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CORNELISSEN, Tom; JANS, Maarten; YPERMAN, Jan; REGGERS, Guy;
SCHREURS, Sonja & CARLEER, Robert (2008) Flash co-pyrolysis of biomass with
polyhydroxybutyrate: Part 1. Influence on bio-oil yield, water content, heating value
and the production of chemicals. In: FUEL, 87(12). p. 2523-2532.

DOI: 10.1016/j.fuel.2008.02.024

Handle: <http://hdl.handle.net/1942/8371>

Flash co-pyrolysis of biomass with polyhydroxybutyrate

part 1. Influence on bio-oil yield, water content, heating value and the production of chemicals

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Abstract

Bio-oil obtained via flash pyrolysis shows potential to be applied as a renewable fuel. However, bio-oil often contains high amounts of water, which is a major drawback for its application. The influence of a biopolymer - polyhydroxybutyrate (PHB) on the pyrolysis of willow is investigated using a semi-continuous home-built pyrolysis reactor. The flash co-pyrolysis of willow/PHB blends (w/w ratio 7:1, 3:1, 2:1 and 1:1) clearly shows particular merits: a synergetic increase in pyrolysis yield, a synergetic reduction of the water content in bio-oil, an increase in heating value, and a production of easily separable chemicals. The occurrence of synergetic interactions is observed based on a comparison between the actual pyrolysis results of the willow/PHB blends, the theoretical pyrolysis results calculated from the reference pyrolysis experiments (pure willow and pure PHB) and their respective w/w ratio. The co-pyrolysis of 1:1 willow/PHB shows the best overall results.

Key words: Flash co-pyrolysis; Willow; Polyhydroxybutyrate; Pyrolytic water; Bio-oil.

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1. Introduction

Ever since the oil crisis in the 1970's, the European Union has become aware of the hazardous impact of its dependence on foreign energy sources, and started investing in the development of an alternative energy strategy in order to reinforce its independence [1]. During the last decade, the search for such an alternative energy strategy was accelerated even more due to the Kyoto Protocol and the ever growing threat of the depletion of fossil fuels, and Global Warming. Many renewable energy sources used in the production of heat and electricity have already been investigated; with wind, solar, water and biomass as the most interesting alternatives. A promising route for the production of alternative energy sources, without competing with the food supply, is the flash pyrolysis of biomass. Flash pyrolysis results in valuable energetic materials: e.g. char (solid), bio-oil (liquid) and gaseous materials [2-4], of which bio-oil has the most potential for a widespread application.

One of the major drawbacks of bio-oil is that it contains high amounts of pyrolytic water. Pyrolytic water is inherently produced during the (flash) pyrolysis of biomass. Nevertheless, the presence of water has both positive and negative effects on bio-oil properties [5, 6]. In literature, the maximum water content is defined as 25 - 26 wt. % [7], while a water content of 15 to 30 % and even more is often reported [6, 8]. In order to increase the applicability of bio-oil and to make its production competitive, the reduction of the water content is of fundamental importance.

The use of co-pyrolytic techniques on biomass/plastic ratios has already been investigated on 'traditional' plastics [9-12]. Biopolymers, which are a special kind of plastic, originate from renewables and/or are biologically degradable. Despite their biodegradability, however, most biopolymers still have to be considered as waste, since it would be ecologically unacceptable to dispose of them in the environment. The flash co-pyrolysis of biomass and biopolymers offers an alternative waste treatment option and may act as an upgrading step during the pyrolysis of biomass. Recently, the flash co-pyrolysis of willow and another biopolymer – PLA (polylactic acid) at 723 K has already been reported

and showed a clear synergetic effect, resulting in an enhanced bio-oil yield with a lower water content and a higher calorific value [13]. Therefore, a myriad of biopolymers, of which polyhydroxybutyrate (PHB) gave the most promising results, has been investigated with a semi-continuous home-built pyrolysis reactor in identical circumstances as for PLA. The findings of this research will be communicated in a future article.

PHB is a naturally occurring biologically degradable polymer, accumulated by many bacteria as carbon and energy reserve material [14, 15]. It can be degraded to water and carbon dioxide under environmental conditions by a variety of bacteria, and shows much potential for its application as an environmentally degradable plastic [16]. The thermal decomposition of PHB has already been studied in detail analytically with the aid of TGA, DSC, Py-MS, Py-GC/MS, and Py-GC-FTIR [17-20]. However, (flash) pyrolysis experiments on PHB combined with subsequent condensation of the condensable pyrolytic gasses produced, has, according to the knowledge of the authors, never been reported.

The goal of the present research is to reduce the amount of pyrolytic water in bio-oil by flash co-pyrolysing biomass (willow) and PHB. In this paper, the influence of the flash co-pyrolysis of willow and PHB on the bio-oil yield, its water content and heating value is discussed. Additionally, for some blends, it was found that not only bio-oil, but also a pure crystalline phase (crystals of crotonic acid) was produced, which is an important next step in the upgrading and separation of bio-oils into chemicals with added value. In a next paper (part 2), the chemical composition of the bio-oil and crystals will be evaluated in terms of the ratio applied in order to propose a general reaction mechanism.

2. Experimental

2.1. Materials

The experiments are performed on pure willow - *Salix*, pure PHB and willow/PHB blends. The willow branches (of which the leaves are not taken into account in this study) are cut and dried at room temperature before being shredded into small particles (~2 mm). A particle size of < 2 mm guarantees a fast inner-heating rate during pyrolysis and thus ensures a flash pyrolysis of the entire particle.

The experiments on willow/PHB blends with a w/w ratio of 7:1, 3:1, 2:1 and 1:1 are investigated and compared with the results obtained for 100% pure willow and 100% pure PHB (reference samples 1 and 2, respectively) to evaluate the effects on the bio-oil yield, its water content, its calorific value and the production of crystals, which are a potential source of chemicals with added value.

2.2. Explorative analysis of pure biomass and PHB

Ultimate Analysis

The CHNS- and O-content of the input materials are determined via two distinct experiments, using a FlashEA 1112 Elemental Analyser of Thermo Electron Corporation. Approximately 2 – 4 mg of sample is introduced into a container, which is injected by an autosampler. Regarding the CHNS-determinations, 5 – 10 mg vanadiumpentoxide is added to the sample as a combustion catalyst. 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT) and L-cystine are used as standards for the CHNS- and O-determinations, respectively.

Thermogravimetric analysis - TGA analysis

Around 30 mg of sample is pyrolysed under approximately 35 ml/min N₂ flow at a heating rate of 10 K/min from room temperature (RT) to 973 K using a DuPont Instruments 951 Thermogravimetric Analyzer.

Thermogravimetric/Mass spectrometric analysis - TG/MS analysis

A TGA Q5000 Thermogravimetric Analyzer of TA Instruments is connected with a Pfeiffer Vacuum ThermoStar mass spectrometer (interfaced at 508 K). Approximately 2 mg of sample is pyrolysed under a helium flow of 100 ml/min at a heating rate of 10 K/min from RT to 873 K. The mass spectrometer is set at the standard ionising voltage of 70 eV with a mass range m/z of 10 – 210 and a scan rate of 5 scans/min.

