Cellulose, hemicellulose and lignin slow steam pyrolysis: Thermal decomposition of biomass components mixtures

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ABSTRACT

Biomass thermochemical decomposition products have been extensively studied as renewable substitutes of fossil fuel. The approach proposed in this work considers vegetal waste as a source of both energy and matter through the production of a vapor phase fuel, highly diluted in steam, suitable to be burned in non-conventional combustion systems and a char with soil amending and fertilizing properties.

To demonstrate the feasibility of such a process an experimental set-up has been designed with the aim to investigate the effect of pressure, heating rate and final temperature in proper variation ranges ($P = 1–5 \times 10^5$ Pa, $HR = 5–40$ K/min, $T = 473–973$ K) on the yields and on the chemical and physical properties of gaseous and solid products. In this paper the effect of temperature at constant pressure ($P = 5 \times 10^5$ Pa) and heating rate ($HR = 5$ K/min) has been investigated in order to explore all the stages of the thermochemical degradation from torrefaction to mild gasification passing through devolatilization. For real biomasses a basic study on characterization of biomass components is needed.

Knowledge of dependences on feedstock nature and process conditions is crucial for the comprehension of phenomena occurring during steam pyrolysis of real complex biomasses and for the optimization of the process operating variables. This study characterizes steam pyrolysis up to 873 K (at pressure $P = 5 \times 10^5$ Pa and heating rate $HR = 5$ K/min) both of three single biomasses constituents (cellulose, hemicellulose and lignin) and of three binary mixtures in order to evaluate possible interactions between the biomass components. The results obtained highlight the importance of the interactions between components, mainly cellulose and lignin, on the yield and characteristics of solid and gaseous products. In particular, strong components interactions have been detected on the specific surface area of the solid product.

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1. Introduction

Nowadays, management of organic waste deriving from agro-food industry is an important issue of international interest for both economic and environmental reasons. A correct management of waste disposal produced by the companies is desirable in order to reduce the burden of this activity on companies’ economic balance and to increase the eco-sustainability of manufacturing processes. A considerable part of agro-food industries wastes is made up of vegetal residues that represent a suitable feedstock for energy and matter recovery technologies. In this framework the production residue can be considered no more as a waste, but as a byproduct characterized by a definite market value. In the framework of a distributed energy generation strategy in which the biomass, representing a residue/waste of processing plants, is processed in proximity of the production sites, waste can represent a resource for the companies in themselves.

Among the possible vegetal biomasses treatment processes, pyrolysis is one of the most suitable as it takes advantage both of a great flexibility and a relatively easy control of products yields and characteristics, thus allowing a tailoring of both process outcome and economic and environmental aspects.

Extensive information is available on pyrolysis processes suitable to allow the exploitation of biomass for energy purposes [1–3]. On the other hand, alternative approaches for material pyrolysis processing aimed at matter recovery and reuse have been suggested [4]. Among those approaches, relevant to the aims of the present paper, there are those aimed at the production of activated carbon from biomasses [5]. Pyrolysis experiments are generally carried out in an inert environment (nitrogen or helium) while an oxygenated gas (steam or CO₂) can be used as pyrolyzing or gasifying agent in dependence on the established thermal conditions. Previous studies dealing with the production of char based activated carbon show the positive effect of steam rather than N₂ and...
214


CO₂ on the liquid quality and physical properties of char [6]. In a flow of steam, the yields of water soluble liquid products increase at the expense of gaseous and solid products given the ability of steam to perform a more efficient penetration of solid matter enhancing desorption, distillation and removal of volatiles and char porosity. On the contrary during pyrolysis in a flow of nitrogen, higher char yields are obtained with lower porosity due to the deposition of carbonaceous material inside char pores [6]. Moreover, steam represents the natural diluent species in MILD combustion processes [7]. In fact, they require fuel mixtures highly diluted beyond flammability limits and pre-heated up to inlet temperatures higher than mixture self-ignition value. This condition is generally achieved by means of an internal or external recirculation of exhausted gases resulting in a fresh reactant flow highly diluted in steam and CO₂. Such peculiar operative conditions make the oxidation process very flexible regarding the utilization of non-conventional fuels, including low calorific value fuels or diluted fuels. In fact the oxidation process evolves under no-deflagrative conditions so that the heat produced by fuel oxidation reactions is not fundamental to sustain the process itself.

Furthermore the dilution of fuels in steam would be a logical strategy to reach MILD operative conditions in industrial facilities following the HODF (Hot Oxidant Diluted Fuel) approach. In addition, steam can improve the oxidation process reducing kinetic characteristic times because it can undergo thermal or chemical decomposition reactions that lead to the generation of OH radicals [8].

