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1. Introduction

In the last decades the problem of CO₂ emission in the atmosphere has driven the industry of power generation towards an increasing use of biomass fuels in addition to conventional fuels.

Figure 1 reports the well known Van Krevelen diagram for a wide variety of solid fuels. It can be seen that biomasses are in general characterized by larger O/C and H/C ratios compared to fossil fuels such as coals. They stand, instead, close to RDFs (refuse derived fuels). As a matter of fact it is not easy to draw a clear demarcation line between biomass and RDFs. Biomass itself is a broad category of materials ranging from raw vegetal materials to solid refuses of industrial and civil origin (wood and agricultural residues, residues of paper, food and dairy industry, sludge of civil origin etc).

A further element of despair in this already very broad category of fuels lies in the content of inorganics and/or metals, which are present in some biomasses at levels distinctively higher than in traditional fuels. Under this respect biomasses appear even more close to industrial wastes. The presence of metals and inorganic matter may produce unusual effects in terms of both energetic and environmental performance.

It has been shown for a variety of solid fuels that the process and reactor design, in particular the temperature level and the inert/oxidizing nature of the gaseous atmosphere, determine the reaction path and affects severely the fate of the organic matter [1-2] but is also expected to determine the fate of inorganic matter and metals.

As far as the organic content is concerned, upon heating under inert atmosphere this undergoes a combination of thermal cracking and condensation reactions, called pyrolysis, producing a gas, a liquid (tar) and a solid product (char). Gaseous species generally include hydrogen, carbon monoxide, methane, carbon dioxide and other incondensable hydrocarbons; tar consists of chemicals, such as methanol, acetone, acetic acid etc. Liquid at room temperature; char is a carbonaceous type solid containing mainly carbon but also the residual inorganic matter.

As shown by Senneca et al. [3] heating of a solid fuel in the presence of oxygen may result in two types of processes depending on the fuel properties and on the process conditions (oxygen concentration, temperature and heating rate). At low temperature (if under isothermal conditions), or at low heating rate (if under non isothermal conditions) thermal
cracking and condensation reactions are assisted and enhanced by parallel oxidative and combustion reactions. Char and tar combustion occur in parallel with thermal cracking as shown by fig. 2A and the resulting gas is rich in CO and CO$_2$. For high enough temperature (under isothermal conditions) or for large particle heating rates (under non isothermal conditions), purely thermally activated pyrolysis overtakes direct combustion and the reaction follows the most typical pattern; pyrolysis occurs first, followed by heterogeneous combustion of the tar and char. The corresponding reduced network is represented in Fig. 2B. It must be noted that volatile matter emission and the formation of an attached or detached volatile flame further contribute to preventing the occurrence of heterogeneous oxidation in this case.

Fig. 1. Van Krevelen diagram

Fig. 2. A Reaction path of oxidative pyrolysis
The presence of metals and inorganic matter in biomass further complicates the scenario and makes it difficult to predict whether a reaction pathway of type A or B would be active. A first consequence is that the yields and the chemical composition of gaseous, liquid and solid products cannot be predicted a-priori and require appropriate consideration of the process conditions. A second consequence concerns the fate of inorganics and metals themselves, which is a matter of utmost importance for environmental reasons. The potential hazard of emission of volatile metals during the pyrolysis/combustion process and of leaching upon disposal of the final residue is indeed a problem that has already been underlined for a number of wastes of industrial origin, such as sludges and wastes obtained from the reclamation of metal from insulated wires and electronic equipments and automobile wastes [4-9], but also for some wastes that may be included in the category of biomass, for instance meat and bone meal [10] and residues of the pulp and paper industry [11].

In conclusions the design of thermal processes aiming at the exploitation of biomass as solid fuels requires a more comprehensive understanding of how process conditions and reactor design affect the efficiency in terms of energy conversion, yields and chemical composition of gaseous, liquid and solid products as well as the fate of inorganic matter. In other words the exploitation of biomass fuels in thermal processes requires biased experimental investigation of its pyrolysis and combustion behaviour. To this end a diversity of techniques at the laboratory scale can be used. The present paper discusses the problems related with the standard laboratory techniques and presents a comprehensive experimental protocol for the characterization of biomass fuels based on thermal analysis and lab-scale reactors. Examples of selected fuels are presented to demonstrate and clarify the issue.

2. Conventional experimental techniques

The most commonly used lab scale technique for the study of thermal processes involving biomass it thermal analysis, because of it apparent simplicity. Thermal analysis is definitely the easiest and most accurate tool to perform proximate analysis but its natural and most valuable goal is the kinetic study.