Thermogravimetric/Fourier Transform – Infrared analysis - TG/FTIR analysis

A DuPont Instruments 951 Thermogravimetric Analyzer, interfaced at 473 K with a gas cell, and coupled with a Bruker Vertex 70 FT-IR spectrometer (resolution: 4 cm⁻¹) is applied. Approximately 30 mg of sample is pyrolysed at a heating rate of 10 K/min from RT to 873 K under a constant helium flow of 100 ml/min.

2.3. Flash (co-)pyrolysis

Flash (co-)pyrolysis of approximately 100 g pure willow, pure PHB and willow/PHB blends is executed at 723 K on a semi-continuous home-built pyrolysis reactor (made out of stainless steel AISI 304) flushed with nitrogen gas, see Figure 1.

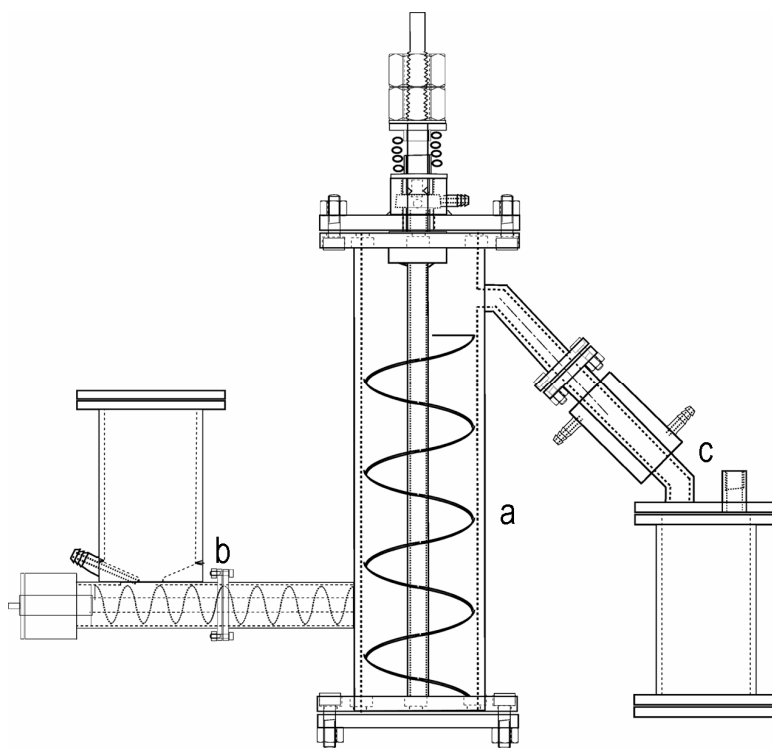


Figure 1: Pyrolysis set-up: a, reactor (at 473 K); b, injection system (at RT in K) with a biomass reservoir; and c, recuperation system (at RT in K) with an additional water cooler.

For a detailed description of the experimental flash pyrolysis set-up and procedure, refer to [13]. Within the reactor (Figure 1, part a), a heat transfer medium (white sand) is constantly moving with the aid of an Archimedical screw. From the moment the sand inside the reactor reaches the pyrolysis temperature of 723 K, the willow, PHB or willow/PHB blend is inserted into the reactor with the aid of a second Archimedical screw (Figure 1, part b). The sample undergoes flash pyrolysis and is converted into volatiles which mainly condense at room temperature (RT) into the recuperation system (Figure 1, part c) as “condensables” (= bio-oil and/or crystals)¹. A flowchart of the pyrolysis is schematically presented in Figure 2.

¹ To the knowledge of the authors, the occurrence of crystals in bio-oil has never been reported. The term “condensables”, which represents the pyrolysis yield, is used to group bio-oil and crystals. An extended pyrolysis flowchart (Figure 2) is added to represent the observations of this research.

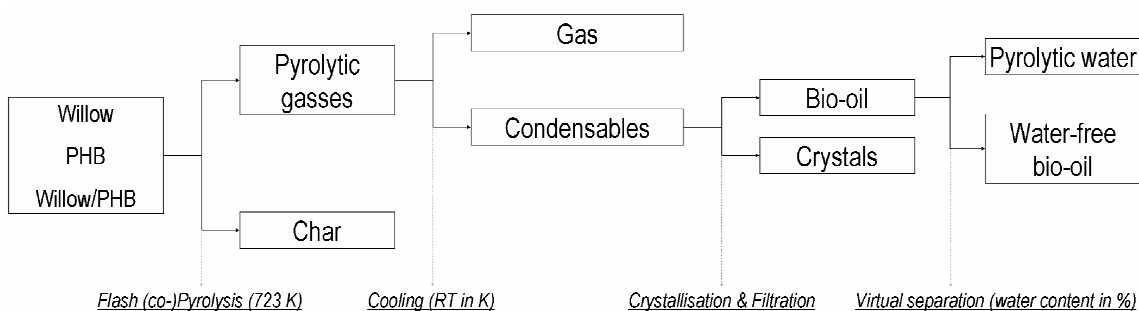


Figure 2: Extended schematic representation of the pyrolysis flowchart.

2.4. Analysis of condensables

Water content

The water content of the bio-oil and crystals is measured using the Dean-Stark method. Approximately 5 to 10 ml sample is introduced into a 250 ml flask, together with approximately 60 ml toluene. Water present in the sample forms an azeotrope with the added toluene, which evaporates at a reduced temperature. During cooling, the azeotrope separates back into water and toluene. Finally, the water is collected in a calibrated reservoir, indicating the amount of water present in the sample.

Calorimetry

The samples (± 1 g) are analysed with an IKA C5003 control calorimeter equipped with an IKA KV 600 Digital water cooler and a Sartorius CP224S analytical balance. Oxygen is connected to the system to pressurise the bomb. Measurements are executed in dynamic mode and the calibration of the system is performed with benzoic acid (palleted, C723) of IKA with a higher heating value (H.H.V.) of 26460 J/g.

Gas Chromatography/Mass Spectrometry – GC/MS

A Varian 3400 gas chromatograph is equipped with a Finnigan TSQ 700 mass selective detector and a DB-WAX capillary fused silica column (30 m x 0.25 mm x 0.25 μ m). The column temperature is programmed from 308 to 533 K at 12 K/min after an initial 1 min isothermal period and kept at the final

temperature for 6 min. Sample injection of 1 μ l of a 1 – 4 % solution in methanol is done in the split less mode while the injector temperature is 533 K.

The mass spectrometer is set at the standard ionising voltage of 70 eV with a mass range m/z of 42 – 500 and a scan rate of 2 scans/sec. The identification of the compounds is accomplished by advising a NIST database containing up to 100.000 data.

3. Results and discussion

The main characteristics of willow and PHB are given in Table 1. Both materials have a high C- and O-content and a relatively low H-content. Additionally, a low N-content and no S is found in willow and PHB. The calorific values of the input materials have been determined as well, PHB having the highest H.H.V. of 22515 J/g.