These considerations have induced to select steam as pyrolyzing agent. As matter of facts, the basic idea behind the research work that produced the results reported in the present paper, is the verification of the feasibility of a steam assisted pyrolysis of biomass for energy and matter recovery. The products of this process being a vapor phase fuel, suitable to be used in non conventional combustion systems (e.g. MILD combustion [8]), and a solid carbon rich residue, known as biochar, with soil amending and fertilizing properties, capable to lock carbon in the soil [9]. Numerous studies have been carried out in inert atmosphere in order to determine the yields of both the char and the condensable and non-condensable pyrolysis products (hereafter indicated as char, gases and liquids, respectively). Extensive information is available on products distribution, among the three abovementioned categories, from several agricultural biomasses [10–18]. However, a detailed chemical characterization is provided only for the gaseous products. In some cases [19–21] char properties have been investigated for activated carbon production. On the contrary, information on the chemical composition of the pyrolysis products liquid (condensable) fraction is not provided or limited only to the identification of the chief functional groups by means of Fourier transform infrared (FT-IR) techniques [22].

In the literature, analysis of pyrolysis processes of various feedstocks has been reported in a wide variety of reactor configurations and experimental conditions. Hence, the consequent variations in the actual conversion conditions, which cannot be easily quantified, make difficult the comparison between the products examined. Moreover, the chemical and structural complexity of biomasses makes it difficult to identify how the products properties are affected by specific operating parameters or feedstock characteristics. To address these issues, a basic study of the mechanism involved in pyrolysis of single biomass components is still required. Knowledge of above mentioned dependences on feedstock nature and process conditions are crucial for the comprehension of phenomena occurring during steam pyrolysis of real complex biomasses and for the optimization of the process operating variables in order to obtain both solid and vapor phase with the desired characteristics.

This paper contributes to the build up of such knowledge by processing three compounds modeling real main biomass components (hemicellulose, cellulose and lignin) and three binary mixtures of them, in weight percentage resembling a typical composition of a vegetal residue. The selection of the feedstock is worth of a detailed discussion. Hemicellulose is a complex, branched and heterogeneous polymeric network, based on pentoses such as xylose and arabinose, hexoses such as glucose, mannose and galactose, and sugar acids. Cellulose is a long chain polysaccharide formed by β-glucose units, linked by β-1,4 glycosidic bonds. Finally, lignin is a racemic, heteropolymer consisting of three hydroxyphenylmethyl alcohol monomers differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols. Except for cellulose, hemicellulose and lignin are present in different forms in real biomasses. For example, hemicellulose can exist in form of xylans, xyloglucans, mannans and mixed linkage β-glucans while the content of p-coumaryl, coniferyl and sinapyl alcohol in lignin is dependent on the source feedstock. Moreover, hemicellulose and lignin present in the raw biomass can be modified on dependence of the extraction method from the biomass matrix [23,24]. In this work cellulose fibers, xylan from beechwood and lignin alkali (Sigma Aldrich) have been chosen as model compounds given the robustness of the knowledge of their behavior in a wide variety of pyrolysis conditions [25–28]. The thermal behavior in presence of steam of the single components and of three binary mixtures of them has been investigated with the aim to evidence and quantify possible interactions between the three components during the process. Future developments of this study will be aimed to the comparison of model mixtures of biomass components and real biomasses.

2. Experimental set-up

2.1. Reactor configuration and operating procedures

The experimental system has been designed taking into account the need to carry out experimental tests under effective thermal control of the processed sample and, at the same time, the possibility to process sample amount high enough to allow the collection of solid and liquid products for off line analysis. In the following a brief description of the experimental apparatus is given, while details have been presented in a previous work [29].

Operating ranges of temperature, heating rate and pressure have been defined elsewhere [29] on the basis of their effect on both products yields and composition and morphology of residual char in order to select the optimal conditions to obtain both a solid and a vapor phase (gas and liquid) with the desired characteristics.

The test reactor, sketched in Fig. 1, consists of a prismatic chamber (width = 0.04 m, height = 0.052 m and length = 0.024 m) in which 6 g of biomass are loaded. The amount of biomass sample has been chosen taking into account the need to obtain solid and liquid products for off-line analysis. In order to limit heat transfer resistance related to a packed bed configuration the sample holder is made up of 5 sample trays allocated uniformly along the rectangular cross-section of the inner reaction chamber where biomass is loaded in a thin layer (approximately 1 mm thick). To limit external heat loss from the jacketed reactor chamber, the steam flows in the jacket, and baffles uniformly distribute the air. Then, the steam flow is reversed so that it enters the reaction environment through a ceramic flow straightener.

