sampling point position as shown in Figure 3, S = storage (Köbbing et al. 2014b).

	IDs	2	3	4	5	6S	7	7S	8	9	10	11	12	13
Moisture	%wt^{ar}	16.0	32.2	62.4	47.0	12.2	30.9	12.8	12.7	20.9	27.5	24.0	51.7	20.0
Ash	%wt^{dry}	3.8	4.2	3.3	4.4	4.3	4.5	2.7	7.1	7.0	7.8	3.3	6.8	5.2
LHV	MJ/kg^{dry}	17.25	16.90	17.52	16.85	17.17	17.43	17.82	16.76	16.96	16.73	17.38	16.44	17.03
C	%wt^{daf}	49.3	49.3	48.8	47.8	49.1	49.4	49.0	49.0	48.7	48.7	49.2	49.2	49.3
H	%wt^{daf}	6.4	6.5	6.4	6.4	6.5	6.4	6.4	6.5	6.2	6.4	6.6	6.7	6.4
N	%wt^{daf}	0.3	0.4	0.3	0.3	0.5	0.5	0.3	0.3	0.3	0.4	0.2	0.4	0.5
O	%wt^{daf}	43.0	42.5	43.4	44.5	42.9	43.0	44.0	43.4	43.9	43.3	43.4	42.4	42.6
S	%wt^{daf}	0.1	0.1	0.2	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1
Cl	%wt^{daf}	0.9	1.2	0.9	0.7	0.8	0.6	0.2	0.7	0.8	1.1	0.5	1.1	1.1
P	mg/kg^{dry}	119	287	61	103	116	176	82	181	86	126	71	240	175

In addition, in Table 4 the metals' content, determined according to the UNI EN 15297, of the three selected samples is reported. In fact, this is another important feature to be considered, since reeds are able to accumulate pollutants due to their phytodepuration potential (Weis & Weis 2004) and after thermochemical conversion processes most of the metals will be concentrated in the ashes.

The thermal behaviour of reeds has been characterised using a simultaneous thermogravimetric analyser (STA 449F3 Netzsch). This technique combines both the heat flux differential scanning calorimetry (DSC) and thermogravimetry (TG). STA analyses were performed at a constant heating rate of 20 °C/min under inert nitrogen atmosphere in a temperature range from 30 to 1000 °C. The evolved gas was further characterised by TG/STA coupled to a gaschromatography-mass spectrometry system and a Fourier Transform Infrared Spectrometer (FT-IR). TG and DTG curves of stems and leaves are shown in Figure 4.

Table 4 – Metals' content and ash melting behaviour of *P. australis* stem tissues. IDs refer to the sampling point position as shown in Figure 3, S = storage (Köbbing et al. 2014b).

IDs	3	4	6S
metals [mg/kg]dry			
As	0.8	0.4	0.7
Cd	0.2	0.1	< 0.1
Cr	5.0	1.2	3.3
Cu	1.0	0.7	0.6
Hg	< 0.1	< 0.1	< 0.1
Mn	62.5	71.2	104.4
Ni	1.5	1.3	1.1
Pb	0.7	1.0	0.5
ash characteristic temperatures [°C]			
deformation	842	839	871
hemispherical	1,047	954	978
flowing	1,115	1,092	1,094

All the profiles show three main reaction mechanisms. The first peak around 100 °C is due to water loss and can thus be attributed to the residual water content of the biomass. Water loss is followed by two reactions (B at around 280–300 °C and C at around 350–380 °C) which are also due to the main weight loss during thermal degradation. Figure 5 shows the Total Ion Current (TIC) chromatogram evaluation at the temperatures corresponding to these two degradation steps.

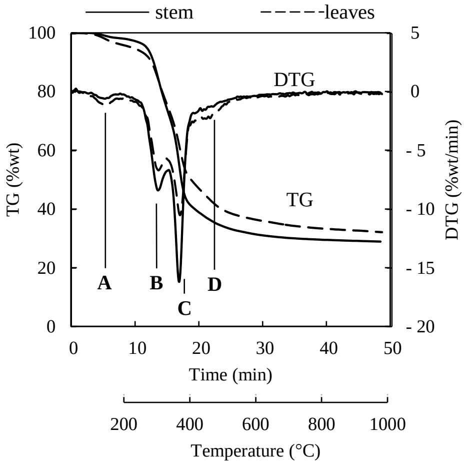


Figure 4 – Comparison between TG and DTG curves of stems and leaves of reed. Circles indicate the temperature at which IR spectra have been extracted; adapted from Patuzzi et al. (2013a).