Table 1: Main characteristics (on dry basis) of willow and PHB.

<u>Characteristics</u>	<u>Willow</u>	<u>PHB</u>
<u>Proximate analysis (%)</u>		
Moisture	1.88	0.17
Volatile	75.27	97.97
Fixed C	21.14	0.80
Ash	1.71	1.06
<u>Ultimate analysis (%)</u>		
Carbon	46.91	55.96
Hydrogen	5.95	7.07
Nitrogen	0.63	0.14
Oxygen	41.69	36.40
H/C molar ratio	1.52	1.52
O/C molar ratio	0.67	0.49
<u>Calorimetric analysis (J/g)</u>		
Higher Heating Value (H.H.V.)	19088	22515

Analytical (co-)pyrolysis

The pyrolysis behaviour of willow, PHB and willow/PHB blends with a w/w ratio of 7:1, 3:1, 2:1 and 1:1 is investigated with the aid of TGA. The mass loss curves and the derivatives of willow, PHB and 1:1 willow/PHB are shown in Figure 3. From the thermograms of the pure materials, the moisture content

can be approximated: after preliminary drying, willow still contains about 1.9 % moisture, while PHB only contains a negligible amount of 0.2 %.

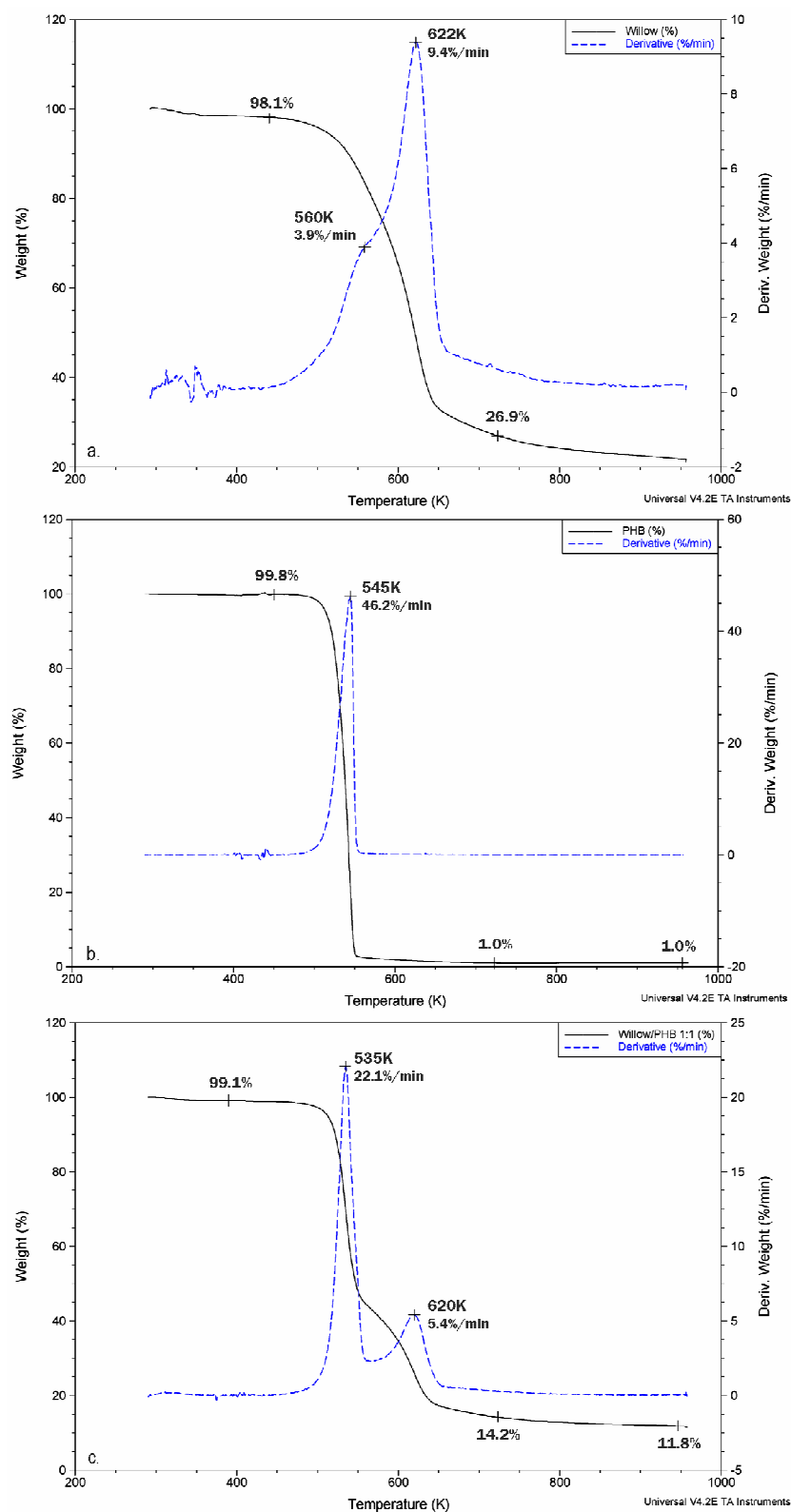


Figure 3: Weight loss and their derivatives of a, willow; b, PHB; and c, 1:1 willow/PHB; obtained by TGA.

As most woody biomass, willow mainly exists of the three basic constituents: cellulose, hemi-cellulose and lignine. Each of these constituents has a specific influence on the TG and DTG profiles of biomass [21-23]. The main decomposition of willow takes place in a temperature range from about 470 up to 670 K, with a maximum decomposition temperature of 622 K (Fig. 3a). PHB on the other hand (Fig. 3b), decomposes in a narrow temperature interval between 480 and 565 K, resulting in a sharp degradation peak with a maximum at 545 K.

The willow/PHB blends (Fig. 3c only shows the thermogram of the 1:1 willow/PHB blend) all give very comparable profiles and are almost a superposition of the individual materials: PHB (maximum decomposition at 545 K) and willow (maximum decomposition at 622 K). Even though willow and PHB are present in the same amount (1:1), the magnitude of the first peak at 545 K, which represents the decomposition of PHB, is excessively higher as compared to the magnitude of the second peak at 622 K, which represents the decomposition of willow. Figure 3 also shows that most of the decomposition reactions are finalised at a temperature of about 670 K, so justifying a flash pyrolysis temperature of 723 K during the semi-continuous pyrolysis experiments, which will be discussed later in this research paper.

From the TG/MS ion-kinetograms of m/z 18 (Figure 4), it can be concluded that pyrolytic water is formed during the intense decomposition of the input materials in the temperature range between 470 and 670 K. Depending on the sample being examined, a one- or two-peak pattern comparable to the DTG-profile (shown in Figure 3) is obtained. A difference in the amount of pyrolytic water produced out of pure willow and pure PHB (reference 1 and 2, respectively) is observed, with the pyrolysis of willow resulting in a higher amount of pyrolytic water. In the case of the 1:1 willow/PHB blend, a relatively high amount of pyrolytic water is detected: the area under the 1:1 curve is significantly higher as compared to the fractional sum of the individual areas of both references (pure willow and pure PHB) in their ion-kinetograms and can be interpreted as an indication that the co-pyrolysis of willow and PHB does not seem to result in a reduction of the amount of pyrolytic water. Additionally it can be noted that a sharp

contrast to the DTG-profile of 1:1 willow/PHB (Figure 3c) is observed: the magnitude of the first peak (at 545 K) in the ion-kinetogram of m/z 18 of 1:1 willow/PHB (Figure 4) is lower compared to the second one (at 622 K), which indicates that the influence of PHB on the production of pyrolytic water is fairly lower compared to willow in the blend.