A schematic diagram of the complete experimental set-up is depicted in Fig. 2. The steam feeding system consists of a steam generator and a super heater, which was regulated by a computer-controlled PID. A valve-controlled steam generator produced steam that was heated to the programmed temperature in the super
heater, and then, the steam entered the reactor jacket. To carry out the process under controlled thermal conditions, the heat flux to the super heater is used as the adjustable variable of the PID, and the temperature of the steam at the entrance of the flow straightener was chosen as the controlling variable. At the exit of the test chamber, an automated sonic-throttled valve was used to regulate the mass flow rate and ensure the proper back-pressure in the chamber. The mass flow rate has been defined in order to minimize the secondary degradation of the condensable species produced from biomass primary pyrolysis and taking into account the optimization of the water content required for the subsequent combustion stage. It is maintained at 0.25 g/s during the tests corresponding to an average residence time of 1.5–3 s for the gas phase in the reactor, depending on the reactor temperature. In addition to the steam flow rate, temperature and pressure are also monitored using N-type thermocouples and pressure transducers along the steam supply line and at the inlet and exit of the test chamber.

The effluent gas produced in the reaction unit passes through a condensation device consisting of a jacketed coil where condensable volatiles cool and condense. At the exit of the condenser, a catch pot submerged in a thermostatic bath at 273 K collects the condensed volatiles for off-line chemical characterization. Driven by a stream of N₂ at a constant flow rate (0.01391/s), not condensed gases flow in a silica gel trap in order to reduce their moisture content before being sampled.

2.2. Materials and methods

In this study beechwood xylan, commercial cellulose fibers and lignin alkali (X4252, C6663, 370,959 from Sigma Aldrich) have been used as feedstock. Three mixtures of two components have been prepared resembling the typical composition of a switch grass [30]. For the sake of simplicity in the following sections it will be referred to the mixtures cellulose/xylan (56:44, %wt), cellulose/lignin (60:40, %wt) and xylan/lignin (54:46, %wt) respectively as Mix C-Xr, Mix C-Lr and Mix X-Lr.

In order to evaluate the effectiveness of thermal control of biomass sample during steam pyrolysis, gas release during steam pyrolysis experiments has been related to their characteristic decomposition temperatures obtained inert atmosphere (N₂) under kinetic regime control. To this aim, thermogravimetric analyses (TGA) of xylan, cellulose and lignin samples have been performed on a Perkin-Elmer Pyris 1 TGA thermogravimetric analyzer by heating 1.5 mg of samples at atmospheric pressure in inert environment (N₂, 20 ml/min) from 303 K up to 873 K at a heating rate of 5 K/min.
Char yield has been determined as the weight loss of the original feedstock. The gas yield has been obtained by online monitoring of gas composition and carrier (N₂) flow rate, while condensable species yield has been evaluated as the amount needed to complete the mass balance with respect to the feedstock sample. A direct evaluation of condensable species yield is not provided, as it should require the evaporation of the process water in which the pyrolysis liquid is dissolved. This operation should determine the loss of some volatile compounds present in the pyrolysis liquid that, on the basis of literature data on the composition of fast pyrolysis oils [31], account for 4.5–7.9% wt of the pyrolysis liquid.

Two replicates of three experimental runs (cellulose, xylan and lignin at T = 703 K) have been performed showing a difference in the yields of solid, gaseous and liquid products lower than 0.3, 0.6 and 0.9% wt. These results guarantee the reliability of the experimental apparatus used in this study.

Chemical analysis of gas phase has been performed using a gas chromatograph equipped with a thermal conductivity detector (TCD) (Agilent 3000 Quad) attached directly to the sampling point. It is comprised of two independent channels, each of them equipped with a specific capillary column and a TCD detector to allow the simultaneous detection of all the species of interest. Column Plot U has been selected to detect CO₂, C₂H₄ and C₂H₆ using helium as carrier gas, while column Molsieve 5Å equipped with pre-column Plot U has been used to separate H₂, N₂, O₂, CH₄ and CO using argon as carrier gas.

The liquid phase has been collected in two separate fractions for off-line analyses:

- nonpolar fractions (NPF), condensed on the walls of the heat exchanger, has been collected by flushing with 0.150 dm³ of dichloromethane (HPLC grade) and
- polar fractions (PF), highly diluted in condensed water, has been collected in the catch pot at the exit of the condenser.