Today it is well known that the most reliable kinetic methods for the analysis of non isothermal TG experiments are the Friedman plot [12,13], the Kissinger±Akahira±Sunose plot [13-15] and the Ozawa-Flynn-Wall method [16,17]. A very important point is that this analysis is easy and reliable in the case of single power law reactions but is more complicated in the case of parallel reactions. Thermal processes of biomass in fact have often
been described using power law kinetic expressions, for a single reaction when one major
event of weight loss is distinguished, for two or more parallel reactions when two or more
stages of weight loss are observed. This choice is made for sake of simplicity and also
because the method for kinetic analysis of TG curves is well consolidated. In the case of
multiple/competitive reactions in series/parallel some methods for kinetic analysis have
been proposed, but there are few examples of their application.
In any case it must be clear that thermogravimetric analysis can be used confidently to
predict the thermal life of a fuel only at relatively low temperature and heating rate.
Outsiders may misunderstand there are serious problems to apply the results of
thermogravimetric analysis to practical operating conditions of pyrolysers/combustors,
where temperature and heating rates are quite different from those of thermogravimetric
analysis.
The potential of thermogravimetric analysis in the study of thermal processes of biomass is
considerably enhanced by the introduction of simultaneous DSC or DTA and analysis of
evolved gas (EGA) by FT-IR and mass-spectrometry. The former technique reveals the
presence of transitions, particularly important for biomasses rich in minerals and metals,
moreover it gives information on the endothermic/exothermic nature of the processes, thus
contributing significantly to interprete the weight changes events detected by the TG curves.
Again outsiders should not be tempted to use the DSC data obtained during simultaneous
TG/DSC experiments of biomass for a quantitative measure of its heat of
pyrolysis/combustion.
Analysis of gaseous species by FT-IR and MS is also very useful to obtain information on the
type of gaseous species evolved throughout a thermal process and to understand the
reaction paths, but also in this case results must be regarded as qualitative more than
quantitative and caution is needed to extend them to real situation. Examples of this type of
equipment are shown in Fig. 3.
For the study of the yields of biomass pyrolysis the most common experimental approach
is the recourse to purposely made lab furnaces equipped for the collection of tar and the
analysis and tar and gases. Different configurations and different collection systems have
been proposed. An example of this type of equipment is shown in Fig. 4. Typically the
sample is located inside a pyrolysis reactor which is heated by an external electrical
furnace with heating rates in the order of 5-50°C/min. The product is conveyed to a set
of consecutive traps for tar condensation at progressively lower temperature. Tar is
analysed off-line typically by Gas Chromatography. Uncondensables are analysed either
of line or online by different analytical tools, such as GC (off-line) or FT-IR or MS
(on-line).
This type of experiments is able to give quantitative data on the yield of biomass pyrolysis,
however the extrapolation of these results to reaction conditions far from those of the
experiment would again be ingenuous.

3. Experimental protocol

The experimental protocol proposed for biomass fuels couples experiments in a
thermobalance with experiments in lab scale reactors and tests of physico-chemical
characterization of the fuels themselves and of their solid products. It therefore includes
three activities.
1. Physico-chemical characterization of the solid
   This includes proximate and ultimate analysis, SEM-EDX, ICP, XRD, Porosimetry by Hg and/or gas adsorption, Granulometric analysis.
   The same set of analysis is applied to the raw sample and to samples of char and ash. The char is obtained in the necessary amount by pyrolysis in a tubular furnace or in a fluidized bed reactor at temperatures in the order of 600-800°C in a flow of nitrogen.
   Ashes are obtained from complete burn-off of the material in lab scale reactors such as tubular furnaces or fluidized bed reactors, in air at temperatures in the order of 800°C.

2. Thermogravimetric analysis
   This includes three sets of experiments:
   TG-IP. pyrolysis under inert conditions;
   TG-OP. oxidative pyrolysis;
   TG-C. combustion of char.
Thermal analysis is carried out in a TG system, possibly coupled with a DSC/EGA equipment for on-line analysis of the gaseous products. It is important that such devices are designed to minimize condensation and secondary reactions in the gas phase. Approximately 10 mg of sample are loaded in the pan in each test. Notably the particle size of the sample must be reduced when possible to 100-200 µm to minimize heat gradients inside the particle and mass transfer limitations. An upward flow of gas of 100-200 mL/min is used.

In pyrolysis experiments (TG-IP and TG-OP) the temperature is raised from 25°C to 110°C and held at 110°C for 5-10 min to release moisture. The sample is then further heated up to 850-900°C at a constant heating rate. Heating rates in the range 5-20°C/min are scanned. During the ramp, 100% He or Ar or N₂ or a mixture of 0.01-21% oxygen in He/Ar/N₂ are used. The sample is finally held at 850-900°C for 30 min, while the gas is switched to 21% O₂ in He/Ar/N₂ to burn the residual char.

In experiments of char combustion (TG-C), the char can be prepared in the thermobalance immediately prior to the combustion test or externally in a lab scale reactor. The char can be then heated in the thermobalance up to 850-900°C at a constant heating rate in a the desired mixture of 0.01-21% oxygen. Alternatively the char is heated in He/Ar/N₂ up to a desired temperature in the range 350-600°C. The gas is then switched to the desired mixture of 0.01-21% oxygen O₂ to burn the char isothermally.

Fig. 4. Lab scale pyrolysis reactor.

It must be noted that the conditions chosen for the thermogravimetric experiments have been used in past experimental campaigns of pyrolysis and combustion of a wide range of solid fuels. In most cases such conditions proved successful to avoid internal gradients of heat and gas concentration as well as particle overheating and guaranteed that reactions took place under kinetic control. However such precautions may result insufficient to guarantee kinetic control in some cases.

The mass recorded during experiments of pyrolysis and oxidative pyrolysis is worked out in order to obtain TG plots of m/m₀ versus T and DTG plots of

$$\frac{dm}{dT} \frac{1}{m_0} = -\frac{df}{dT} \frac{m_o - m_{\infty}}{m_0}$$

versus T.
where \( m, m_o \) and \( m_\infty \) are the actual weight of the sample, the initial weight of sample (after the dehumidification stage in pyrolysis and oxidative pyrolysis experiments) and the weight of the sample residue at the end of the experiment, respectively.

Results were fitted to a power law expression:

\[
-\frac{1}{m_o} \frac{dm}{dt} = k_o \exp\left(\frac{-E}{RT}\right) \left(1 - \frac{m}{m_o}\right)^\alpha 
\]  

(1)

The kinetic parameters of equation (1) can be obtained by non linear regression analysis of the DTG curves according to the Friedman and Kissinger methods using general-purpose regression tools. Data from experiments at heating rate \( (H\alpha) \) below 20°C/min are used.

The mass loss recorded during experiments of char combustion is further worked out to calculate:

- the carbon conversion degree \( f = (m_o - m)/(m_o - m_\infty) \)
  
  \( m, m_o \) and \( m_\infty \) being the actual weight of the sample, the initial weight of sample and the weight of the sample residue at the end of the experiment;

- the instantaneous rate of carbon conversion \( df/dt \)

Assuming that a power law kinetic expression of the type

\[
\frac{df}{dt} = A(f) \cdot k_o \exp\left(\frac{-E}{RT}\right) p_g^\alpha 
\]

(2)

is a good approximation in most cases, where \( p_g \) is the partial pressure of the oxygen and \( A(f) \) describes the evolution of instantaneous conversion rate along burn-off.

