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Co-pyrolysis of wood and plastics: Influence of plastic type and content on product yield, gas composition and quality

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ABSTRACT

In recent years, the world has witnessed a rapid rise in waste production and energy demand, which has increased interests in waste to energy processes, particularly the co-pyrolysis of wood and plastic waste. Nonetheless, for plastic waste, most research studies narrowly focus on polyolefins because of their abundance in waste streams and their high oil yields from pyrolysis. In this paper, we study the co-pyrolysis of non-polyolefins – polystyrene (PS) and polyvinyl chloride (PVC) – and poplar wood (PW), in order to investigate the synergistic effect of PS and PVC content on product yield, gas specie yield and heating value. The experiments were performed using a fixed-bed reactor, heated to 750 °C at a rate of 20 °C/min under nitrogen atmosphere. Our results show that PVC has a large positive synergy on char yield with a maximum value of 8 wt% at 30 wt% PVC content, whereas PS only showed a slightly positive synergy (2.5 wt% maximum). Concerning oil and gas production, PS provides a small synergy. However, PVC showed a significant positive synergy on oil yield with a maximum value of 11 wt% at 50 wt% PVC content, which was linked to a strong negative synergy in gas production. Regarding gas specie yields, the addition of PS led to positive synergies in the formation of H_2, CH_4, CO and CO_2, although insignificant interactions were observed for C_xH_y compounds. Furthermore, by comparing the distribution of chloride species in the products of co-pyrolysis with PVC, using experimental and theoretical methods, we discovered that the negative synergy in HCl yield observed was mainly due to the dissolution of HCl in the water fraction of the condensed oil phase, rather than the formation of chlorinated organic compounds, as suggested in previous literature works. Our study therefore consolidates the understanding of the synergistic interactions between wood, PS and PVC co-pyrolysis, under conditions that favour gas production.

1. Introduction

The rapid growth in world population over the last century combined with industrial development and urbanization has resulted in two major issues: the sharp increase in waste production and demand for energy. In Europe, the current generation rates of wood and plastic waste are 70.5 and 26.2 Mt/yr which are accompanied by low recycling rates of 31% and 17% respectively [1]. Hence, research into opportunities for converting wood and plastic waste to energy is strongly needed. Pyrolysis is a promising technique for recovering energy inherent in combustible solid waste which involves the thermal decomposition of the waste in an inert atmosphere to yield three primary products: gas (H_2, CO, CO_2, CH_4 and light hydrocarbons), liquid hydrocarbons (tars and oils) and char (carbon material).

In recent years, co-pyrolysis of woody biomass and plastic waste has gained considerable research interest mainly due to the positive contribution of plastics to the product yield and the calorific value of the oil produced [2–6]. According to Johannes et al. [7], the interactions or synergy between biomass and plastics depends on various factors including the type and contact of the fuel components, pyrolysis duration, temperature and heating rate, and catalysts. Hence, it is not surprising that conflicting reports sometimes arise in literature concerning the differences between the actual and predicted yields of the pyrolysis products, where the predicted yields are calculated as linearly proportional to the contributions of the pure components. For example, Grieco and Baldi [8] observed insignificant interactions between low density polyethylene (LDPE) and beech wood during co-pyrolysis in a capsule at heating rates of 0.1 and 1 °C/s. However, Yang et al. [9] observed a significant synegistic effect on oil yield when LDPE and cedar wood were co-pyrolyzed at 600 °C in a dropdown tube reactor at rapid heating rates.

Research works on the co-pyrolysis of biomass and plastic waste

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Table 1
Proximate analysis (as-received basis) of wood and plastic samples.

	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)	LHV (MJ/kg)
PW	8.0	2.0	85.1	4.0	17.1
PS	0.0	0.0	99.6	0.4	39.8
PVC	0.0	0.0	95.8	4.2	19.3

Table 2
Ultimate analysis (dry ash-free basis) of wood and plastic samples.