Polar fraction of pyrolysis liquid has been dried at T = 40°C, diluted in acetone (0.1% wt) and injected in a GC/MS (HP6890/HP5975) for qualitative analysis. The gas chromatograph is equipped with a DB-1701 capillary column (60 m × 0.25 mm i.d., 0.25-mm film thickness). Helium has been used as carrier gas with a constant flow of 1.0 ml/min. The oven temperature has been programmed from 313 (6 min) to 373 K at a heating rate of 3 K/min and held for 1 min, than it was raised to 523 K at a heating rate of 10 K/min and held at 523 K for 8 min. A sample volume of 1 ml has been injected. The MS has been operated in electron ionization mode, and a m/z range from 30 to 400 Da/e has been scanned.

The H/C and O/C atomic ratio of liquid phase has been measured by a Perkin-Elmer 2400 CHNSO elemental analyzer. Oxygen content has been evaluated from mass balance closure neglecting the presence of inorganics in the raw component.

Finally, char properties has been investigated. SEM analysis has been performed to analyze char structure and surface area (BET surface) has been evaluated by generating seven-point isotherm at 77 K for N₂ adsorption (Autosorb-1, Quantachrome) using 30 mg of char sample. Before the analysis, char sample has been degassed placing it in a glass cell and heating it at 473 K under vacuum conditions.

3. Results and discussion

The experimental tests have been conducted at a constant heating rate (HRₚ = 5 K/min) and pressure (P = 5 × 10⁵ Pa). The single biomass components have been processed up to two final temperatures, Tₑ = 703, 873 K, while the binary mixtures have been pyrolyzed up to a final temperature Tₑ = 873 K. Products yields, gas and liquid composition and char physical properties have been evaluated in order to better understand thermal behavior of single biomass components and to study possible interactions between cellulose, xylan and lignin during thermal degradation.

3.1. Steam pyrolysis of biomass components

As known from previous studies on biomass pyrolysis and steam gasification [32] characteristic temperatures of biomass thermal degradation are not affected by the presence of steam instead of inert gas, at least up to 873 K. Moreover, literature data [33] obtained in a sealed vessel at elevated pressure (3–15 MPa) only shows a mild influence of pressure on characteristic decomposition temperature of cellulose during pyrolysis. Consequently a comparison between the characteristic temperatures of biomass components thermal degradation in kinetic regime and in the reactor used in this study could allow the evaluation of the effectiveness of thermal control of the process. To this aim in this study, characteristic temperatures obtained from weight loss curves in TG tests carried out at atmospheric pressure in N₂ and 5 K/min have been compared with characteristic temperatures derived following the thermal evolution (expressed as compound releasing rate measured at STP conditions) of the main gaseous species (CO, CO₂, H₂, CH₄, C₂H₄ and C₂H₆) of cellulose, xylan and lignin steam pyrolysis. In Fig. 3 mass loss rate of xylan, cellulose and lignin is presented while in Fig. 4 releasing rate of gaseous species evolving from steam pyrolysis of biomass components is given.

The analysis of differential thermogravimetric (DTG) curves shows that xylan and lignin are less stable than cellulose and starts their decomposition, respectively, at 500 K and 470 K, while cellulose degradation begins at about 600 K. Xylan and cellulose degradation is qualitatively similar as it happens in a narrow range of temperature, though mass loss rate of cellulose appears sharper than the one observed in the case of xylan. On the contrary, lignin pyrolysis is spread over a wider temperature range. As it can be deduced from TGA experiments xylan primary degradation consists of two overlapped steps represented by two peaks in the DTG curves. The first peak presents a maximum at 520 K and is representative of the cleavage of the glycosidic bonds between xylan units and the decomposition of side chain structures; the second peak can be ascribed to the opening of xylan unit [34] that happens at higher temperature as it can be seen from the maximum set at 580 K. Decarbonylation reactions, in the first reaction
step, are responsible of CO release [34]; on the contrary, the second peak is linked to CO2 release mainly due to the cleavage of acetyl groups linked to the xylan unit [28]. The separation between the two reaction steps observed in TG experiments disappears in the steam pyrolysis tests as it can be deduced from Fig. 4 where it is evident the complete overlapping of CO and CO2 releasing curves; on the other hand temperature range of xylan primary pyrolysis (500–600 K) corresponds to the one observed in TGA experiments. At temperature higher than 600 K the release of CH4, C2 and H2 is due mainly to the instability of intermediate condensable species produced during primary degradation and reaches a maximum at about 770 K. At T > 830 K a rapid increase in CO2 and H2 releasing rate is observed and is probably due to the onset of char gasification reactions.