Accordingly the time \( \tau_{0.5} \) required to achieve 50% conversion reads:

\[
\tau_{0.5} = \frac{1}{k_o} \exp\left(\frac{E}{RT}\right) p_g^\alpha \int_0^{0.5} \frac{df}{A(f)} 
\]

(3)

and the reaction rate averaged over the first 50% conversion:

\[
\bar{R}_{0.5} = \frac{0.5}{\tau_{0.5}} = k_o \cdot \frac{0.5}{\tau_{0.5}} \exp\left(\frac{-E}{RT}\right) p_g^\alpha 
\]

(4)

kinetic parameters of equation (4) can be obtained by non linear regression analysis of average reaction rate over the conversion interval \( f=[0, 0.5] \) at different temperature and different values of oxygen partial pressure. Alternatively an average over a larger conversion interval can be adopted.

### 3. Experiments in lab scale reactors

These include:

- **TR-IP-SH**: Experiments of inert pyrolysis with slow heating.
- **TR-OP-SH**: Experiments of oxidative pyrolysis with slow heating.
- **TR-IP-I**: Experiments of inert pyrolysis under isothermal conditions.
- **TR-OP-I**: Experiments of oxidative pyrolysis under isothermal conditions.
- **TR-CC-SH**: Experiments of char combustion with slow heating.
- **TR-CC-I**: Experiments of char combustion under isothermal conditions.
In experiments of slow pyrolysis (TR-IP-SH and TR-OP-SH) typically tubular reactors are used heated externally by electric furnaces at 5-10°C/min. The vessel with the sample is placed inside the reactor from the very beginning of the experiment and heated accordingly. In experiments of pyrolysis under isothermal conditions (TR-IP-I and TR-OP-I) the sample is fed to the already hot reactor at a given temperature, typically in the range 600-850°C. Inert pyrolysis is carried out using helium, while for oxidative pyrolysis inert gas is mixed with a small quantity (0.1-5%) of O\(_2\). The reaction products are quickly cooled down as they flow through bubblers held at 0°C and -12°C respectively. Tar captured by the bubblers are characterized off line by GC or simulated distillation. The gas which passes through the bubblers is sent directly to a gas analysis system, possibly a micro-GC in order to analyse the gaseous products on line. These experiments allow to measure the overall yield in gas-tar and solid products. Further data concern the composition of the tar cumulatively produced during the test and the profiles of gaseous species evolved as a function of time/temperature.

In experiments of char combustion at slow heating rate (TR-CC-SH) the same tubular reactor and experimental procedure as for experiments of slow pyrolysis can be used. In experiments of char combustion under isothermal conditions (TR-CC-I) the reactor used for experiments of isothermal pyrolysis can be used or alternatively small scale fluidized bed reactors. In fluidized bed reactors a bed of inert material such as quartzite can be used with particle size typically between 300-400 µm. Particles are fed from the top of the reactor at a fixed temperature (between 500-900°C). During char combustion experiments the gas is initially nitrogen. After pyrolysis is complete, the gas is switched from nitrogen to an O\(_2\)/N\(_2\) mixture (with O\(_2\) at values between 4-15%). The profiles of CO and CO\(_2\) evolved as a function of time can be worked out to evaluate char combustion rate according to the following expressions:

\[
R = \frac{f}{t_g} \int_{t_R}^{t_R+\tau} \left( c_{CO} + c_{CO2} \right) Q \, dt
\]

\[f: \text{ carbon conversion degree} \]

\[t_R, t_R+\tau: \text{ reaction time, time when oxygen feed started, s} \]

\[c_{CO}, c_{CO2}: \text{ concentration of CO e CO}_2, \text{ mol/l} \]

\[Q: \text{ gas flow rate, l/s} \]

\[n_C: \text{ moles of carbon fed with the solid fuel, mol} \]

4. Examples of sample preparation and physico-chemical characterization tests

In order to explain the experimental protocol proposed in the previous paragraph, results will be presented here for a set of different biomasses as well as for other carbon rich materials. The examples have been selected so as to show typical and problematic cases. As a first example the case of meat and bone meal (MBM) has been chosen, from a previously published paper [10]. MBM char was prepared in an electrically heated tubular furnace at 650°C for 5min in a flow of nitrogen. Ashes of MBM were produced in the same electrically heated tubular furnace at 800°C in a flow of air.
Elemental analysis, SEM, ICP and granulometric analysis have been carried out on the above samples. The following instruments have been used: LECO CHN 2000 and Perkin Elmer CHNOS elemental analysers, a Philips XL30 SEM equipped for EDAX analysis, an Agilent 7500 CE ICP-MS, a Mastersizer 2000 granulometer of Malvern Instruments. Results are reported in Table 1 and in Fig. 5.

The granulometric analysis of MBM indicate that the sample has a quite dispersed particle size distribution with average particle diameter of 250 µm. In the SEM picture of MBM some smooth and roughly cylindrical particles can be recognized within the bulk of the material. The EDAX analysis reveals large amounts of C, O, Ca, P. In comparison the roughly cylindrical particles are poor in Ca and P and quite rich in C and S.

![SEM picture of MBM](image)

The ICP analyses indicates that raw MBM contains large amounts of Na and Ca, followed by K, Mg and by small amounts of Fe, Zn, Al, Sr with traces of Ba, Mn, Cr, Co, Pb. The same metals are found in ashes of MBM produced in the electrical furnace at 800°C, however upon ashing the amounts of Ca, Mg increase by a factor of 3, those of Al, Na, Fe, Zn by a factor of 2; K significantly decreases. XRD of MBM reveals that the only crystalline substance present in MBM is Apatite (Ca10(PO4)6(OH)2).

