

SLOW STEAM PYROLYSIS OF CELLULOSE, HEMICELLULOSE AND LIGNIN. INTERACTIONS BETWEEN COMPONENTS IN SURROGATE MIXTURES

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Abstract

Biomass thermochemical decomposition products have been extensively studied as renewable substitutes of conventional 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 for real biomasses a basic study on characterization of biomass components is needed. 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 main biomass components. The results obtained highlight the importance of the interactions between components, mainly cellulose and lignin, on the yield and characteristics of both solid and gaseous products.

Introduction

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.

The basic idea behind this research work is the verification of the feasibility of a steam assisted pyrolysis of biomass aimed to the production of a vapor phase fuel, suitable to be used in non conventional combustion systems (e.g. MILD combustion [1]), and a solid carbon rich residue, known as biochar, with soil amending and fertilizing properties [2].

Analysis of pyrolysis processes of various feedstocks have been reported in a wide variety of reactor configurations and experimental conditions [3-5] making difficult

the comparison between the products examined. A basic study of the mechanism involved in pyrolysis of single biomass components is still required 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 comparing the thermal behavior of single biomass model components (xylan from beechwood, cellulose and lignin alkali) and of three binary mixtures of them allowing to evidence and quantify possible interactions between the three components during the process.

Experimental set-up

Reactor configuration and operating procedures

The test reactor, described in details in [6], consists of a prismatic chamber where 5 sample trays are allocated uniformly along the rectangular cross-section of a jacketed reactor chamber. The steam flows in the jacket, then, its flow is reversed so that it enters the reaction environment and invests tangentially the biomass sample (sample mass=6 g) placed on the sample trays. Steam mass flow rate corresponds to an average residence time of 1.5-3 s for the gas phase in the reactor, depending on the reactor temperature. Before being sampled, the effluent gas passes through a condensation device where condensed volatiles are collected for off-line chemical characterization. The experimental tests have been conducted at a constant heating rate ($HR_{sp}=5$ K/min) and pressure ($P=5\times 10^5$ Pa). The single biomass components have been processed up to two final temperatures, $T_f=703$, 873 K, while the binary mixtures have been pyrolyzed up to $T_f=873$ K.

Materials and methods

In this study beechwood xylan, cellulose fibers and lignin alkali (X4252, C6663, 370959 from Sigma Aldrich) have been used as feedstock. Three mixtures of two components have been prepared resembling the typical composition of a switch grass. 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 C-X_r, C-L_r and X-L_r. 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. Chemical analysis of gas phase has been performed using a two channel gas chromatograph equipped with two thermal conductivity detector (TCD) (Agilent 3000 Quad). The liquid phase has been collected in two separate fractions, a nonpolar fractions (NPF) condensed on the walls of the heat exchanger and a polar fractions (PF), highly diluted in condensed water. The H/C and O/C atomic ratio of liquid phase has been measured by a Perkin–Elmer 2400 CHNSO elemental analyzer. Finally, SEM analysis has been performed to analyze char structure and surface area (BET surface) has been evaluated (Autosorb-1, Quantachrome).

Results and discussion

Steam pyrolysis of biomass components

The results obtained from steam pyrolysis of xylan show that 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 CH_4 , C_2 and H_2 is due mainly to the instability of intermediate condensable species produced during primary degradation. At $T > 830$ K a rapid increase in CO_2 and H_2 releasing rate is observed and is probably due to the onset of char gasification reactions.

From CO and CO_2 releasing rate, reported in fig.1, it is evident that primary degradation of cellulose, consisting in decarbonilation and decarboxylation reactions, occurs in a narrow temperature range (600-680 K) in agreement with literature TG data [7]. The release of CO , CH_4 and C_2 at $T > 700$ K gives evidence of the onset of secondary degradation reactions. The release of H_2 is negligible in the examined temperature range.