TGA experiments show that cellulose primary pyrolysis occurs at temperature higher than xylan and in a narrower temperature range (600–680 K). As known from the literature, decarboxylation and decarboxylation reactions produce mainly CO and CO2 [28]. As it is evident from CO and CO2 releasing rate, reported in Fig. 4, primary degradation occurs in the same temperature range observed in TG experiments, reaches a maximum at T = 650 K and decreases rapidly at higher temperatures. The release of CO, CH4 and C2 at T > 700 K gives evidence of the onset of secondary degradation reactions whose activity reaches a maximum at T = 760–790 K. The release of H2 is negligible in the examined temperature range.

According to the literature data [28-35] TG experiments show that lignin pyrolysis covers a wide temperature range (400–750 K), though mass loss rate is lower than the one observed for xylan and cellulose.

At T < 500 K mass loss could be due to the cracking of hydroxyl groups in lateral chains of lignin structure. At higher temperature CO2 and CO are released from the cleavage of C–C bonds. Unlike to what happens for xylan and cellulose, in the case of lignin, light hydrocarbons (mainly CH4) evolve from primary pyrolysis of lignin between 620 and 730 K. The release of these species at higher temperature can be ascribed to secondary degradation of primary unstable volatile species.

In Table 1 the yields of char, liquid and gaseous products are shown.

For all the three biomass components a reduction of char yield at increasing temperature is observed. In the examined range of temperature lignin shows the highest char yield, while cellulose is characterized by the lowest one even though it appears significantly higher if compared with the literature data [32,35] probably due to the effect of pressure. In fact, as suggested by previous studies that evaluated the effect of pressure on coal pyrolysis [36], the vapor pressure of tar precursors increases with pressure, resulting in an enhancement of cross-linking reactions that give rise to char and gas formation at low temperatures with respect to the vaporization of such precursors. Moreover, the porous structure of cellulose may determine an increase of the residence time of the vapors during pyrolysis of the solid substrate promoting the secondary reactions that lead to the formation of char and gas. Finally char forming reactions are reported to be autocatalyzed by steam [33].

At low temperature (Tt = 703 K) steam pyrolysis of xylan and cellulose produces mainly condensable species whose yield is, respectively, 53.3 and 70.4%wt, while liquid yield observed for lignin is significantly lower (40.4%wt). At higher temperature liquid yields remain quite constant probably due to the onset of secondary degradation reactions of volatiles produced at lower temperatures.

This is confirmed by observing gas yields and compositions. At low temperature gas phase for all the three components is mainly made up of CO2 and CO except for lignin that show CH4 yield comparable with CO yield even at low temperature. As previously observed in the phenomenological analysis of steam pyrolysis of biomass components, CO2 is the main product of primary degradation of all the three components, though, in the case of xylan, decarboxylation reactions are responsible of a significant release of

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Table 1

<table>
<thead>
<tr>
<th>Yields of products and gaseous species and HHV of gas phase evolving from steam pyrolysis of biomass components at two temperatures.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<tr>
<td></td>
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<tr>
<td>Char (%wt)</td>
</tr>
<tr>
<td>Liquid (%wt)</td>
</tr>
<tr>
<td>Gas (%wt)</td>
</tr>
<tr>
<td>CO (%wt)</td>
</tr>
<tr>
<td>CO2 (%wt)</td>
</tr>
<tr>
<td>H2 (%wt)</td>
</tr>
<tr>
<td>CH4 (%wt)</td>
</tr>
<tr>
<td>C2H6 (%wt)</td>
</tr>
<tr>
<td>C3H8 (%wt)</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
</tr>
</tbody>
</table>
Table 2

Compounds identified in the polar fraction of steam pyrolysis liquids of biomass components. HHV of non polar and polar fraction of liquid collected from the process at \( T_f = 873 \) K.