	C (%)	H (%)	O (%)	N (%)	S (%)	Cl (%)
PW	49.9	6.4	42.7	1.0	0.0	0.01
PS	92.4	7.8	0.0	0.0	0.0	0.0
PVC	38.7	4.8	0.0	0.0	0.0	56.5

have principally focused on the influence of temperature, heating rate and reaction time on product yield and quality [10–13]. Nonetheless, some authors, such as Oyedun et al. [14] have shown that the type and plastic content in the sample also play an important role. Unfortunately, the few studies on the influence of plastic content on product yield are narrowly-focused on polyolefins (polyethylene (PE) or polypropylene (PP)) because this plastic type generates high oil yields and is the most abundant in waste streams [15,8,16]. Consequently, the operating conditions chosen for these studies aim at maximising oil yields for liquid fuel production and involve low temperatures (400–500 °C), and short gas residence times (< 15 min). Furthermore, with respect to research works on the influence of plastic content in biomass on gas composition and heating value, Grieco et al. [8] and Paradela et al.[12] have observed significant interactions. However, Paradela et al. [12] conducted their experiments with a fixed plastic waste mixture of 56 wt % PE, 17 wt% PS and 27 wt% PP and Grieco et al. [8] performed theirs using only PE as the plastic type. Hence, there remains a knowledge gap in literature about the contribution of non-polyolefins such as PS and PVC on the gas composition and heating value derived from co-pyrolysis with biomass.

Thus, in this work, we will investigate the influence of PS and PVC content in wood on the co-pyrolysis product yields, gas specie yields and heating value, under conditions that favour gas production: high temperature, low heating rate and long gas residence time.

2. Experimental methods

2.1. Wood and plastic samples

The materials used for the tests were poplar wood (PW), PVC and PS, whose characterstics are displayed in Tables 1 and 2. The particle size of each pure material was less than 1 mm. Several wood/plastic mixtures for each plastic type were prepared having different plastic contents: 0-5-10-30-50-100 wt% plastic.

2.2. Pyrolysis reactor and procedure

Fig. 1 gives a schematic representation of the experimental setup. For each test, 10 g of sample was placed in a quartz crucible. The sample was heated in a furnace to 750 °C at a heating rate of 20 °C/min under nitrogen atmosphere (33 mL/min) and was maintained at this temperature for 30 min before being cooled to room temperature. These operating conditions allowed a reaction time of 66 min which is sufficient for secondary cracking of volatiles to occur in order to form more gas and secondary char. At the reactor outlet, the volatile oil was condensed in an impinger bottle filled with cotton wool and cooled to 0 °C. Thus, in this case, the term 'oil' represents a mixture of bio-tar, oil, wax and small amounts of water produced from the pyrolysis process. For experiments with PVC, the oil condenser was replaced with two impinger bottles containing aqueous solutions of KOH to trap HCl gas. Next, the total amount of the non-condensable gas produced from pyrolysis was collected in a Tedlar bag. Its composition was analyzed by a micro-gas chromatograph (Micro-GC, A3000 Agilent). The quantification of HCl concentration in the aqueous phase was conducted using X-ray fluorescence (XRF, PANanalytical).

The char yield was calculated by dividing the weight loss of the sample and crucible before and after pyrolysis by the total initial sample mass. The gas yield y_{gas}, was calculated based on the following equations:

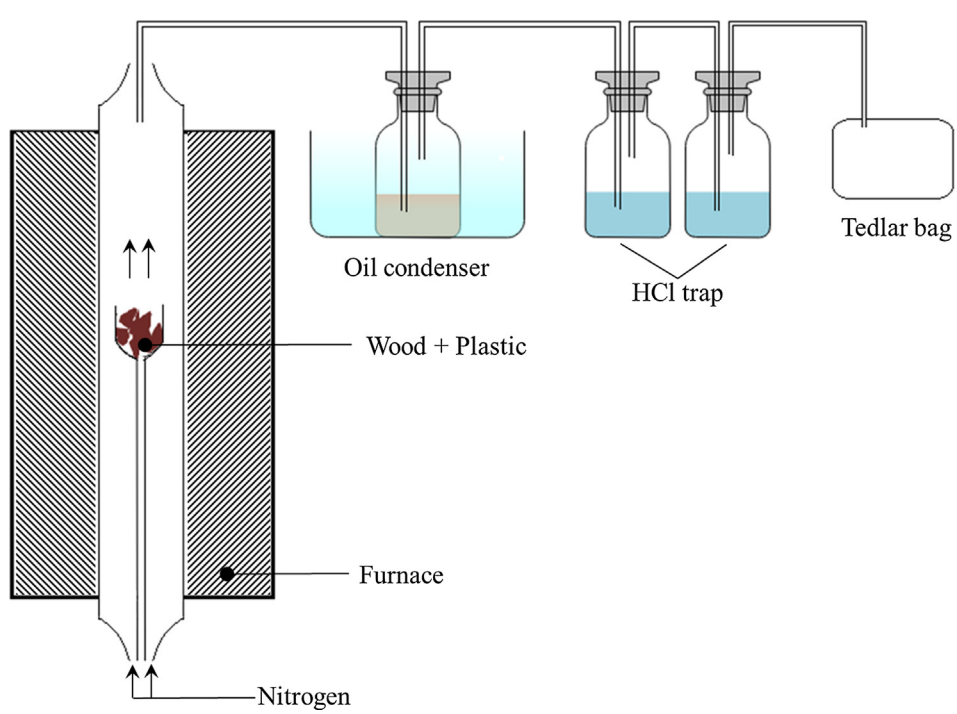
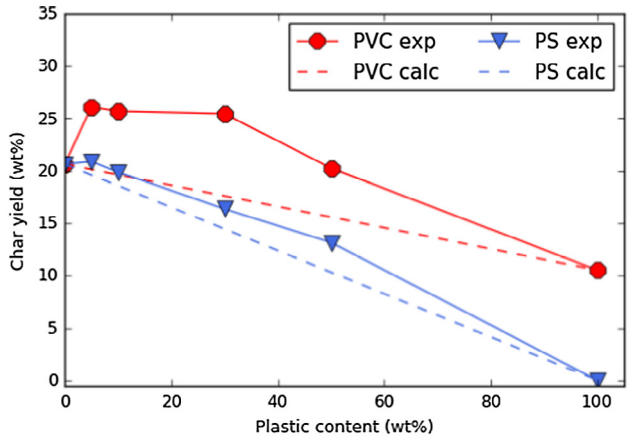
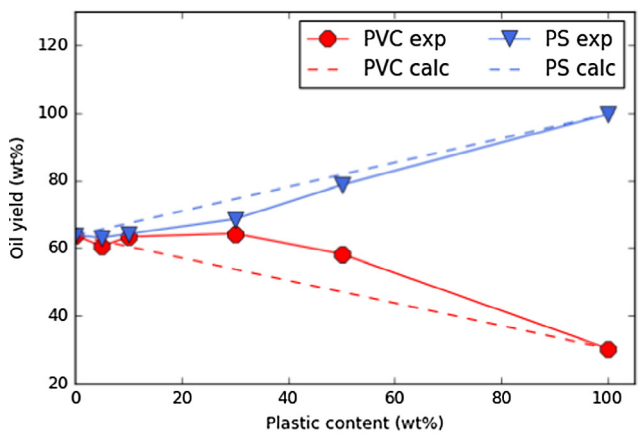