In order to provide a good example of the tests of characterization of the microstructural properties the case of three biomass materials, investigated in ref. [18] will also be reported: namely, wood chips (Pinus radiata), pine seed shells and exhausted olive husk. Porosimetric analysis was carried out on the raw materials, on chars and on partially reacted chars. Char samples were prepared in a bubbling fluidised bed reactor operated with nitrogen at 850°C for 5min. A selection of char particles prepared in the fluidised bed reactor were embedded in a in epoxy resin and cut. Cross-sections were observed under a scanning electron microscope (Philips XL30 with LaB6 filament) at magnifications up to 50 times. Some char samples were ground and sieved to particle size ≤300 µm and further reacted with air or up to 10% carbon conversion in an electrically heated tubular furnace operated at 440°C in air.
### Proximate analysis of MBM

<table>
<thead>
<tr>
<th>Component</th>
<th>Value (as received w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>6</td>
</tr>
<tr>
<td>Ash</td>
<td>20</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>10</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>64</td>
</tr>
</tbody>
</table>

### Ultimate analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>MBM (as received, w%)</th>
<th>MBM char (w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>43.4</td>
<td>31.1</td>
</tr>
<tr>
<td>H</td>
<td>6.4</td>
<td>1.7</td>
</tr>
<tr>
<td>N</td>
<td>9.2</td>
<td>5.1</td>
</tr>
<tr>
<td>S</td>
<td>0.4</td>
<td>n.d.</td>
</tr>
<tr>
<td>Cl</td>
<td>0.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>P</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

### Heating Value of MBM (d.b. %w)

<table>
<thead>
<tr>
<th></th>
<th>Value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV</td>
<td>15.50</td>
</tr>
<tr>
<td>LHV</td>
<td>14.47</td>
</tr>
</tbody>
</table>

### ICP analysis of raw and ashed material

<table>
<thead>
<tr>
<th>Element</th>
<th>MBM (as received, ppm)</th>
<th>Ash (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>57</td>
<td>108</td>
</tr>
<tr>
<td>Na</td>
<td>11422</td>
<td>19498</td>
</tr>
<tr>
<td>Fe</td>
<td>138</td>
<td>331</td>
</tr>
<tr>
<td>Ca</td>
<td>19832</td>
<td>58541</td>
</tr>
<tr>
<td>K</td>
<td>3910</td>
<td>808</td>
</tr>
<tr>
<td>Mg</td>
<td>1777</td>
<td>5150</td>
</tr>
<tr>
<td>Ba</td>
<td>11</td>
<td>78</td>
</tr>
<tr>
<td>Mn</td>
<td>8</td>
<td>31</td>
</tr>
<tr>
<td>Sr</td>
<td>37</td>
<td>140</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
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<tr>
<td>Va</td>
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<td>0</td>
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<tr>
<td>Ni</td>
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<td>8</td>
</tr>
<tr>
<td>Zn</td>
<td>70</td>
<td>139</td>
</tr>
<tr>
<td>Ce</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>La</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>9</td>
</tr>
</tbody>
</table>

### Granulometric analysis

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>MBM</th>
<th>EP1</th>
<th>EP3</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (0.1)</td>
<td>6</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>d (0.5)</td>
<td>124</td>
<td>44</td>
<td>8</td>
</tr>
<tr>
<td>d (0.9)</td>
<td>706</td>
<td>162</td>
<td>51</td>
</tr>
<tr>
<td>Mean d (Surface weighted)</td>
<td>16</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Mean d (Volume weighted)</td>
<td>252</td>
<td>73</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 1. Characterization of MBM
The analysis included mercury intrusion porosimetry, adsorption of $N_2$ at 77K and of $CO_2$ at 273K. The porosimetric station consisted in a high-pressure mercury porosimeter Carlo Erba 2000 equipped with a Macropore unit and a Carlo Erba Sorptomatic 1900. Mercury porosimetry allowed to evaluate the pore size distribution of char in the size range of $200 \mu m > dp > 75 \AA$ and the % porosity, $\varepsilon$. Nitrogen adsorption results allowed to evaluate BET surface areas. Data of carbon dioxide adsorption were analysed according to Dubinin Radushkevich method to evaluate micropore volumes.

Figures 6 A-C show the cross-sections of char particles of wood chips, pine seed shells and olive husk observed under the scanning electron microscope. The micrographs show that char from wood chips and pine seed shells has a highly anisotropic pore structure characterized by parallel channels running in the axial direction (orthogonal to the paper sheet). This is a consequence of the fibrous structure of the parent biomass. Large pores and cavities are also evident in the case of olive husk char, but the orientation appears to be random. A comparison of the three micrographs shows that the solid matrix of the char from wood chips is the most porous, while that of pine seed shell char is the most compact.

The cumulative pore size distribution on volume basis for the chars of the three biomass fuels is reported in Figure 7. Table 2 reports the overall char porosity and density calculated from porosimetric data. Table 3 reports the BET surface area and the micropore volume of unconverted char samples and of char reacted with air or with carbon dioxide up to 10% carbon conversion.

It can be observed that wood chip char is characterized by the lowest density and the largest porosity, which consists predominantly of macropores (>1μm). Wood chip char has also the smallest micropore volume of the three chars (0.17 cm$^3$/g). Moreover micropore volume of wood chip chars is scarcely affected by partial conversion both with air and with carbon dioxide. BET area of wood chip char is negligible after pyrolysis, it increases to 300m$^2$/g after 10% combustion. Noteworthy the increase in BET surface with the progress of carbon consumption can be related with the opening up and development of mesopores, while the increase of micropore volume can be related with the evolution of microporosity [19]. The observed results therefore suggest that reaction of wood chip char with oxygen opens up larger pores (macro and mesopores). The extent and the role of microporosity is very limited in wood chip char.