<table>
<thead>
<tr>
<th>Component</th>
<th>Xylan</th>
<th>Cellulose</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Butanone</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2-Dimethoxybutane</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>2-Pentanone,4-hydroxy-4-methyl</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>2/5H-furanone</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Furan</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4:3:6-Dianhydro-β,D-glucopyranose</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Idroquinone</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>5-Hydroxymethyl,2-furaldehyde</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Syringol</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2 Benzendiol,4-methyl</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Vanillin</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetovanillone</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzenzetic acid, 4-hydroxy,3-methoxy</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>1,6-Anhydro-β-D-glucofuranose</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>HHV PF at 873 K, MJ/kg</td>
<td>17.5</td>
<td>17.4</td>
<td>23.7</td>
</tr>
<tr>
<td>HHV NPF at 873 K, MJ/kg</td>
<td>24.5</td>
<td>16.4</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Table 3

BET surface of char produced from steam pyrolysis of biomass components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Xylan</th>
<th>Cellulose</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface (m²/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_f = 703 )</td>
<td>1.2</td>
<td>8</td>
<td>0.4</td>
</tr>
<tr>
<td>( T_f = 873 )</td>
<td>15</td>
<td>428</td>
<td>0</td>
</tr>
</tbody>
</table>

CO. Moreover, in the case of lignin, depolymerization and decomposition of the original aromatic matrix determines the release of CH₄ even at low temperature. The presence of CH₄ is responsible of the highest Higher Heating Value (HHV) observed for gas deriving from lignin steam pyrolysis even at low temperature. At higher temperature gas yields deriving from biomass components increase mainly due to the release of CO₂ and CO. The increase of CO yield is higher than the one observed for CO₂ yield. This consideration together with the onset of negligible amounts of H₂ and hydrocarbons (mainly CH₄ and C₂H₆) at higher temperature confirms a weak influence of secondary degradation reactions on gas composition. For all the biomass components HHV increases with temperature and it reaches the highest value for the gas deriving from lignin thanks to its highest content of CH₄ and H₂.

In Table 2 qualitative analysis of polar fraction (PF) obtained from steam pyrolysis of the three components at \( T_f = 873 \) K is presented along with HHV of polar and non polar liquid fractions.

Condensable species identified in the water soluble fraction of liquid deriving from cellulose and xylan are carbohydrates, carboxylic acids and ketones produced from glycosidic rupture and cracking of polysaccharides. The presence of levoglucosan gives evidence of the competition between glycosidic rupture whose main product is levoglucosan, and transglycosylation mechanism leading to hydroxycetaldehyde production. Finally, aromatic compounds are the main constituents of liquid derived from lignin.

Elemental analysis of the polar and non polar fractions of pyrolysiss liquids has been used for the evaluation of their high calorific value \[37\]. The analysis shows that lignin produces a liquid phase characterized by a lower O/C ratio with respect to the liquid deriving from cellulose and xylan responsible of its higher calorific value. Moreover, except for liquid derived from cellulose, HHV of non polar fraction of liquids obtained from steam pyrolysis of biomass components is higher than the one evaluated for the polar fraction.

In Table 3 BET surface of char produced from steam pyrolysis of biomass components is shown. Cellulose is the main responsible of biomass char porosity. In fact, char produced by cellulose under steam atmosphere is characterized by a surface values comparable with those observed for cellulose that underwent chemical alkaline activation at the same final temperature \[38\] and exceed by 75% the BET of cellulose-based activated carbon produced by physical activation in nitrogen at thermal conditions \[38\]. On the contrary xylan and lignin give a char with a very compact structure. These results are supported by SEM micrographs of the three components and their char processed at \( T_f = 873 \) K, reported in Fig. 5. Xylan particles have irregular shapes characterized by a broad size distribution. Raw particles present a rough surface with cracks. Thermal treatment induces an aggregation of the raw particles and a smoothing of the surface due to the formation of a melt phase during pyrolysis. The devolatilization determines the formation of a non uniform porosity with larger pores reaching 50 μm in size. Cellulose fibers preserve their original structures during the process as a result of the slow release of volatiles at a low heating rate, although their diameter undergoes a reduction of approximately 40%. Several repeatable SEM micrographs (not shown in this paper) reveal that roughness of fiber surface does not disappear during pyrolysis and that specific surface area development is mainly due to the reduction of fiber walls, which determines the formation of a hollow core fiber. Finally, lignin undergoes drastic changes in structure during pyrolysis. Raw material presents spherical shape with a broad size distribution and a macroporous structures. High temperatures induce the melting and the coalescence of the original material that appear as a single particle with shining, compact and smooth surface.

The results obtained from the experiments of steam pyrolysis carried out on biomass components allow to infer the following considerations:

- The proposed experimental apparatus is suitable to study the behavior of the desired biomass during steam pyrolysis following the gas species release along reactor temperature.
- For all the three main biomass components an increase of final pyrolysis temperature up to 873 K determines an improvement of the products characteristics (char porosity, vapor phase yield and heating value) related to the use of both char as amending agent and vapor phase as fuel; further experiments should be carried out at higher temperatures (up to a limit of 973 K) to study the influence of steam on such characteristics.
- As for products characteristics, it is possible to conclude that cellulose contributes more than the other two components to produce a char with an high surface area (BET surface at 873 K is equal to 428 m²/g), while lignin is important for the production of a vapor phase with an higher heating value giving the highest content of CH₄ in the gas phase and of CO in the liquid phase.