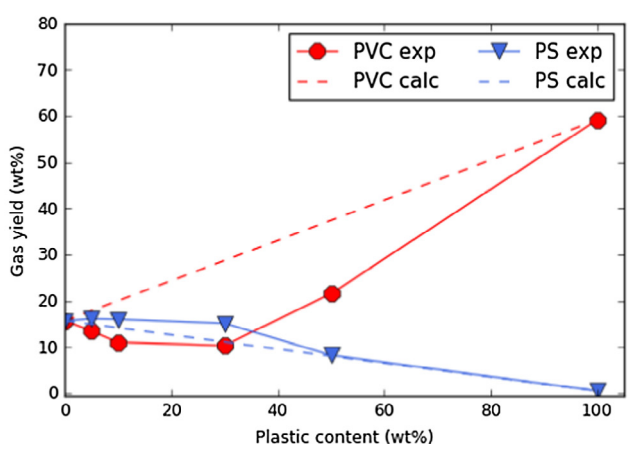
Fig. 1. Experimental setup of pyrolysis equipments.



(a) Char yield



(b) Oil yield



(c) Gas yield

Fig. 2. Influence of plastic type and content on product yield.

$$V_{gas} = \frac{Q_{N_2} t}{x_{N_2}} \tag{1}$$

$$y_{gas} = \frac{\sum_i^n (\rho_i x_i) V_{gas}}{m_s} \tag{2}$$

where V_{gas} is the total gas volume, Q_{N_2} and x_{N_2} are the volumetric flowrate and volume fraction of the nitrogen carrier gas respectively, t is the reaction time, ρ_i and x_i are the density and volume fraction of each gas specie i, measured at normal temperature and pressure, and m_s is the initial sample mass. To estimate the oil yield, the difference between the yields of char and gas was calculated.

The gas lower heating value LHV_{gas} in units of MJ/Nm^3 was estimated based on the lower heating values of each gas specie i (MJ/kg), using the following equation:

$$LHV_{gas} = \sum_i^n LHV_i \rho_i x_i \tag{3}$$

To evaluate the synergy between poplar wood and the plastic samples, the theoretical product yields were calculated according to the following formula:

$$y_{calc} = w_1 y_1 + w_2 y_2 \tag{4}$$

where y_1 and y_2 are the pyrolysis yields of pure wood and plastic; w_1 and w_2 are the mass proportions of wood and plastic in the sample respectively. Therefore, the interaction or synergy parameter Δy, is the difference between the experimental and calculated product yields from co-pyrolysis.

$$\Delta y = y_{exp} - y_{calc} \tag{5}$$

3. Results

3.1. Effect on char yield

Fig. 2 and Table 3 present the yields of char, oil and gas with respect to the different plastic contents in the samples. It can be seen in Table 3 that the char yield from pure PW pyrolysis is 20.6 wt% whereas half as much char is produced from pure PVC (10.5 wt%) and virtually no char is produced from pure PS. Williams et al. [17] have obtained similar values for char yield from the pyrolysis of these pure plastics.

Regarding the co-pyrolysis of PW and PS, a small positive synergy can be observed in Fig. 2a with a maximum difference of approximately 2.5 wt% between the experimental and theoretical char yield. This indicates that the presence of PS promotes secondary reactions of volatiles, such as condensation and repolymerisation, to form secondary char.

For co-pyrolysis with PVC, a strong positive synergy can be seen in Fig. 2a, where the maximum synergy of 8 wt% occurs at a PVC content of 30 wt%. Cepeliogullar and Putun [18] have also obtained significantly higher char yields compared with the theoretical yield for a mixture of 1:1 weight ratio of PVC and biomass (hazelnut shell, sunflower residues and E. rigida). An explanation for this phenomenon could be drawn from the work of Matsuzawa et al. [19,20] who suggest that HCl produced from PVC pyrolysis promotes the dehydration and cross-linking of cellulose in biomass, which in turn promotes the charring of cellulose.