Olive husk generates a char that is denser than wood chips char and relatively less macroporous. The pore size distribution is indeed shifted toward smaller pore sizes. Micropore volume of the unconverted char is comparable with that of wood chips (0.18 cm$^3$/g) but increases by 40% after combustion. BET surface increases up to 320m$^2$/g after combustion. Altogether results of porosimetric analysis suggest that olive husk char possess a more extensive network of mesopores compared to wood chip char and again quite modest microporosity. Moreover mesoporosity develops along with reaction with oxygen.

The char obtained from pyrolysis of pine seed shells has the smallest pore size distribution and the highest density of the three biomass chars investigated. Its micropore volume is 0.23 cm$^3$/g and increases by 32% after combustion indicating a considerable activation of small pores especially by carbon dioxide. BET area reaches 580 m$^2$/g after combustion suggesting that mesoporosity is significantly developed by oxygen. Altogether results indicate that pine seed shell char contains a large portion of micro and mesopores prone to be activated by the reaction.
Table 2. Results of Hg-porosimetry on three biomass chars

<table>
<thead>
<tr>
<th>Char Type</th>
<th>Average Pore Diameter [μm]</th>
<th>% Particle Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood chips char</td>
<td>17</td>
<td>91</td>
</tr>
<tr>
<td>Olive husk char</td>
<td>7.5</td>
<td>80</td>
</tr>
<tr>
<td>Pine seed shells char</td>
<td>17.5</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 3. Results of gas adsorption on unreacted and partially reacted biomass chars

<table>
<thead>
<tr>
<th>Char Type</th>
<th>BET Area (N2) [m²/g]</th>
<th>Micropore Volume (CO₂) [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted char</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood chips char</td>
<td>&lt; 1</td>
<td>0.165</td>
</tr>
<tr>
<td>Olive husk char</td>
<td>&lt; 1</td>
<td>0.183</td>
</tr>
<tr>
<td>Pine seed shells char</td>
<td>&lt; 1</td>
<td>0.232</td>
</tr>
<tr>
<td>Char reacted with air up to 10% conversion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood chips char</td>
<td>296</td>
<td>0.175</td>
</tr>
<tr>
<td>Olive husk char</td>
<td>320</td>
<td>0.256</td>
</tr>
<tr>
<td>Pine seed shells char</td>
<td>579</td>
<td>0.307</td>
</tr>
</tbody>
</table>

A last example is reported to demonstrate the study of the fate of metals by SEM, ICP and XRD analysis. The case reported here refers to a bitumen like refuse of the oil industry, particularly riched in Mo and V. Although this is not a biomass fuel, it is presented here because it is particularly instructive of the problematic related to the presence of metals.

In addition to the raw material, also char, ashes, a sample of leached material and a sample of char at intermediate burn-off have been characterized. The char was prepared in a tubular reactor at 600°C in a flow of nitrogen. Ashes were obtained from complete burn-off of the material in the same reactor in the excess of 800°C. Partial conversion of the char was accomplished at 600°C in air. Additionally a sample was obtained by overnight leaching of the raw material in pentane.

SEM and ICP analysis were carried out using a Philips XL30 SEM equipped for EDAX analysis and an Agilent 7500 CE ICP-MS. XRD measurements were made with a Brucker D8 ADVANCE diffractometer in reflection mode from 3°(2θ) to 70°(2θ) with a step size of 0.03°(2θ) with an energy dispersive detector Sol-X. Porosimetric analysis was carried out by nitrogen adsorption at 77K with a Carlo Erba Sorptomatic.

Results are reported in Tables 4-5 and in Fig 8. Notably the raw material has a very high carbon content and good calorific value (PCS 34050 kJ/kg). It contains also non-negligible contents of selected heteroatoms and several impurities, such as S, Cl, Ca, V, Fe, Ni, Mo. These metals, identified also by XRD, form different crystalline phases: V1.87FeS4, S8V5.44, V2NiS4, V2Fe0.67S4, V3S4 and V2MoS4. XRD reveals also the presence of a sharp peak at 2θ=26° indicative of the presence of graphitic carbon, probably resulting from catalytic graphitization. The BET area is 200m²/g.

Notably during vacuum treatment prior to nitrogen adsorption tests the sample released a large quantity of sticky and intensely odorous volatile matter. This sticky matter removed under vacuum could also be removed by mild heat treatment up to 150°C or alternatively by leaching the sample with organic solvents such as pentane, as already explained. The proximate and ultimate analyses and the ICP analysis confirm that such pre-treatments removed mainly volatile organic matter with very low boiling point which impregnated the raw sample, while metals remained in the sample.
Fig. 6. SEM picture of cross-section of biomass chars. A. Wood chips; B. Pine seed shells; C. Olive husk
Upon pyrolysis in nitrogen at 600°C volatile organic matter is further lost whereas metals mainly remain in the solid residue. Results from XRD characterization of the char surprisingly show that the sample becomes less graphitic in nature. When the char is burnt with air in the excess of 800°C the carbon content gradually decreases and the concentration...
of metals increases. XRD reveals the appearance of vanadium oxides (VO₂ and V₂O₃) and a renewed increase in graphitic order. The ash composition has been characterized by ICP, and results are reported in Table 5. If one considers that ash residue remaining after complete burn off of the raw fuel represents about 10% of the original sample mass, one would expect that the content of metals in the ash residue should be nearly ten times the corresponding amount in the raw sample. Inspection of Table 5 suggests that this is not the case. To better appreciate the partitioning of metals between the solid residue and the leachate (for samples leached with pentane) or the gas phase (for char remaining after pyrolysis and for the ash residue remaining after combustion), a partitioning factor α has been reported for all but the raw samples and for each metal. Based on an ash-tracing concept, the partitioning factor α has been defined as:

$$\alpha = \frac{w_{i,k}}{w_{i,raw}}$$

where $w_{i,k}$ represents the amount of metal i in sample k (k=pentane-leached sample, char, ash) and $w_{i,raw}$ the amount of the same metal in the raw sample. Similarly, $w_{ref,k}$ and $w_{ref,raw}$ represent the amounts of a reference metal in sample k and in the raw sample, respectively. The reference metal was selected so as to meet two constraints: stability upon both heat treatment and combustion, abundance so as to minimize uncertainties associated with its quantification. After consideration of different candidates, Nickel proved to be the better suited reference metal. Analysis of the partitioning factors provides a clear picture of the relative stability of the different metals upon pentane-leaching, fuel pyrolysis and combustion, which can be related to the departure of α from unity. Most metals are relatively stable upon pyrolysis (with possible exceptions of sodium and lead). More pronounced is the effect of combustion on selected metals: extensive depletion of Se, Sb, Cd and Hg is observed. The more pronounced effect is no doubt that associated with Mo, whose abundant content in the raw residue is only marginally retained in the ash residue after combustion, possibly because of the large volatility of this metal in the oxidized state.

<table>
<thead>
<tr>
<th>Raw sample</th>
<th>Pentane-leached sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>Volatiles</td>
<td>22.1-23.8</td>
</tr>
<tr>
<td>Ashes</td>
<td>8.7-10.9</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>66.7-67.5</td>
</tr>
</tbody>
</table>

Table 4. Analysis (a.r. w%) of refuses of the oil industry. *Minimum and maximum values.
Table 5. ICP analysis of inorganics and metal partitioning factors of refuses of the oil industry

<table>
<thead>
<tr>
<th>Raw sample</th>
<th>Pentane-leached sample</th>
<th>Char</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>ppm</td>
<td>α</td>
<td>ppm</td>
</tr>
<tr>
<td>Na</td>
<td>3896</td>
<td>3757</td>
<td>0.97</td>
</tr>
<tr>
<td>Mg</td>
<td>105</td>
<td>99</td>
<td>0.95</td>
</tr>
<tr>
<td>Al</td>
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<td>320</td>
<td>0.91</td>
</tr>
<tr>
<td>P</td>
<td>19</td>
<td>10</td>
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</tr>
<tr>
<td>K</td>
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</tr>
<tr>
<td>Ca</td>
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</tr>
<tr>
<td>Ti</td>
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<td>15</td>
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</tr>
<tr>
<td>V</td>
<td>12720</td>
<td>12360</td>
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</tr>
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<td>Cr</td>
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<tr>
<td>Mn</td>
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<td>Cu</td>
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<tr>
<td>Cd</td>
<td>51</td>
<td>49</td>
<td>0.97</td>
</tr>
</tbody>
</table>

5. Examples of thermogravimetric analysis

TG-IP/TG-OP/TG-C results for typical biomass

The results of thermal analysis carried out on some of the previously mentioned fuels will be reported in this section in order to provide examples of typical as well as more problematic results as regards TG-IP, TG-OP and TG-C experiments. Notably the TG analysis was carried out in a Netzsch STA 409 CD TG/DSC equipped with a special Skimmer device and a quadrupole Mass Spectrometer Balzers QMG422 (0-300 a.m.u.). This device, described in detail in ref [20] and shown in Fig. 3, enables on-line analysis of gaseous products while minimizing condensation and secondary reactions in the gas phase.

Pine seed shells provide a good example of the typical biomass behaviour during TG-IP and TG-OP experiments. The TG-DTG curves are reported in Fig. 9. The DTG curves exhibit a single peak anticipated by a shoulder. The peak temperature increases with the heating rate. The char residue is around 25% at all heating rates.

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Fig. 9. TG-DTG curves from experiments TG-IP and TG-OP on a typical biomass.

With 5% oxygen at 5°C/min two stages of weight loss are observed: the first stage, accounts for the loss of volatile matter, the second one accounts for conversion of char, leaving behind only residual ash. The first DTG peak is anticipated by 25°C compared to the case of inert pyrolysis. Altogether results of pyrolysis under inert and oxidative conditions indicate a reaction path of the type described in Fig. 2B.

Completely different results have been obtained for coals [2] which, upon oxidative pyrolysis experience a single stage of weight loss with peak at quite higher temperatures (around 670°C at 5°C/min), according to the reaction path of reported in fig. 2A.

DTG curves of the type shown can be analysed easily according to the Friedmann and the Kissinger methods in order to obtain kinetic parameters. Notably large values of the parameter $\alpha$ are commonly obtained when a single reaction model of the type of eqn. (1) is applied to a set of multiple parallel reactions with a broad distribution of activation energies. For ligno-cellulosic materials in fact a wide range of kinetic schemes have been used, including two parallel reactions, nucleation models, discrete activation energy models. The adoption of a single reaction model is a relatively good simplification in the case of pine seed shells, it may be an oversimplification in the case of other biomasses, nevertheless it remains useful for calculations within a first order approximation.

Fig. 10-11 report results of TG-C experiments on pine seed shell char and other biomasses. In particular the procedure followed to assess the kinetics of char–combustion reaction is exemplified assuming a power law expression of the type in eqn. (2).
Fig. 10. Instantaneous char combustion rate vs burn-off for a typical biomass.

Fig. 11. Arrhenius plots for combustion of three biomass chars.
The instantaneous carbon conversion rate has been normalised with respect to the time $\tau_{0.5}$. By this procedure data points at different temperature and oxygen partial pressure overlay and a regression curve can be drawn, which gives the variation of the rate of carbon conversion along burnoff ($A(t)$).

It is important to observe that the Arrhenius plots in the temperature range investigated are reasonably linear. This allows to obtain the kinetic parameters for char combustion from regression over all data points in the figure. At higher temperature the slope of the Arrhenius plot might decrease as a consequence of the onset of mass transfer limitations to the rate of combustion. In this case only the linear portion of the Arrhenius plot should be used to obtain kinetic data.