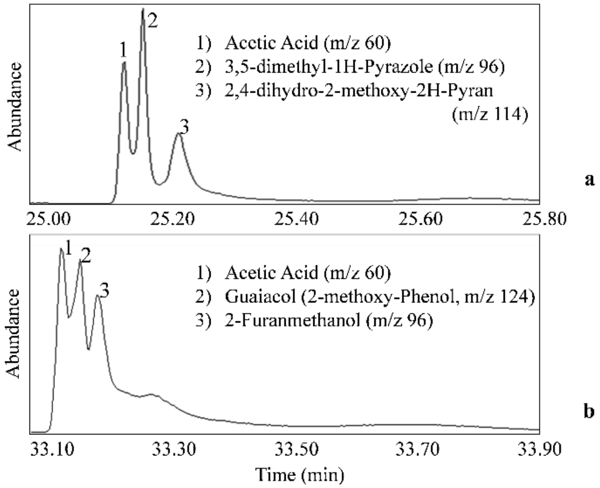


Figure 5 – Total Ion Current (TIC) chromatogram evaluation at [a] 2nd TG step (≈ 280 °C) and [b] 3rd TG step (≈ 350 °C) (Patuzzi et al. 2013a).

The residual mass at 700 °C is 30.17 % and 34.63 % for stems and leaves, respectively; as a consequence, considering the average biomass distribution in *P. australis* proposed by Shi et al. (2010), i.e. about 71 % in stem and 29 % in leaves, the weighted average conversion is 31.5 %.

In order to better define the quality of the evolved gas during thermal conversion, FTIR spectra were recorded at four selected temperatures (Table 5), corresponding to three main reactions during thermal degradation. There are no qualitative differences between the IR spectra of stem and leaves. As example, the results for the stem samples are shown in Figure 6.

Table 5 – Temperatures at which FTIR spectra of the various samples have been recorded: A moisture loss; B first reaction; C second reaction; D almost completed reactions; adapted from Patuzzi et al. (2013a).

Plant part	temperature [°C]			
	A	B	C	D
stem	102.4	281.7	353.7	429.8
leaves	101.6	280.7	352.2	556.0

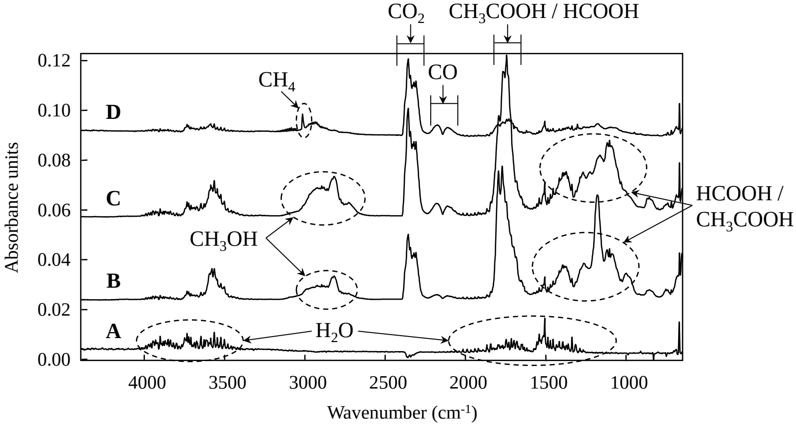


Figure 6 – FT IR spectra of the stem sample (A ≈ 105 °C, B ≈ 280 °C, C ≈ 350 °C, D ≈ 560 °C); adapted from Patuzzi et al. (2013).

The moisture loss of biomass samples attributed to the first peak (A) was confirmed by the FTIR spectra recorded at 100 °C. At higher temperatures, i.e. around 300 °C methanol (CH_3OH), acetic acid (CH_3COOH) and formic acid ($HCOOH$) could be detected. These three compounds are still present up to 350 °C but not at temperatures higher than 450–500 °C. In addition, carbon dioxide (CO_2) release increased from temperatures around 300 °C to temperatures around 350 °C and then decreased at around 450–500 °C. At this latter temperature, methane (CH_4) could also be detected in the evolved gases. This is in accordance to thermodynamic equilibrium calculation, as well as the increasing trend of carbon monoxide (CO).