3.2. Effect on oil and gas yields

As shown in Table 3, the oil and gas yield of pure PW is 63.7 wt% and 15.7 wt%. Pure PS generates a high oil yield of 99.5 wt%, due to its relatively high volatile and low ash content (Table 1). Thus, the oil yield from PS/PW co-pyrolysis increases with PS content, which follows a similar trend reported in literature for co-pyrolysis with other biomass types at temperatures of roughly 400 °C [3,21–23]. However, in Fig. 2b, a negative synergy can be observed for PS/PW co-pyrolysis, which has not yet been demonstrated in literature. Oyedun et al. [14] have found from thermogravimetric analysis, that lower temperature and energy are required to pyrolyze PS/biomass blends than are required for the pyrolysis of other mixtures such as HDPE/biomass. It is therefore possible, in our opinion, that the oil formed at lower temperatures in the presence of PS has more time to undergo secondary cracking reactions to produce more gaseous products, and thereby decrease the overall oil

Table 3
Product yield from the pyrolysis of PW, PVC, PS and their mixtures

	PVC			PS		
Plastic Content (wt%)	Char (wt%)	Gas (wt%)	Oil* (wt%)	Char (wt%)	Gas (wt%)	Oil* (wt%)
0 (100 wt% PW)	20.6	15.7	63.7	20.6	15.7	63.7
5	26.1	13.5	60.5	20.9	16.1	63.0
10	25.7	11.0	63.3	19.9	16.0	64.2
30	25.4	10.3	64.2	16.3	15.1	68.6
50	20.2	21.5	58.2	13.1	8.30	78.6
100	10.5	59.2	30.3	0.00	0.50	99.5

* Calculated by difference and represents a mixture of bio-tar, oil, wax and water.

yield. This suggestion is supported by the observation, in Fig. 2c, that the gas yield increases relative to the predicted yield for PS contents below 50 wt%.

Pure PVC has a relatively low oil yield (30.3 wt%) and high gas yield (59.2 wt%) compared to PW and PS. By observing Fig. 2b, the co-pyrolysis of PVC and PW has a positive synergistic effect on oil yield, with a maximum synergy of 11 wt% at 50 wt% PVC content. A corresponding strongly negative synergy in gas yield can be seen in Fig. 2c, where the maximum synergy of 18 wt% occurs at 30 wt% PVC content. Zhou et al. [24] have recently observed a significant increase in oil yield for mixtures of PVC with three biomass components – hemicellulose, cellulose and lignin – during fast co-pyrolysis at 800 °C in a fixed bed reactor. They propose that the biomass and/or bio-char can act as a catalyst to promote chain scission of PVC, resulting in the increased production of chlorinated oil compounds. This theory will be examined in Section 3.5.

3.3. Effect on gas specie yields

Table 4 displays the yield of light gases derived from the co-pyrolysis of the different plastic and wood samples, and Table 5 shows the yield of the heavier hydrocarbon gases produced, which we will conveniently refer to as C_xH_y. In Fig. 3, the variation of the various gas specie yields as a function of plastic content is presented, which reveals non-linear trends and therefore, the existence of interactions between PW and plastics.

Concerning PS, the yields of the gas species generally decrease as PS content in PW increases because oil production is favoured by this plastic (Fig. 2b). However, significant positive synergies can be observed for H_2, CH_4, CO and CO_2, and to a lesser degree for C_xH_y compounds. This implies, that secondary reactions occur between PS and the wood volatile products to promote the formation of lighter gases.

In Fig. 3, we can observe that PVC contents below 50 wt% in PW results in negative synergies for CH_4, C_xH_y, CO and CO_2 yields. This indicates that interactions between PVC and PW favours the production of oxygenated hydrocarbons in the oil and char products. Nonetheless, a positive synergy for H_2 yield can be seen, which in our opinion, may be due to enhanced condensation and cyclization reactions of polyene species produced from the dechlorination of PVC. These cyclization reactions of polyene take place via both radical and molecular mechanisms to form H_2, polycyclic aromatic hydrocarbons (PAH) and char [25]. Our proposed mechanism for enhanced H_2 production is supported by the recent works of Çepelioullar et al. [18,26] who obtained an increased amount of PAH from the co-pyrolysis of PVC and biomass mixtures.