3.2. Analysis biomass components interactions

In this section the possible interactions between biomass components are discussed comparing the results obtained processing binary mixtures of the three components with the data of ideal mixtures calculated by the superposition of the results obtained from xylan, cellulose and lignin steam pyrolysis (named in the following Mix C-Xₕ, C-L and X-L) in the same weight percentage of real mixtures. In Figs. 6–8 the releasing rate of the main gaseous species evolving from the process are presented as function of the process temperature. The yields of the process products and of the detected gaseous compounds are reported in Table 4.

As observed in previous literature \[39,40\] the interaction between cellulose and xylan affects weakly liquid and gas yields that are higher than the one expected, while char yield is lower.
In particular, release of CO₂ and CO during primary degradation of both the components is enhanced in agreement with the lower char yield and higher liquid yield observed. The production of CO at higher temperatures, mainly due to secondary reactions is depressed, while a weak increase in the release of the other secondary species (H₂ and hydrocarbons) is observed indicating an effect of the presence of xylan on the secondary degradation reaction path of cellulose volatiles species. HHV of gas phase does not change significantly with respect to the one expected for the ideal mixtures calculated by the superposition of the results obtained from xylan and cellulose.

In the mixture of cellulose and lignin, char and liquid yields are significantly influenced by the interaction between the two components in agreement with previous literature data [40]. In fact, char yield is lower than the one expected, while liquid yield is higher. Gas yield and composition, and consequently gas HHV, is only weakly affected by the presence of two components in the mixture, even though the analysis of Fig. 6 shows that CO release is enhanced at temperature corresponding to cellulose degradation and it is depressed at higher temperature when lignin carbonization and secondary degradation of cellulose volatile species occur. It appears that the release of others secondary species is not affected by the concurrent presence of cellulose and lignin as releasing rate of H₂ and light hydrocarbons is comparable to the one expected from the superposition of the corresponding curves obtained from cellulose and lignin. It can be postulated that lignin inhibits the thermal polymerization of levoglucosan formed from cellulose and enhances the formation of the low molecular weight products from cellulose.

![SEM micrographs of raw feedstock and char obtained at T_f=873 K from xylan (Char X), cellulose (Char C) and lignin (Char L).](image)

**Fig. 5.** SEM micrographs of raw feedstock and char obtained at T_f=873 K from xylan (Char X), cellulose (Char C) and lignin (Char L).

![Releasing rate of gas compounds, expressed as ml/s at STP conditions, resulting from steam pyrolysis of Mix C-Xr (---) and Mix C-Xc (---) as a function of temperature.](image)

**Fig. 6.** Releasing rate of gas compounds, expressed as ml/s at STP conditions, resulting from steam pyrolysis of Mix C-Xr (---) and Mix C-Xc (---) as a function of temperature.
with changes in the secondary degradations mechanisms of volatiles species and reduced yield of char.

Finally, the mixture of xylan and lignin shows a char yield comparable with the one expected. Even if xylan primary degradation is delayed (as appears from CO₂ releasing rate in Fig. 8) the extent of primary pyrolysis of xylan is not altered by the presence of lignin as it can be deduced observing the curves of CO₂ and CO (Fig. 6).

Table 4

<table>
<thead>
<tr>
<th>Products</th>
<th>Mix C-Xc</th>
<th>Mix C-Lc</th>
<th>Mix C-Lr</th>
<th>Mix C-Lc</th>
<th>Mix X-Lc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char (wt%)</td>
<td>16.7</td>
<td>19.7</td>
<td>24.52</td>
<td>30.01</td>
<td>35.67</td>
</tr>
<tr>
<td>Liquid (wt%)</td>
<td>63.2</td>
<td>61.9</td>
<td>63.57</td>
<td>57.13</td>
<td>38.18</td>
</tr>
<tr>
<td>Gas (wt%)</td>
<td>20.1</td>
<td>18.5</td>
<td>11.91</td>
<td>12.87</td>
<td>26.15</td>
</tr>
<tr>
<td>CO (wt%)</td>
<td>3.44</td>
<td>4.22</td>
<td>4.07</td>
<td>3.73</td>
<td>1.98</td>
</tr>
<tr>
<td>CO₂ (wt%)</td>
<td>15.02</td>
<td>13.18</td>
<td>6.24</td>
<td>7.57</td>
<td>21.63</td>
</tr>
<tr>
<td>H₂ (wt%)</td>
<td>0.29</td>
<td>0.18</td>
<td>0.16</td>
<td>0.18</td>
<td>0.51</td>
</tr>
<tr>
<td>CH₄ (wt%)</td>
<td>0.84</td>
<td>0.64</td>
<td>1.22</td>
<td>1.20</td>
<td>1.76</td>
</tr>
<tr>
<td>C₂H₄ (wt%)</td>
<td>0.12</td>
<td>0.09</td>
<td>0.08</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>C₂H₆ (wt%)</td>
<td>0.36</td>
<td>0.21</td>
<td>0.14</td>
<td>0.15</td>
<td>0.21</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>7.34</td>
<td>6.65</td>
<td>12.0</td>
<td>11.41</td>
<td>7.80</td>
</tr>
</tbody>
</table>