An additional information which can be readily obtained from Fig. 11 is the scale of reactivity of different chars: in the case shown it is evident that olive husk char is the most reactive of the three samples.

**TG-IP/TG-OP/TG-C results for metal rich materials**

Olive husk and MBM provide examples of atypical TG results that can be obtained for fuels with high inorganic or metal content as regards the effect of oxygen during pyrolysis. As shown in Fig. 12 the presence of oxygen during pyrolysis of this type of fuels does not enhance the mass loss, on the contrary the pyrolytic scission seems to be delayed.

![Olive husk TG curves](image)

Fig. 12. TG curves of olive husk during TG-IP and TG-OP experiments

This apparently anomalous trend can be related to the high metal and inorganic content of these biomasses which promote formation of oxidized complexes. The uptake of oxygen partly compensates the mass loss due to pyrolysis at moderate temperature. At higher temperature complexes are released and eventually lead to complete burnout above 500°C.

The case of the bitumen like residue, particularly rich in Mo and V, will also be presented here, because it is considered very useful to explain this phenomenology. The results of TG-IP and TG-OP tests for this material are reported in Figs. 13-14 TG-DTG-DSC curves are complemented by MS curves.
Under inert conditions between 150 and 300°C distinct peaks can be recognized in MS profiles corresponding to M/e equal to 29, 43, 41, 57, 56. Although it is not possible to achieve a full identification of the chemical species corresponding to these values of M/e, it is likely that alkanes (propane M/e 29, butane M/e 43,29; pentane M/e 43, 57) and butene (M/e 41, 56) are produced in this temperature range. The complete spectrum at 200°C reveals the release also of species with high molecular mass: M/e 81, 95-98, 104, 118, 140, 154, 160, 164, 176, 180. In the temperature range 350-800°C a large MS peak identified as hydrogen is observed, which may be due to dehydrogenation/aromatization reactions and breakage/condensation of higher molecular weight chains.

When mild oxidizing conditions are established (pO2=0.001bar) the pattern does not change significantly up to 400°C, although above 450°C the weight loss increases from 2 to 9%. When strongly oxidizing conditions are established (pO2=0.21 bar) a totally different behaviour is observed: up to 350°C the weight loss is depressed. Combustion takes off above 450°C with a marked heat release resulting in 90% weight loss. MS curves are not reported, but it is CO and CO2 are the major products in this case.

The presence of solid state reactions under oxidizing conditions at moderate temperature at the expense of metals is supported by the evidence during experiment DTG-OP of a small though noticeable DSC peak at 350°C and by results of XRD that show the formation of vanadium and molibdenum oxides.

![Fig. 13. TG-DTG-DSC curves from experiments TG-IP and TG-OP of a residue of the oil industry.](image)

6. Examples of lab scale experiments


Examples of results of pyrolysis in ab scale reactors with the specific aim of studying the yields in tar and gas under different pyrolysis conditions are reported for the bitumen like
residue of oil residue already mentioned before. In particular, the effect of inert vs mild oxidizing conditions and the effect of slow vs fast heating are presented. Pyrolysis and oxidative pyrolysis experiments have been carried out in the tubular reactor described in Fig. 4. The reaction products were quickly cooled down as they flowed through 250ml bubblers held at 0°C and -12°C respectively. Tar captured by the bubblers has been characterized off line by means of simulated distillation. The gas which passed through the bubblers was sent directly to a micro-GC Agilent 3000° equipped with four columns (Molesieve MS5A, Poraplot U, Poraplot alumina and OV1) in order to analyse the gaseous products on line.

Fig. 14. MS curves from experiments TG-IP of a residue of the oil industry.

The overall char yield was between 19-22% in all the tests. The tar yield was around 10% but turned out to be rather scattered. The analysis of the tars collected by the bubblers is reported in Tab. 6. The weight fractions corresponding to different boiling points are reported. It can be observed that tar produced from slow pyrolysis under inert conditions has a minor fraction of components with boiling point between 170-300°C, a 60% weight fraction has boiling point in the range 350-500°C and 30% above 500°C. These figures are consistent with the weight loss measured by TGA. Tar obtained by fast pyrolysis under inert conditions and by slow pyrolysis with a mild oxidizing atmosphere both contain a larger fraction with boiling point below 350°C.

The composition of the gas leaving the bubblers during an experiment of slow pyrolysis in He are reported in Fig. 15. It can be observed that hydrocarbons with more than two carbon atoms are released in two stages. The first, more pronounced one, occurs between 150-400°C, the second between 400 and 600°C. Methane is instead released over the entire temperature range of the experiment. Under moderately oxidizing conditions similar profiles are obtained up to 300°C, but at higher temperatures CO₂ is produced at the expense of methane and other hydrocarbons.
Figure 16 reports the cumulative yields of different gaseous species throughout pyrolysis in the tubular reactor under different conditions. It can be observed that during slow heating rate pyrolysis in helium the product gas contains mainly CH\textsubscript{4} (90%) and small percentages of CO, CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{6} (3-5% each). The presence of oxygen in the pyrolysis atmosphere at low concentration levels (0.1%) produces a gas with 50% di CO\textsubscript{2} and 40% CH\textsubscript{4}. Upon fast heating pyrolysis rate under inert conditions produces a rather different gas, with a marked increase in C\textsubscript{2}H\textsubscript{4}, which becomes the most abundant species, followed by CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, CO, CO\textsubscript{2}.