It is interesting to observe in Fig. 3b that although HCl yield increases as a function of PVC content, a strong negative synergy can be observed, whereby HCl gas yield was found to decrease by 53.6 wt% when PVC content was decreased from 100 to 30 wt.%. This result is consistent with a recent TG-FTIR analysis by Zhou et al. [27] who report that, compared to pure PVC pyrolysis, the maximum HCl peak strongly weakens when PVC is co-pyrolysed with orange peel and tissue paper in a 1:1 weight ratio mixture. Furthermore, Kuramochi et al. [28] have reported a significant reduction in HCl emission when demolition wood is co-pyrolyzed with 1 wt% PVC film. However, the mechanism for HCl-biomass interaction is not well-defined in literature [29]. Kuramochi et al. [28] have pyrolyzed mixtures of PVC with three constituents of biomass (cellulose, hemicellulose and lignin) separately. Their results show that cellulose has an insignificant effect on HCl emission, whereas hemicellulose, and lignin to a lesser extent, reduce HCl emissions by fixing most of the Cl molecules in the char product. A contradictory result has been presented by Zhou et al. [30] who have found that cellulose can also decrease HCl emission to a similar degree as hemicellulose and lignin. To further add to the confusion, another recent work by the same author suggests that the Cl molecules are fixed in the liquid product to form chlorinated oil compounds [24]. It is therefore evident that more investigations are needed to better understand the mechanisms that govern the interactions between HCl and biomass during co-pyrolysis with PVC. This point will be further addressed in Section 3.5.

3.4. Effect on gas heating value

Table 6 and Fig. 4 present the evolution of the gas lower heating value (LHV) with plastic content. Factors that can increase the LHV of a gas include high concentrations of hydrogen and hydrocarbons. Fig. 4 shows that at conditions of normal temperature (20 °C) and atmospheric pressure, the LHV of gas derived from pure PW pyrolysis is about 19 MJ/Nm^3, while higher LHV values are observed for pure PS and PVC in the order of 23 and 26 MJ/Nm^3 respectively. However, the gas LHV is observed to not vary significantly with plastic content below 50 wt%, because the hydrogen and carbon content of these plastics preferentially distribute to the oil product of PS, and the char and HCl gas products of PVC.

3.5. Effect of PVC content on chlorine distribution

Fig. 5 presents the distribution of Cl molecules in the char, gas and condensed oil (bio-tar, oil, wax and water) products as a function of the

Table 4
Light gas yields from the pyrolysis of PW, PVC, PS and their mixtures.

	PVC					PS			
Plastic Content (wt%)	H_2 (wt%)	CH_4 (wt%)	CO (wt%)	CO_2 (wt%)	HCl (wt%)	H_2 (wt%)	CH_4 (wt%)	CO (wt%)	CO_2 (wt%)
0 (100 wt% PW)	0.16	1.54	6.10	7.17	0.10	0.16	1.54	6.10	7.17
5	0.20	1.36	4.80	6.15	0.48	0.18	1.59	6.66	6.89
10	0.19	1.12	3.85	4.97	0.56	0.18	1.59	6.52	6.95
30	0.25	1.24	3.57	3.62	1.19	0.21	1.52	6.20	6.53
50	0.26	1.31	3.73	3.66	11.90	0.15	0.87	3.46	3.34
100	0.36	2.50	0.07	0.05	54.79	0.03	0.18	0.15	0.03

Table 5
Hydrocarbon gas (C_xH_y) yields from the pyrolysis of PW, PVC, PS and their mixtures.