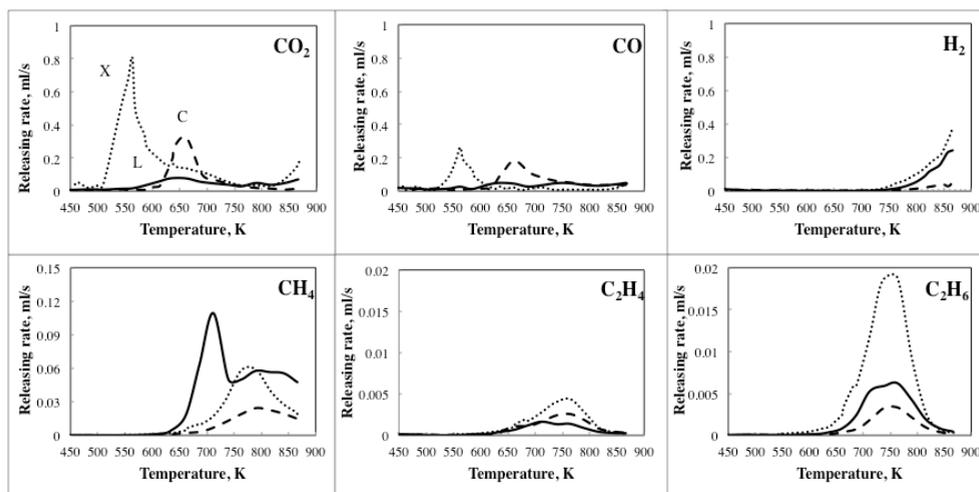


Figure 1. Releasing rate of gas compounds resulting from steam pyrolysis of xylan (.....), cellulose (---) and lignin (—) as a function of temperature.

According to literature TG experiments [7] 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 CO_2 and CO are released from the cleavage of C-C bonds. Light hydrocarbons (mainly CH_4) 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 and characteristics of char, liquid and gaseous products are shown. For all the three biomasses 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 literature data [7] probably due to the effect of pressure [8] and of autocatalytic effect of steam on charring reactions [9]. At low temperature ($T_f=703$ K) steam pyrolysis of xylan and cellulose produces mainly condensables species, while liquid yield observed for lignin is significantly lower.

	<i>Xylan</i>		<i>Cellulose</i>		<i>Lignin</i>	
	$T_f=703$	$T_f=873$	$T_f=703$	$T_f=873$	$T_f=703$	$T_f=873$
Char (% wt)	29.7	22.4	21.0	17.5	55.9	48.5
Liquid (% wt)	53.3	53.2	70.4	68.7	40.4	40.0
Gas (% wt)	16.9	24.4	8.6	13.8	3.7	11.5
CO (%wt)	2.20	3.25	2.59	4.98	0.38	1.87
CO ₂ (% wt)	14.65	19.67	6.00	8.08	3.04	6.82
H ₂ (% wt)	0.00	0.30	0.00	0.08	0.00	0.33
CH ₄ (% wt)	0.04	0.74	0.02	0.56	0.20	2.15
C ₂ H ₄ (% wt)	0.02	0.09	0.02	0.09	0.01	0.06
C ₂ H ₆ (% wt)	0.04	0.36	0.01	0.10	0.02	0.23
HHV gas (MJ/kg)	1.64	5.70	3.33	7.38	4.54	17.34
HHV PF (MJ/kg)	n.a.	17.5	n.a.	17.4	n.a.	23.7
HHV NPF (MJ/kg)	n.a.	24.5	n.a.	16.4	n.a.	30.0
BET surface char (m ² /g)	n.a.	15	n.a.	428	n.a.	0

Table 1. Yields and characteristics of products from steam pyrolysis of biomass components at two temperatures.

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. These results are consistent with the phenomenological analysis of steam pyrolysis of biomass components previously carried out. 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 not 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.

The analysis polar and non polar fractions of pyrolysis liquids 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 (table 1). 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 1 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 value that exceed by 75% the BET of cellulose-based activated carbon produced by physical activation in nitrogen at comparable thermal conditions [10]. On the contrary xylan and lignin give a char with a very compact structure.

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 C-X_c, C-L_c and X-L_c) in the same weight percentage of real mixtures. The yields of the process products and of the detected gaseous compounds are reported in table 2. As observed in previous literature [11, 12] 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 [12]. 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. 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 [12] 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. Liquid yield is lower and gas yield is higher mainly due to the enhanced release of CO₂ (whose releasing rate as function of temperature is not reported here for the lack of the room) in the final stage of the process (at T>800K).

The increment of CO₂ and H₂ at T>800K 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.