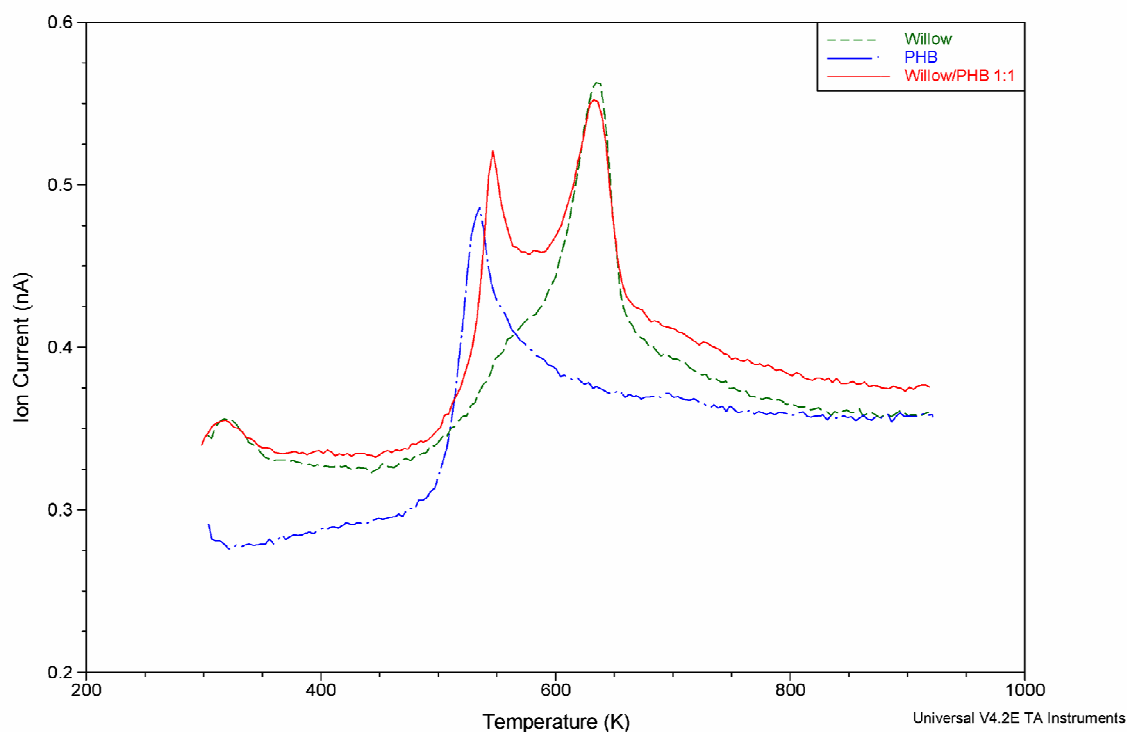


Figure 4: Evolution of mass '18' in function of temperature (= ion-kinetogram of m/z 18) for willow, PHB, and 1:1 willow/PHB; obtained by TG/MS.

Other masses e.g. m/z 16, 28, 29, 44, 45, and 46; potentially representing the release of methane, carbon monoxide, typical fragments of aldehydes and/or ketones, carbon dioxide, typical fragments of alcohols and/or ethers, and typical fragments of acids, respectively, have also been evaluated by TG/MS and showed patterns comparable to those of the ion-kinetograms of m/z 18.

Additionally, TG/MS exposes the formation of a specific component during the decomposition of PHB and the willow/PHB blends at approximately 545 K: m/z 86 increases in direct relation with the addition

of PHB (Figure 5). This trend is also observed for m/z 39, 41, 68, and 69. These m/z values are characteristic signals of crotonic or butenoic acid².

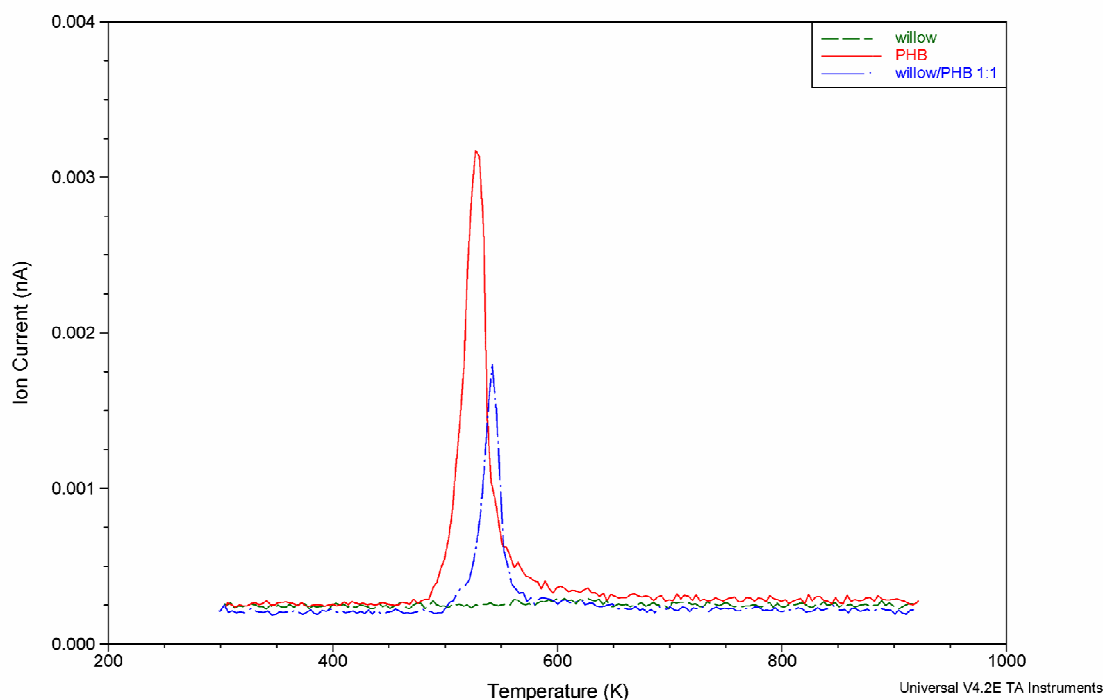


Figure 5: The ion-kinetogram of m/z 86, representing the production of crotonic acid during the (co-)pyrolysis of willow, PHB and 1:1 willow/PHB; obtained by TG/MS.