7.5 Reed conversion scenarios: Experimental and modelling investigation

7.5.1 Experimental analysis

Several pyrolysis experimental tests have been performed in a bench scale apparatus setting different process temperatures (300 °C, 450 °C, 550 °C, 600 °C and 700 °C), setting the heating rate of the oven equal to 50 °C min^{-1}. The bench scale pyrolysis apparatus – set up at the Free University of Bozen-Bolzano and schematically presented in Figure 7 – consists of a tubular electric furnace, a tubular reactor, a condenser, a series of impinger bottles for the collection of tars and a module for gas sampling and measurement. The furnace is able to reach the maximum temperature of 1050 °C. The reactor (20 mm diameter, 45 mm length) is placed inside the furnace. Reactor and condenser are made out of quartz, which has a high resistance to temperature and chemicals, high purity and high stability.

The atmosphere inside the reactor is kept inert by nitrogen flow. The gas produced inside the reactor flows through the condenser, where it is cooled. The tar collection is then performed in a series of six impinger bottles, according to the technical specification UNI CEN/TS 15439; the first impinger bottle acts as a moisture collector; all the bottles except the last one are filled with isopropanol, an organic solvent suitable for tar capture. Except the first and the fourth, all the bottles are equipped with G0 frits (i.e., sintered glass filters with a nominal pore size in the range 160–250 μm). The first, second and fourth bottle are kept at 35/40 °C with water as cooling liquid, while the others are cooled at –15/–20 °C with a mixture of salt/ice/water. The gas suction device consists of a drying tower, a rotameter, a dry running rotary vane vacuum pump and a dry gas volume meter (measurement range: 0.4–6.0 m^3h^{-1}; accuracy: 0.09% at 1.2 m^3h^{-1}, –0.2% at 0.4 and 6.0 m^3). For each test, the tar–isopropanol solution has been collected and analysed by GC–MS technique. PAH have been separated on a DB5 MS column (J&W Scientific) and detected by a high resolution ($R > 10.000$) mass spectrometer (GC–HRMS, MAT95XL, Thermo Scientific). PAH have been identified by the addition of deuterated internal standards.

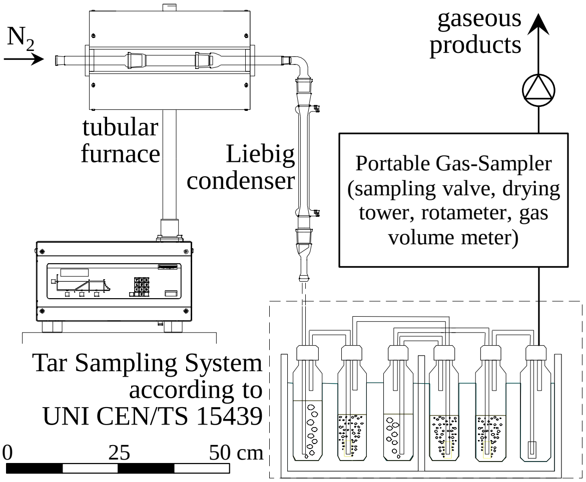


Figure 7 – Set-up of the bench-scale batch pyrolysis/torrefaction system (Patuzzi et al. 2013b).

The detected PAH concentrations are reported in Figure 8. The main detected compounds are: naphthalene, phenanthrene, fluoranthene, acenapthene, acenaphthylene, dibenzo[al]pyrene, indeno[cd]pyrene and pyrene. The total PAH concentration, as well as the concentration of most of the main compounds, show a clear increasing trend with the temperature. This behaviour is in good agreement with the literature (Garcia-Perez & Metcalf 2008).

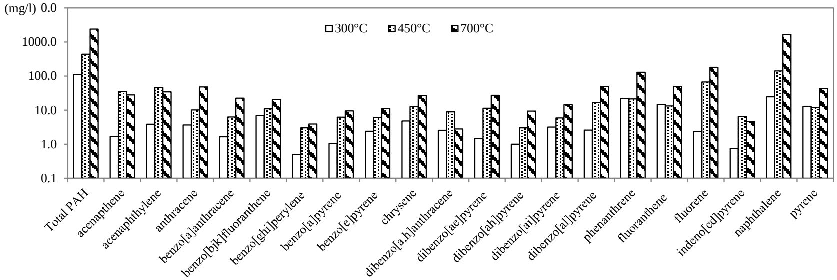


Figure 8 – PAH concentration in the condensed tar samples (Patuzzi et al. 2013b).