releasing rate at low temperature. Liquid yield is lower and gas yield is higher mainly due to the enhanced release of CO₂ in the final stage of the process (at T > 800 K). The increment of CO₂ and H₂ at T > 800 K may be probably due to a local increment of temperature induced by the heterogeneous gasification reactions of xylan char. Secondary degradation reactions are weakly affected by the interaction between the two components that favors the release of CH₄ with respect to heavier hydrocarbons. The higher content of CO₂ in gas phase with respect to the one expected determines a significant reduction of HHV of gas phase.

Analysis of char residues, whose specific surface area is given in Table 5, shows a strong interaction between the solid residues of the biomass components resulting in a BET surface significantly

Table 5

<table>
<thead>
<tr>
<th>Products</th>
<th>Mix C-Xc</th>
<th>Mix C-Xc</th>
<th>Mix C-Lc</th>
<th>Mix C-Lc</th>
<th>Mix X-Lc</th>
<th>Mix X-Lc</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface (m²/g)</td>
<td>138</td>
<td>245</td>
<td>147</td>
<td>256</td>
<td>2</td>
<td>7</td>
</tr>
</tbody>
</table>
lower than the one expected. A reduction of 43% of the expected surface area is observed in the case of Mix C-X, and Mix C-L. As it is evident from Fig. 9, representing SEM micrographs of char deriving from binary mixture of the three components, xylan forms globular structures that embed cellulose fibers. As reported in previous studies related to adsorption of xylan on cellulose fibers, cellulosic materials treated in autoclave with solutions of 4-O-methyl glucuronoxylan result covered with globular xylan assemblies of various sizes both on fibers surface and pores [42], thus preserving a considerable part of the fibers wall porosity and specific surface area. The above results obtained for Mix C-L, and Mix X-L, are confirmed by SEM results that show the formation of a plastic-like char in both mixture containing lignin as a result of the melting of this component that embeds and smooths cellulose fibers surface and xylan char surface [43].

From the results obtained processing binary mixtures of the three main biomass components it can be deduced that steam pyrolysis of a single component in biomass is always affected by the presence of other component. In particular it can be observed that:

- even though the interactions between cellulose and xylan affect weakly the products yields and gas phase compositions, significant changes in char porosity occur determining a reduction of 43% of BET surface with respect to the one calculated by the superposition of the results obtained from the single components;
- thermal degradation of cellulose is influenced by the presence of lignin that seems to favor the decomposition of levoglucosan to form lower molecular weight compounds at expense of levoglucosan polymerization; it results in an increase of liquid yield at expense of char yield; as xylan, the presence of lignin during steam pyrolysis of cellulose determine a strong (43%) reduction of char surface area;
- the interactions between xylan and lignin during steam pyrolysis determine a higher CO$_2$ release with respect to the one calculated for the ideal mixture probably due to an early onset of char gasification reactions. The higher gas yields observed correspond to a reduction of its HHV and to an increment in liquid yield. Significant changes in char surface area are observed though they are not worth to note given the compact char structure of the single components.

4. Conclusions

Results obtained in this study allow to conclude that the selection of a suitable vegetal feedstock for biofuel and biochar production has to account for the biomass chemical composition. It has been observed that:

- cellulose represents the main source of char characterized by high surface area, while lignin is responsible of the production of a vapor phase with the highest HHV;
- interactions between biomass components cannot be neglected as they are responsible of the reduction of HHV value of gas phase in the case of xylan–lignin mixture and a decrease of BET surface of char in all mixtures examined.

Further investigations will be carried out in order to evaluate the interactions among the three components and to compare the behavior of a real biomass with a ternary model mixture characterized by the same content of the three components.

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References