Additionally, TG/FT-IR experiments have also been performed on pure willow, pure PHB and the four willow/PHB blends. The TG/FT-IR spectra extracted at 545 K and 622 K (the main decomposition temperatures of PHB and willow, respectively) of the evolving pyrolytic gases of pure willow, pure PHB and 1:1 willow/PHB are visualised in Figure 6, where a comparison between the different FT-IR spectra at their respective temperature, e.g. 545 K (left) and 622 K (right), is made.

At 545 K, the pure PHB and 1:1 willow/PHB FT-IR spectra are nearly identical. Only a few differences are observed: 1. the willow/PHB blend shows a relatively higher response for CO_2 ($2300 - 2400 \text{ cm}^{-1}$) compared to pure PHB, and 2. the band pattern at 1150 cm^{-1} (most probably referring to C-O vibrations) slightly differs between pure PHB and 1:1 willow/PHB. The decomposition of 1:1 willow/PHB at 545 K is

² The formation of crotonic acid during the thermal degradation of pure PHB has already been observed in the evolving pyrolytic gases and is discussed in literature [17-20,24].

clearly dominated by and can almost completely be attributed to the degradation of PHB, indicating that yet no significant interactions occur during the analytic co-pyrolysis.



Figure 6: FT-IR spectra of the evolving gasses at 545 K (left) and 622 K (right); a, overlay; b, for willow; c, PHB; and d, 1:1 willow/PHB; obtained by TG/FT-IR.

At 622 K, on the other hand, the FT-IR spectrum of 1:1 willow/PHB resembles the FT-IR spectrum of willow the most. However, the spectrum features are also affected by PHB. This can possibly be explained by tailing of the PHB decomposition (consult the 3D diagrams in Figure 8 where such tailing is also observed). All three FT-IR spectra at 622 K show the presence of CO₂ (and CO), but the actual peak pattern of CO₂ slightly differs for all three inputs. The response for CO₂ is the highest in the 1:1 willow/PHB spectrum. This observation can be an indication towards another degradation mechanism occurring during the co-pyrolysis of willow and PHB, and which results in an increased production of CO₂.

Figure 7, which contains some minor artefacts due to background subtraction, shows the evolution of CO and CO₂ as a function of temperature for pure willow, pure PHB, and 1:1 willow/PHB. The evolving gasses monitored by TG/FT-IR contain much more CO₂ than CO, with PHB (Figure 7b) producing only a negligible amount of CO. The CO₂-profile of the 1:1 willow/PHB blend obtained by TG/FT-IR (shown in Figure 7c) resembles the profile for water obtained by TG/MS of that same blend (ion-kinetogram *m/z* 18, Figure 4)³.

In both the FT-IR spectra at 545 K and 622 K (Figure 6) and in the 3D-diagrams (Figure 8), obtained by plotting the absorbance (Y) of the evolving gasses as a function of the wave number (X) and temperature (Z), the most abundant peaks are represented by the carbonyl functionalities located at 1800 – 1690 cm⁻¹.

³ TG/MS and TG/FT-IR are two complementary techniques: TG/MS is specific for water and CO₂, but to a lesser extent for CO; while TG/FT-IR is specific for CO and CO₂, but to a lesser extent for water because of interferences.

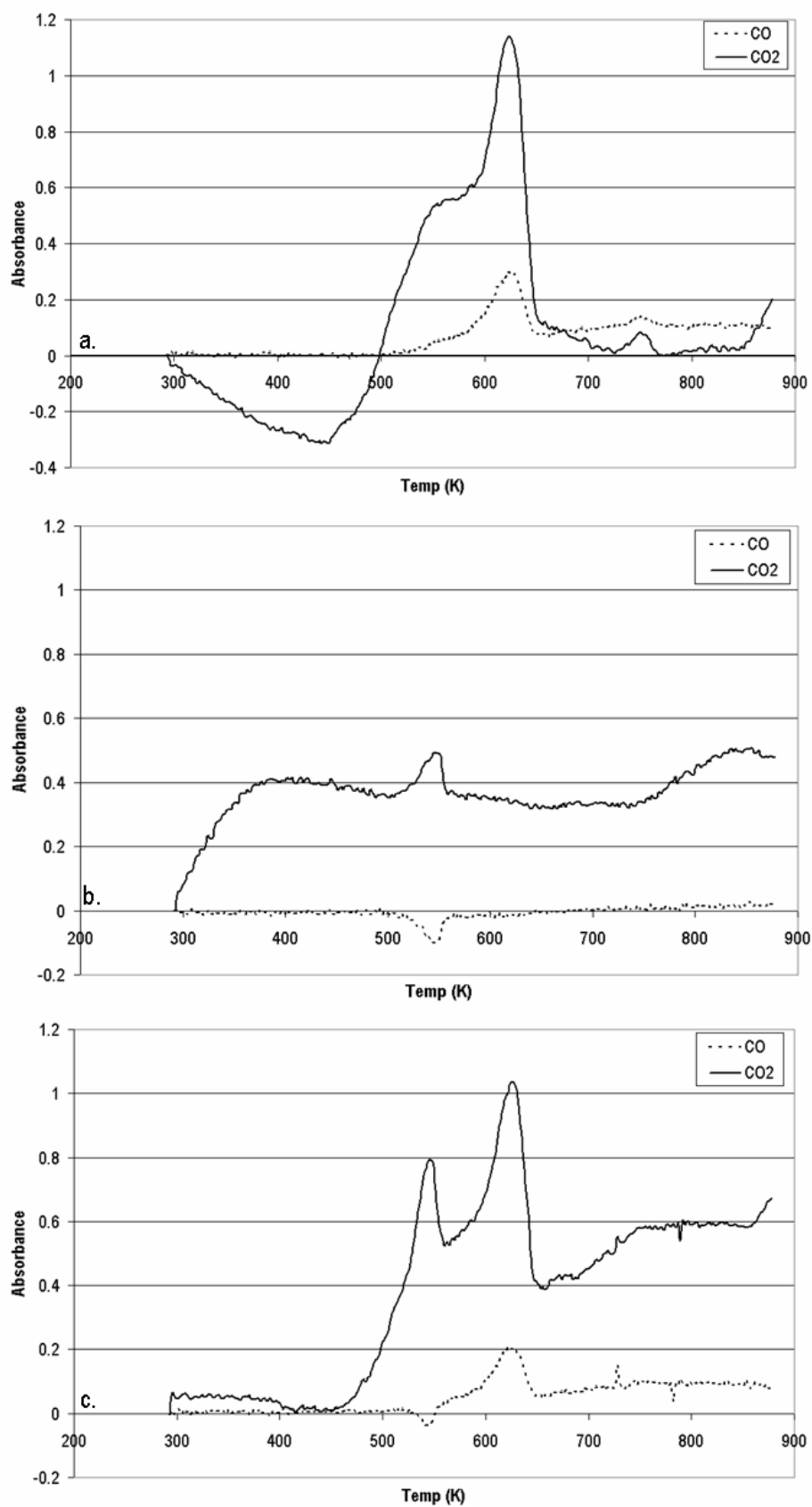


Figure 7: The evolution of CO and CO₂ during the thermal decomposition of a, willow; b, PHB; and c, 1:1 willow/PHB; obtained by TG/FT-IR.