Plastic Content (wt%)	PVC C_2H_4 (wt%)	PVC C_2H_6 (wt%)	PVC C_3H_8 (wt%)	PS C_2H_4 (wt%)	PS C_2H_6 (wt%)	PS C_3H_8 (wt%)
0 (100 wt% PW)	0.26	0.20	0.19	0.26	0.20	0.19
5	0.19	0.12	0.13	0.38	0.18	0.22
10	0.13	0.12	0.11	0.34	0.18	0.24
30	0.18	0.17	0.13	0.34	0.15	0.15
50	0.23	0.29	0.17	0.28	0.10	0.09
100	0.69	0.45	0.24	0.09	0.01	0.00

PVC content in the sample mixture with PW. The Cl content in the char and condensed gas products were analysed using X-ray fluorescence (XRF, PANanalytical) and the Cl content in oil was calculated by difference. The corresponding yields of Cl in the pyrolysis products were then determined on the basis of the initial mass of Cl in the PVC/PW samples. It can be observed in Fig. 5 that products from pure PW pyrolysis contain insignificant amounts of Cl whereas for pure PVC, 96.9 wt % of Cl is released in the gas phase, thus leaving only 2.9 and 0.04 wt% Cl in the oil and char phase respectively. Compared to the products of pure PVC pyrolysis, the Cl yield decreases in the gas phase by 89.9 wt% when the PVC content is lowered from 100 wt% to 30 wt%, and the corresponding Cl yields in the oil and char products increase by 76.2 and 13.8 wt% respectively. Furthermore, even at a low PVC content of 5 wt%, the Cl distribution in oil is significantly higher than in the char and gas phases. Hence, it is clear that the Cl molecules from co-pyrolysis