The total PAH content has been normalised respect to the initial biomass sample, obtaining an increasing PAH yield with the temperature (2.75 mg g^{-1}, 15.84 mg g^{-1} and 74.41 mg g^{-1} at 300 °C, 450 °C and 700 °C, respectively). In pyrolysis tar, a PAH content ranging from 7.0 to 12.6 % at 400 °C to 21. 4 % at 800 °C have been reported for lignocellulosics (Ku & Mun 2006).

7.5.2 Modelling of a CHP plant based on reed gasification

Starting from the composition and the lower heating value of the reed samples collected both in water and on the land, the average composition and lower heating value have been calculated (Table 6), assuming a moisture content of 10 %, a typical value that can be reached after an air-drying pre-treatment. The average elemental composition and calorific value have been used as input in multi-stage model of a CHP biomass plant (Prando et al. 2013). The power plant layout (Figure 9) consists of a first section where the producer gas is produced and a second section where the producer gas is exploited to generate electrical and thermal power. The producer gas production section has been modelled as a fixed bed air gasifier operating in ideal conditions which can simulate the pyrolysis and air gasification process. The chemical reaction can be endothermic or exothermic depending on the process conditions. In the first case, the heat is provided by a burner, which is fed through a producer gas spilling, while for exothermic operation the heat is supposed to be discharged. Before feeding the CHP plant, producer gas is piped through heat-recovery and clean-up sections.

The first stage of the model is the gasification unit, simulated through an enhanced gas-solid equilibrium approach, previously tested versus experimental available data and based on the minimisation of the Gibbs free energy (Baratieri et al. 2008). This allowed the estimation of the theoretical yield and equilibrium composition of the reaction products (producer gas and char) of reed thermochemical conversion processes (pyrolysis and gasification). The model consists of a code written in Matlab environment that handle chemical reaction equilibria, implementing the Cantera software library, a collection of object-oriented software tools for problems involving chemical kinetics, thermodynamics and transport phenomena (Goodwin 2011).

Figure 10 shows the producer gas molar composition for reed pyrolyzed at different temperatures and a process pressure of 1 bar. According to Baratieri et al. (2008), methane and carbon dioxide formation are favoured at lower temperatures, and at higher temperatures carbon monoxide and hydrogen are the dominant equilibrium products. This is mainly due to the increasing importance of the endothermic water gas reaction, which causes a corresponding decrease of the producer gas steam content (generated by the drying of the feedstock). Furthermore, carbon dioxide trend goes through a maximum according to its exothermic formation and endothermic conversion.

The equilibrium composition versus the equivalence ratio (ER, ratio between the oxygen fed to the gasifier and the stoichiometric quantity of oxygen needed for the complete oxidation of the species) has also been evaluated (Figure 11). The increase of the ER parameter causes a proportional increase of the N_2 molar fraction due to the greater amount of air fed to the reactor (Baratieri et al. 2008).

Table 6 – Average composition of reeds (as received basis), used as input of the thermodynamic equilibrium model (Köbbing et al. 2014b).

moisture	ash	C	H	N	O	S	LHV
[%wt^{ar}]							[MJ/kg^{ar}]
10.0	4.7	39.6	5.2	0.3	40.1	0.1	15.07

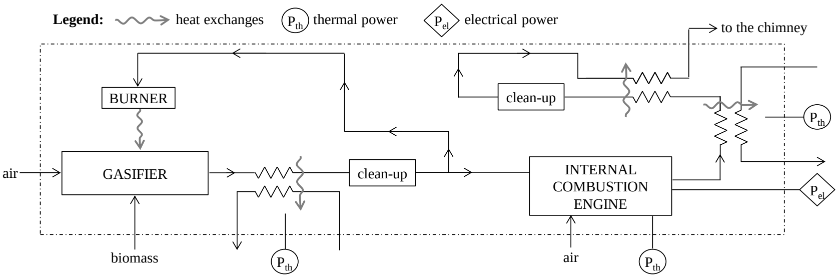


Figure 9 – Schematic representation of the considered CHP power plant layout; adapted from Prando et al. (2013).