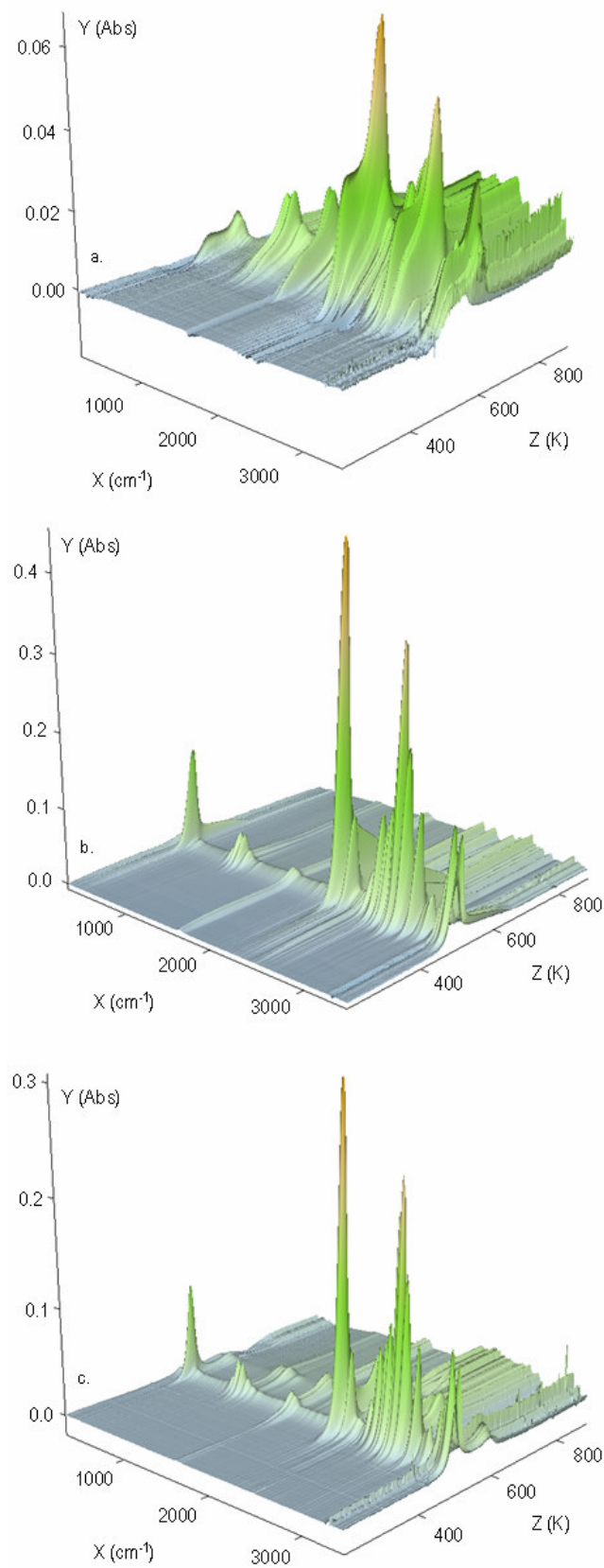


Figure 8: 3D TG/FT-IR diagrams of a, willow; b, PHB; and c, 1:1 willow/PHB with X: Wave number (cm^{-1}) ; Y: Absorbance Units (Abs); Z: Temperature (K).

Figure 9 specifically focuses on the evolution of these carbonyl functionalities, expressed as the overall intensity within a specific spectral window ($1876 - 1696 \text{ cm}^{-1}$) as a function of temperature. The most abundant peak is obtained from PHB, and the least one from willow, while the 1:1 blend is located somewhere inbetween. This trend is observed for almost all functionalities and their respective spectral windows. In general, it can be concluded that the overall evolution of functional groups as a function of temperature (obtained by TG/FT-IR), ignoring the small temperature differences due to the experimental set-up, resembles the DTG-profiles shown in Figure 3, indicating that no significant reactions seem to occur during the co-pyrolysis of willow and PHB in analytic circumstances.

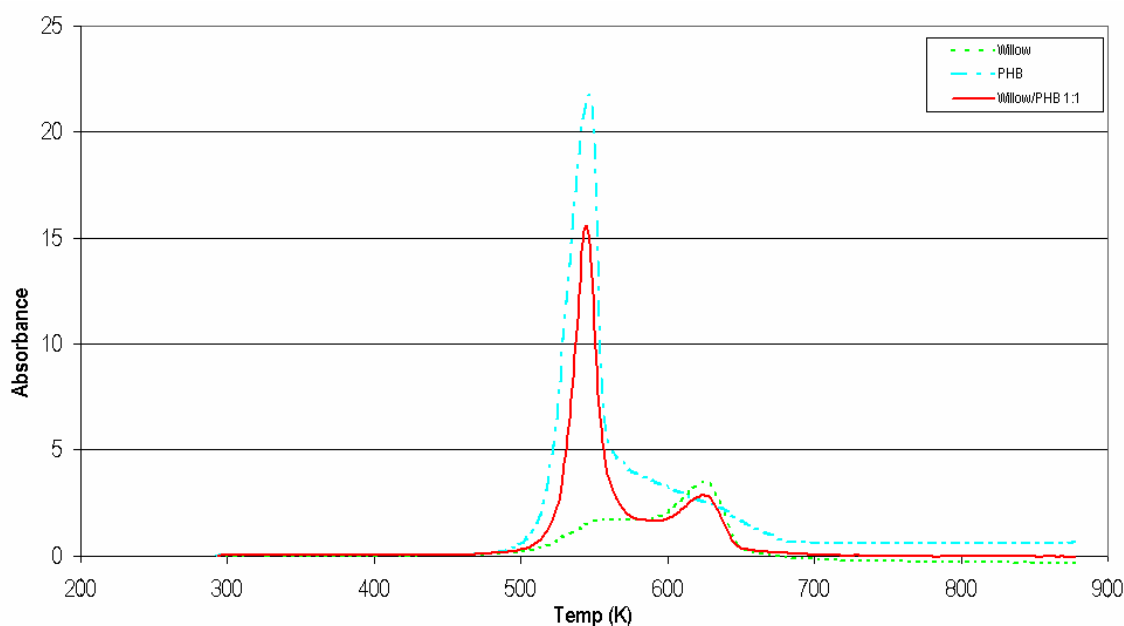


Figure 9: Traces of carbonyl functionalities ($1876 - 1696 \text{ cm}^{-1}$) for willow, PHB, and 1:1 willow/PHB; obtained by TG/FT-IR.

So far, different analytic pyrolysis techniques have been performed in order to grasp some ideas on the general pyrolysis mechanisms that might occur during the co-pyrolysis of willow and PHB. However, all experiments have been applied analytically based on slow pyrolysis, while during the semi-continuous (co-)pyrolysis experiments flash pyrolysis is induced. In the second part of this research, the results of the flash (co-)pyrolysis experiments performed on the semi-continuous home-built pyrolysis reactor (Figure 1) will be discussed.