<table>
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<tr>
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<th>Experiment TR-IP-SH</th>
<th>Experiment TR-OP-SH</th>
<th>Experiment TR-OP-I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st bubbler</td>
<td>2nd bubbler</td>
<td>1st bubbler</td>
</tr>
<tr>
<td>&lt;170</td>
<td>0</td>
<td>0</td>
<td>&lt;170</td>
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<tr>
<td>170-350</td>
<td>4.7</td>
<td>12.3</td>
<td>18</td>
</tr>
<tr>
<td>350-500</td>
<td>61.5</td>
<td>55.8</td>
<td>58</td>
</tr>
<tr>
<td>500-800</td>
<td>33.8</td>
<td>31.9</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 6. Boiling points of tar collected during pyrolysis in lab scale reactor of a residue of the oil industry

Char combustion (TR-CC-SH, TR-CC-I)

Char combustion experiments have been carried out in a fluidized bed reactor (FB-C) consisting of a 1.1 m long quartz tube with 20 mm id. The tube is heated by a vertical electrical furnace with 110 mm ID and length 750 mm. Gas flows bottom up and passes through a distributor positioned at the centre of the tube. The gas flow rate is 100NL/h. A bed of 20mm quartzite is used with particle size between 300-400 µm. Exhaust gas is analysed on line by ABB IR analysers. In each test initially the bed is fluidized by nitrogen. One single particle of approximately 5mm diameter is fed from the top of the reactor at a fixed temperature (between 500-600°C). After pyrolysis is complete, the gas is switched from nitrogen to an O\textsubscript{2}/N\textsubscript{2} mixture (with O\textsubscript{2} at values between 4-15%).

Figure 17 shows typical results of a fluidized bed experiment. In the example reported in this figure the particle was fed at t=100s under inert conditions. The bed was at 600°C. The progress of pyrolysis can be followed from the profile of CH\textsubscript{4}. The time of pyrolysis in this experiment was 58s. At time t=800s oxygen was let into the reactor at the desired level of concentration (15% in the example), this produced a fast increase of combustion products. The CO and CO\textsubscript{2} profiles obtained during this stage are reported in the figure and show that char combustion took 430s. Notably in all the experiments devolatilization took roughly 60s. Pyrolysis time was indeed not affected by the operating conditions, in the range investigated, suggesting that the process was dominated by heat and mass transfer effects.

The char combustion time increased from 430s to 1500s when the temperature was lowered from 600 to 500°C at a value of oxygen concentration of 15% and from 430s to 1700s when oxygen concentration was lowered from 15 to 4 % at the temperature of 600°C. A regression of data of average rate of char combustion at different temperature and oxygen concentration allows to estimate the values of kinetic parameters.
Fig. 15. Gas evolved during TR-IP experiment of a residue of the oil industry.

Fig. 16. Analysis of gas evolved during TR-IP experiment of a residue of the oil industry.
Fig. 17. Profiles of $O_2$, CO and $CO_2$ released during an experiment of TRCCI at 600°C in the fluidized bed reactor for a residue of the oil industry

7. Conclusions

An experimental procedure has been proposed to investigate at a lab-scale the potential of biomasses as fuels for pyrolysis and combustion processes. The experimental work coupled physico-chemical characterization tests with pyrolysis under inert and oxidizing conditions and char combustion using different experimental techniques. Thermogravimetric analysis provides useful information on the temperature range in which pyrolysis/combustion of the fuel can be carried out and allows to estimate the rate and kinetics of the reactive processes. Moreover it provides useful information on the effect of...
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inert/oxidative conditions on the products yield. Examples reported in this paper show that the presence of oxygen upon heating favours pyrolysis reactions in many cases, but when biomasses have a high content of metals and inorganic matter the presence of oxygen hinders the pyrolytic reactions at low-moderate temperature through formation of oxygen complexes.

Tests of pyrolysis in lab scale reactors show that the composition of the pyrolysis gas and tar are strongly affected by the heating rate and by the presence of even minor concentrations of oxygen. As far as gas composition is concerned, slow heating under rigorously inert conditions produces mainly methane and minor amounts of hydrogen, methane, propane, ethylene, CO, CO₂. When heating is carried out in an even mild oxidizing atmosphere the gas produced contains mainly CO₂ and CH₄ and modest amounts of alkanes and alkenes of higher order. As far as tar is concerned, both fast heating and the presence of oxygen increase the low boiling point fraction.

Experiments in a fluidized bed reactor allows to estimate the time of pyrolysis and of char combustion under different conditions. Characterization of the solid products by ICP and XRD allows to investigate the fate of mineral matter and metals. The examples reported for some metal rich fuels show that metals mainly remain in the solid residue during pyrolysis under rigorously inert conditions (up to 600°C). On the contrary pyrolysis under oxidizing conditions and char combustion at temperatures in excess of 800°C produce the oxidation and loss of selected volatile metals, most likely in their oxidized forms. This result has severe environmental implications and needs to be taken into account in process design.

8. Acknowledgments

Several people contributed to the work and are gratefully acknowledged, in particular Mr Vitale Stanzione for ICP and GC analysis, Dr Paola Ammendola and Dr Giovanna Ruoppolo for pyrolysis experiments in the tubular reactor, Mr Sabato Russo for SEM analysis. Special thanks to Mr Luciano Cortese for the valuable support in several aspects of the experimental work and Dr Riccardo Chirone for guidance and assistance.

9. References

Alternative energy sources have become a hot topic in recent years. The supply of fossil fuel, which provides about 95 percent of total energy demand today, will eventually run out in a few decades. By contrast, biomass and biofuel have the potential to become one of the major global primary energy source along with other alternate energy sources in the years to come. A wide variety of biomass conversion options with different performance characteristics exists. The goal of this book is to provide the readers with current state of art about biomass and bioenergy production and some other environmental technologies such as Wastewater treatment, Biosorption and Bio-economics. Organized around providing recent methodology, current state of modelling and techniques of parameter estimation in gasification process are presented at length. As such, this volume can be used by undergraduate and graduate students as a reference book and by the researchers and environmental engineers for reviewing the current state of knowledge on biomass and bioenergy production, biosorption and wastewater treatment.

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