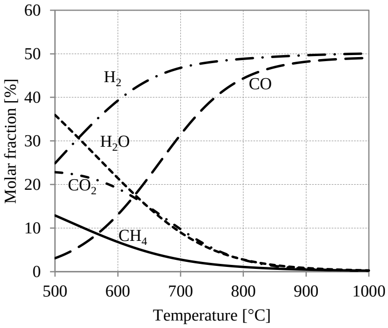
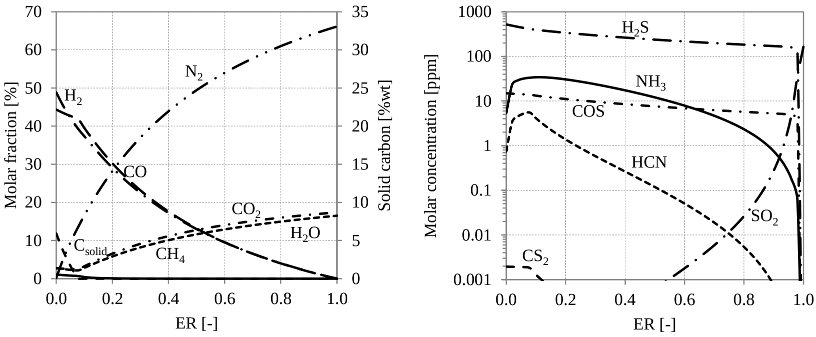


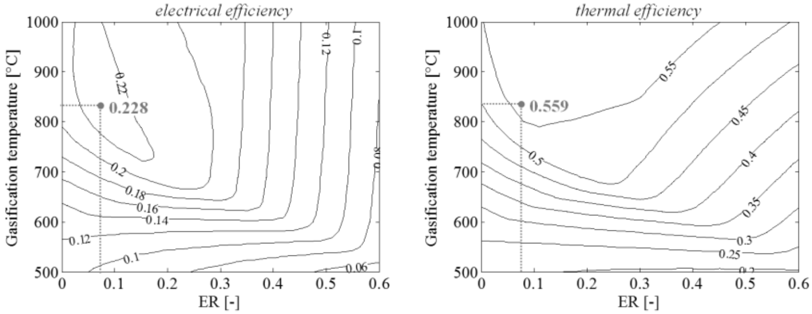
Figure 10 – Producer gas equilibrium composition versus process temperature under pyrolysis conditions and pressure of 1 bar (Köbbing et al. 2014b).

The producer gas heating value represents the useful energy output from the gasification process. An increase of the amount of gasifying agent tends to lower the producer gas LHV, mainly decreasing its CH_4 and H_2 molar concentrations. The global enthalpy variation along the conversion process has been computed taking into account all the enthalpy fluxes i.e. enthalpies of the biomass, reaction products and gasifying agents. This quantity, if positive (or negative), represents the amount of energy that has to be supplied to (or is released by) the process itself. The net process enthalpy variation is an increasing function of the process temperature. In addition, a rising of ER determine an increase of the partial oxidation process exothermicity (Baratieri et al. 2008).



a b

Figure 11 – Producer gas equilibrium composition and solid carbon versus equivalence ratio under partial oxidation and steam gasification of reed at 800°C and 1 bar; [a] major and [b] minor components (Köbbing et al. 2014b).



a b

Figure 12 – Contour line representation of the CHP [a] electrical and [b] thermal efficiencies that can be achieved under different gasifier operating conditions. The highlighted values are the ones assumed for the scenario evaluation (Köbbing et al. 2014b).

The efficiency of the whole CHP system has been evaluated supplementing the simulation of the gasification stage with the energy balance of the cogeneration set (i.e., internal combustion engine). The electrical efficiency is maximised when the gasifier is operated at 870 °C and ER=0.06. Under these conditions the thermal and electrical conversion efficiency results equal to 55.9 % and 22.8 %, respectively (Figure 12). These values have been used in the scenarios evaluated in Chapter 8.

7.6 Conclusion

Several reed samples collected within the Wuliangsuhai Lake wetland area have been characterised by means of elemental and calorimetric analysis. The results show that reed is characterised by a remarkable energy content that is comparable to the one of traditional woody biomass. Nonetheless, the high ash content and the relatively low ash melting temperatures are both aspects that should be carefully taken into account in the design of a thermal degradation plant.

In addition, the application of advanced analytical techniques (TG/STA-IR-GC-MS), supplemented by the experimental pyrolysis tests at different temperatures, in a bench scale apparatus, have given useful insight into the thermal degradation process of common reed (*P. australis*). The STA analysis highlighted two main degradation steps, one at around 280 °C and the other at around 350 °C. According to the pyrolysis tests, the PAH concentration in the collected tar, as well as, the concentration of most of the main compounds shows a clear increasing trend with the temperature.

Finally, starting from the measured reed composition, the reed-to-energy pathways through pyrolysis and gasification processes have been further assessed applying a thermodynamic equilibrium approach. Based on both modelling and experimental results, *P. australis* can be considered an attractive natural biomass resource both acting as a second generation feedstock and as phytoextractant for its metal accumulation potential.

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