Flash (co-)pyrolysis

The flash pyrolysis of willow and the flash co-pyrolysis of 7:1 and 3:1 willow/PHB, with the semi-continuous home-built pyrolysis reactor, result into a 'normal' brown viscous bio-oil. However, as soon as a sufficient amount of PHB is added (2:1 and 1:1 willow/PHB), crystals are formed in the bio-oil (after condensation; Figure 1, part c). After complete crystallisation, the bio-oil is filtered and the crystals are readily separated from the bio-oil (Figure 2). The pyrolysis of pure PHB, on the other hand, only results in the production of such crystals. The crystals contain no water and are characterised with the aid of GC/MS as crotonic acid or butenoic acid⁴.

Table 2 summarises the pyrolysis yields and efficiencies of the flash (co-)pyrolysis of pure willow, pure PHB and willow/PHB blends with a w/w-ratio of 7:1, 3:1; 2:1 and 1:1; performed with the semi-continuous home-built pyrolysis reactor. In Table 2, 'condensables' is used to group bio-oil and crystals, while in Table 3 a subdivision of 'condensables' into bio-oil and crystals is made. Additionally, Table 3 virtually subdivides bio-oil into water-free bio-oil and pyrolytic water based on the water content⁵. Based on these results, some conclusions can be drawn.

Table 2: Pyrolysis yields and efficiencies of the condensables, char and gas productions in function of the willow/PHB w/w ratios. The gas yield is calculated by difference.

	<u>Willow</u>	<u>7:1</u>	<u>3:1</u>	<u>2:1</u>	<u>1:1</u>	<u>PHB</u>
<u>Input (m%)</u>						
Willow	100.00	85.80	73.94	64.68	50.06	0.00
PHB	0.00	14.20	26.06	35.32	49.94	100.00
<u>Output (m%)</u>						
Condensables	49.71	53.29	57.76	59.38	64.24	68.67
Char	22.22	22.28	16.20	13.80	9.50	0.49
Gasses (by diff.)	28.07	24.43	26.04	26.82	26.26	30.84

⁴Input (m%) is calculated on dry basis.

⁴ The presence of crotonic acid in the pyrolytic gasses was already observed in this research with the aid of TG/MS (*m/z* 39, 41, 68, 69, and 86). The entire compositional analysis of the bio-oil and crystals will be discussed in more detail in a future article.

⁵ For a complete schematic representation of the pyrolysis flowchart refer to Figure 2.

Table 3: Subdivision of condensables into crystals and bio-oil; and virtually of bio-oil into water-free bio-oil and pyrolytic water based on the water content; obtained from 100 g input.

	<u>Willow</u>	<u>7:1</u>	<u>3:1</u>	<u>2:1</u>	<u>1:1</u>	<u>PHB</u>
Cristals (g)	0.00	0.00	0.00	9.20	29.70	68.67
Bio-oil (g)	49.71	53.29	57.76	50.18	34.54	0.00
Water content (m%)	36.65	26.87	21.00	20.26	15.95	0.00
Water-free Bio-oil (g)	31.49	38.97	45.63	40.01	29.03	0.00
Pyrolytic Water (g)	18.22	14.32	12.13	10.17	5.51	0.00

First, the yield in condensables (Table 2) increases in direct relation to the addition of PHB. Additionally, a synergy⁶ can be calculated, i.e. an increased yield in condensables compared to the sum of the fractional experimental values of both inputs is achieved. Table 4 summarises the synergy (in %) in the total yield in condensables obtained by the flash co-pyrolysis of the 7:1, 3:1, 2:1 and 1:1 blends. The synergy is calculated based on the yield in condensables of the two reference materials (pure willow and pure PHB) and their respective w/w ratio, and the yield in condensables obtained by the actual flash co-pyrolysis of the blends. The synergy in the total yield in condensables culminates in the 1:1 w/w-ratio, and reaches almost +9%⁷. Third, the presence of a synergy is confirmed in Table 4, where the production of pyrolytic water is lower compared to the sum of the fractional experimental values of both inputs. Again, the synergy peaks at the 1:1 w/w-ratio resulting into a decrease of almost – 40%⁸. Finally, the yield in water-free bio-oil also shows a synergy for all willow/PHB blends (Table 4). Here, however, the most pronounced synergy is obtained for the 2:1 willow/PHB blend reaching + 96.4%⁹. The maximum yield in water-free bio-oil (in absolute terms (Table 3)), on the contrary, is obtained during the co-pyrolysis of 3:1 willow/PHB, representing a yield of 45.63 m%.

⁶ The occurrence of synergetic interactions is observed based on a comparison between the actual pyrolysis results of the willow/PHB blends, the theoretical pyrolysis results calculated from the reference pyrolysis experiments (pure willow and pure PHB) and their respective w/w ratio.

⁷ The theoretical yield in condensables = $[(50.06\text{g} \times 49.71\% + 49.94\text{g} \times 68.67\%)/100] = 59.18\text{ m\%}$, while the actual yield in condensables is 64.24 m%, thus an increase of 5.06 m% or $[(5.06 \times 100)/59.18] = + 8.55\%$.

⁸ The theoretical yield in pyrolytic water = $[(50.06\text{g} \times 18.22\% + 49.94\text{g} \times 0.00\%)/100] = 9.12\text{ m\%}$, while the actual yield in pyrolytic water is 5.51 m%, thus a decrease of 3.61 m% or $[(3.61 \times 100)/9.12] = - 39.59\%$.

⁹ The theoretical yield in water-free bio-oil = $[(64.68\text{g} \times 31.49\% + 35.32\text{g} \times 0.00\%)/100] = 20.37\text{ m\%}$, while the actual yield in water-free bio-oil is 40.01 m%, thus an increase of 19.64 m% or $[(19.64 \times 100)/20.37] = + 96.44\%$.

Table 4: Synergy (in %) in the total yield in condensables, the water-free bio-oil yield and the amount of pyrolytic water; calculated by ' $[(\text{Actual}-\text{Theoretical})/\text{Theoretical}]*100\%$ '. Willow and PHB (*in bold*) are considered as the references. Small differences can be found due to rounding error.

Bio-oil	Total yield in condensables			Water-free bio-oil yield			Amount of pyrolytic water		
	Theoretical (m%)	Actual (m%)	Synergy (%)	Theoretical (m%)	Actual (m%)	Synergy (%)	Theoretical (m%)	Actual (m%)	Synergy (%)
<i>Willow</i>	49.7	49.7	-	31.5	31.5	-	18.2	18.2	-
7:1 willow/PHB	52.4	53.3	1.7	27.0	39.0	44.2	15.6	14.3	-8.4
3:1 willow/PHB	54.7	57.8	5.7	23.3	45.6	96.0	13.5	12.1	-10.0
2:1 willow/PHB	56.4	59.4	5.3	20.4	40.0	96.4	11.8	10.2	-13.7
1:1 willow/PHB	59.2	64.2	8.6	15.8	29.0	84.2	9.1	5.5	-39.6
<i>PHB</i>	68.7	68.7	-	0.0	0.0	-	0.0	0.0	-

On the other hand, it is observed that the production of crystals is lower in comparison with the sum of the fractional experiments. However, after a preliminary GC/MS analysis of the different bio-oils, it is worth mentioning that the amount of dissolved crotonic acid in bio-oil increases in accordance with the addition of PHB. Further research is conducted to quantify the total amount of crotonic acid produced during flash co-pyrolysis.