	<i>C-X_r</i>	<i>C-X_c</i>	<i>C-L_r</i>	<i>C-L_c</i>	<i>X-L_r</i>	<i>X-L_c</i>
Char (% wt)	16.7	19.7	24.52	30.01	35.67	36.46
Liquid (% wt)	63.2	61.9	63.57	57.13	38.18	46.10
Gas (% wt)	20.1	18.5	11.91	12.87	26.15	17.46
CO (% wt)	3.44	4.22	4.07	3.73	1.98	2.51
CO ₂ (% wt)	15.02	13.18	6.24	7.57	21.63	12.76
H ₂ (% wt)	0.29	0.18	0.16	0.18	0.51	0.31
CH ₄ (% wt)	0.84	0.64	1.22	1.20	1.76	1.49
C ₂ H ₄ (% wt)	0.12	0.09	0.08	0.08	0.06	0.08
C ₂ H ₆ (% wt)	0.36	0.21	0.14	0.15	0.21	0.29
HHV (MJ/kg)	7.34	6.65	12.0	11.41	7.80	11.12
BET surface char (m ² /g)	138	245	147	256	2	7

Table 2. Yields and properties of products from steam pyrolysis of real (*C-X_r*, *C-L_r* and *X-L_r*) and ideal (*C-X_c*, *C-L_c* and *X-L_c*) binary mixtures of biomass components.

Analysis of char residues, whose specific surface area is given in table 2, shows a strong interaction between the solid residues of the biomass components resulting in a BET surface significantly lower than the one expected. A reduction of 43% of the expected surface area is observed in the case of mixtures *C-X_r* and *C-L_r*. SEM micrographs of char deriving from binary mixture of the three components, not reported for the lack of the room, show that xylan forms globular structures that embed cellulose fibers, thus preserving a considerable part of the fibers wall porosity and specific surface area, while lignin form a plastic-like char in both mixture containing lignin as a result of the melting of this component that embeds and smooths cellulose and xylan char surface.

Conclusions

Results obtained in this study allow to conclude that the selection of a suitable vegetal feedstock for biofuel and biochar production have 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 produces the 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.

References

- [1] Cavaliere, A., de Joannon, M., “Mild Combustion” *Prog. Ener. Combust. Sci.* 30:329-366 (2004)
- [2] Lehmann, J., Gaunt, J., Rondon, M., “Bio-char sequestration in terrestrial ecosystems-A review”, *Mit. & Adapt. Strat. for Global Change.* 11:403-427 (2006)
- [3] Di Blasi, C., Signorelli, G., Di Russo, C., Rea, G., “Product distribution from pyrolysis of wood and agricultural residues”, *Ind. Eng. Chem. Res.* 38:2216-2224 (1999)
- [4] Antal, M.J., Croiset, E., Dai, X., De Almeida, C., Mok, W.S.L., Norberg, N., Richard, J.R., Majthoub, M.A., “High-yield biomass charcoal”, *Energy Fuels.* 10:652-658 (1996)
- [5] Guo, J., Lua, A.C., “Characterization of char pyrolyzed from oil palm stones for the preparation of activated carbon”, *J. Anal. Appl. Pyrolysis.* 46:113-125 (1998)
- [6] Giudicianni, P., Cavaliere, A., Ragucci, R., “S³O²PHIA (Solid Self-Reforming with Separation of Organic Part from Hetero-Inorganic Atoms) process as novel approach able to enhance eco-compatibility of thermochemical biomass degradation processes” *Proc. PTSE*, Ischia, Italy. 2010.
- [7] Yang, W., Yan, R., Chen, H., Lee, D.H., Zheng, C., “Characteristics of hemicellulose, cellulose and lignin pyrolysis”, *Fuel.* 86:1781-1788 (2007)
- [8] Wall, T.F., Liu, G.S., Wua, H.W., Roberts, D.G., Benfell, K.E., Gupta, S., Lucas, J.A., Harris, D.J., “The effects of pressure on coal reactions during pulverised coal combustion and gasification”, *Prog. Energy Combust. Sci.* 28:405-433 (2002)
- [9] Varhegyi, G., Szabo, P., “Kinetics of the thermal decomposition of cellulose in sealed vessels at elevated pressures. Effects of the presence of water on the reaction mechanism”, *J. Anal. Appl. Pyrolysis.* 26:159-174 (1993)
- [10] Khezami, L., Chetouani, A., Taouk, B., Capart, R., “Production and characterisation of activated carbon from wood components in powder: Cellulose, lignin, xylan”, *Powder Technol.* 157:48-56 (2005)
- [11] Yang, H.P., Yan, R., Chen, H.P., Zheng, C.G., Lee, D.H., Liang, D.T., “In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin”, *Energy Fuel.* 20:388-393 (2006)
- [12] Wang, S., Guo, X., Wang, K., Luo, Z., “Influence of the interaction of components on the pyrolysis behavior of biomass”, *J. Anal. Appl. Pyrolysis.* 91:183-189 (2011)