In general, it can be concluded that the flash co-pyrolysis of willow and PHB results in a bio-oil with added value, and that the preferred w/w-ratio of willow/PHB depends on the specific goal of the flash co-pyrolysis.

The averaged experimental H.H.V.'s obtained by calorimetry of the respective bio-oils are summarised in Table 5. The addition of PHB clearly shows an additional advantage, i.e. an increase in H.H.V. of the bio-oil compared with bio-oil of pure willow (16103 J/g), directly correlated with the addition of PHB. One of the main reasons for the increase in H.H.V. seems to be the decrease of the water content. Even though the crystals are economically more attractive as high value feedstock, they show to have the highest H.H.V., reaching 23104 J/g.

Table 5: H.H.V.'s of bio-oils in Joule per gram and the synergetic increase (in %) in the energy recuperation; calculated by $[(\text{Actual}-\text{Theoretical})/\text{Theoretical}]*100\%$. Willow and PHB (*in bold*) are considered as the references. The H.H.V. of the crystals equals 23104 J/g. Small differences can be found due to rounding error.

Bio-oil	H.H.V. (J/g)	Energy recuperation		
		Theoretical (m%)	Actual (m%)	Synergy (%)
<i>Willow</i>	16103	41.9	41.9	-
7:1 willow/PHB	18023	46.0	49.1	6.7
3:1 willow/PHB	19040	49.4	55.0	11.5
2:1 willow/PHB	19107	52.0	57.7	10.9
1:1 willow/PHB	20217	56.2	66.6	18.5
<i>PHB</i>	-	70.2	70.5	-

Taking into account the pyrolysis yields in condensables (Table 2 and 3), the H.H.V.'s of the input materials (Table 1), of the bio-oil (Table 5) and the crystals (H.H.V. = 23104 J/g), an energy recuperation ranging from 42% to 70% for the pyrolysis of pure willow and pure PHB, respectively, is

obtained (Table 5). The co-pyrolysis of 1:1 willow/PHB approximates the energy recuperation obtained from pure PHB (67%¹⁰ - 70%¹¹, respectively). It can be concluded that the co-pyrolysis of the different w/w-ratios results in an increased energy recuperation compared to the sum of the fractional experimental values of both references (= synergy), and thus makes the co-pyrolysis of willow and PHB an energetic and economic attractive route. Table 5 summarises the theoretical energy recuperation calculated based on the flash pyrolysis results of the two reference materials (pure willow and pure PHB) and their respective w/w ratio, the actual energy recuperation obtained by the flash co-pyrolysis of the blends, and the synergetic increase in the energy recuperation for the 7:1, 3:1, 2:1 and 1:1 blend (in %). Again, the synergy culminates for the 1:1 willow/PHB blend and reaches +18.5%¹².

Therefore, it can be stated that the flash co-pyrolysis of the 3:1 willow/PHB blend results in the highest bio-oil and water-free bio-oil yield (57.76 m% and 45.63 m%, respectively), while the 1:1 willow/PHB blend results in the highest synergetic decrease (almost -40%) in the amount of pyrolytic water, the highest synergetic increase of the yield in condensables(+9%) and the highest synergetic increase in energy recuperation (+18.5%).

Even though the explorative analysis (e.g. TGA, TG/MS and TG/FT-IR) did not result in any conclusive evidence regarding interactions between willow and PHB during (slow) co-pyrolysis, nor regarding a decrease in the amount of pyrolytic water in the evolving gasses (as was observed for the co-pyrolysis of willow and PLA in earlier research [13]), a synergetic reduction of the water content and of the amount of pyrolytic water produced during the flash co-pyrolysis of willow and PHB with the semi-continuous home-built pyrolysis reactor is achieved. Additionally, a synergetic increase in pyrolysis

¹⁰ The energy recuperation = $[(34.54\text{g} \times 20217\text{ J/g} + 29.70\text{g} \times 23104\text{ J/g}) \times 100 / (50.06\text{g} \times 19088\text{ J/g} + 49.94\text{g} \times 22515\text{ J/g})] = 66.56\%$ in condensables for the 1:1 willow/PHB flash co-pyrolysis.

¹¹ The energy recuperation = $[(68.67\text{g} \times 23104\text{ J/g}) \times 100 / (100\text{g} \times 22515\text{ J/g})] = 70.47\%$ in condensables for the flash pyrolysis of pure PHB.

¹² The theoretical energy recuperation = $[(50.06\text{g} \times 41.94\% + 49.94\text{g} \times 70.47\%) / 100] = 56.19\%$, while the actual energy recuperation is 66.56 %, thus an increase of 10.37 % or $[(10.37 \times 100) / 56.19] = +18.46\%$.

yield, water-free bio-oil yield and energy recuperation is observed. The obtained synergy points out that the (flash) co-pyrolysis of willow and PHB results in unexpected observations. Therefore, the synergy can only be explained by additional reactions (and different reaction circumstances) during flash co-pyrolysis in the semi-continuous pyrolysis reactor.

Due to the fact that biomass, and more specifically willow, decomposes in three stages, some possible general reactions can be proposed: 1. the decomposition of lignine and/or hemicellulose results in volatiles which react with PHB, followed by subsequent reactions with cellulose; 2. the decomposition of PHB results in volatiles which react with willow (cellulose, hemicellulose and/or lignin); 3. lignine and/or hemicellulose and PHB interact during the decomposition and result in altered volatiles, which in turn can additionally react with cellulose. The proposed reactions and interactions can occur: 1. during the decomposition and/or 2. between the volatiles after decomposition and/or 3. between the condensables of willow and PHB. In this research, TG/FT-IR explicitly showed that the decomposition of the blends at 545 K is almost completely attributable to the degradation of PHB, indicating that the first proposed reaction is unlikely to occur. Additional research is in progress in order to formulate an unambiguous answer to these proposals and will be communicated in part 2.

4. Conclusions

The flash co-pyrolysis of willow and PHB at 723 K results in an increased pyrolysis yield and bio-oil with a reduced water content. A synergistic effect was observed to increase along with the addition of PHB, with a maximum for the 1:1 w/w ratio. Additionally, an increased energy recuperation compared to the sum of the fractional experimental values of both materials is achieved, making the co-pyrolysis of willow and PHB an energetic and economic attractive route. Finally, the flash co-pyrolysis of willow and PHB also resulted in an uninitiated phase-separation between bio-oil and crystals (crotonic acid), which are a potential source of value-added speciality chemicals.

5. Acknowledgements

The authors like to thank M. Vanhamel for her help with the TG/FTIR analysis and Biomer for the PHB samples. This study fits into an association scholarship between Xios and University Hasselt.

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