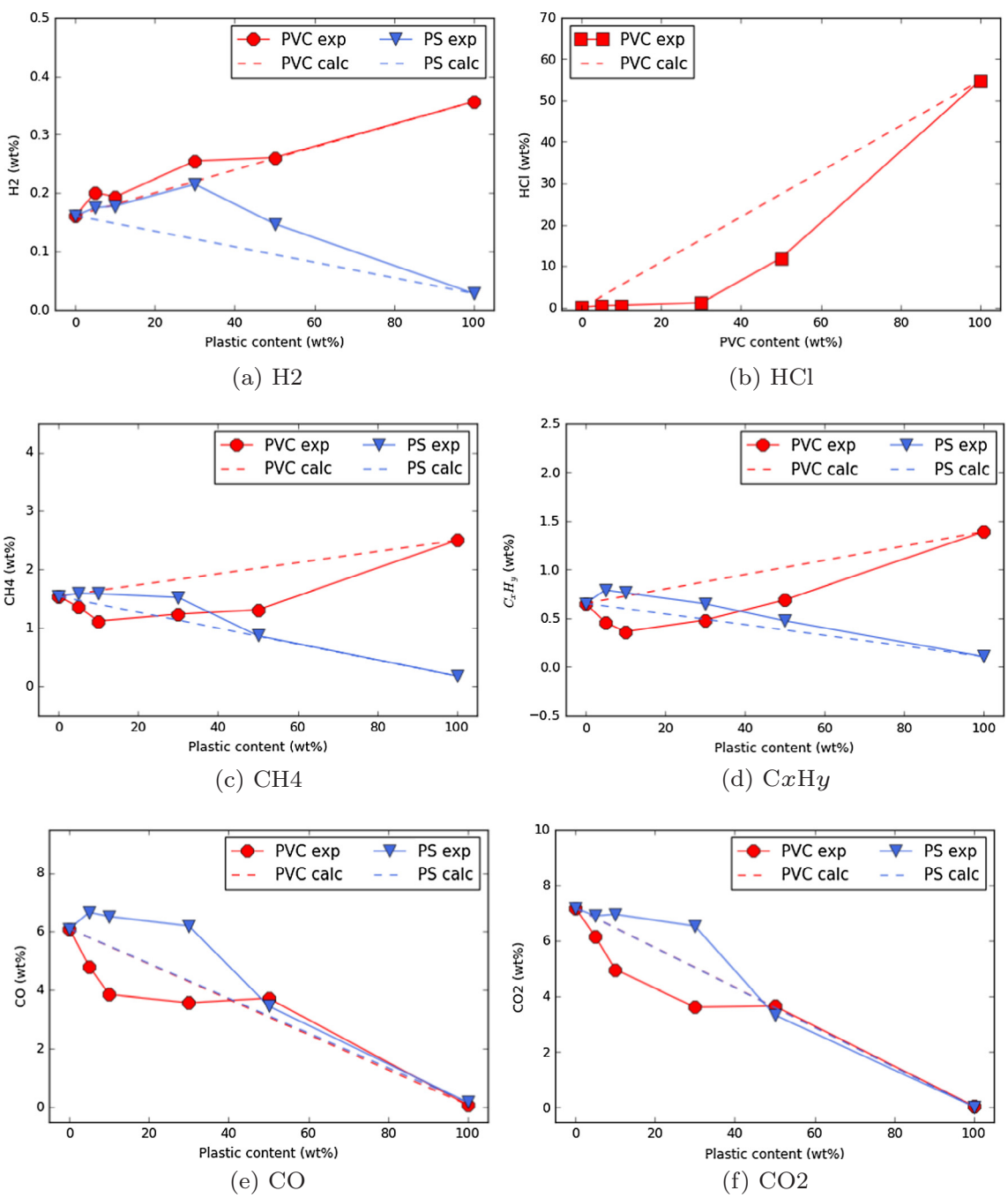


Fig. 3. Influence of plastic type and content on gas composition.

Table 6
Gas lower heating value (MJ/Nm3) from the pyrolysis of PW, PVC, PS and their mixtures.

	PVC	PS
0 (100 wt% PW)	18.9	18.9
5	18.2	19.0
10	17.9	19.0
30	18.2	18.3
50	18.5	19.0
100	25.6	22.8

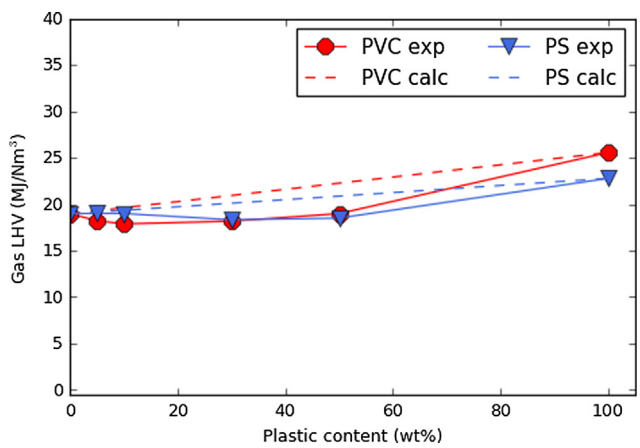


Fig. 4. Influence of plastic type and content on gas heating value.

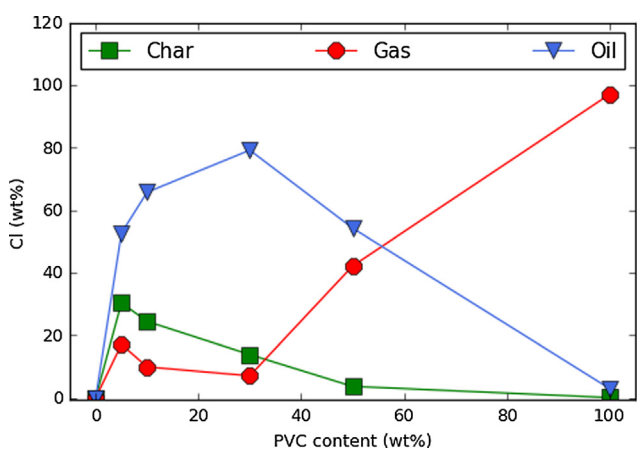


Fig. 5. Influence of PVC content on distribution of chlorine in char, gas and oil products.

of PVC/PW are preferentially trapped in the oil product. Our result therefore supports the aforementioned hypothesis presented by Zhou et al. [24] that the Cl molecules are fixed in the oil product.

A further investigation was made to predict the distribution of chloride species in the char, gas and oil products, using thermodynamic equilibrium calculations based on the Gibbs free energy minimization approach. These calculations were performed using FactSage V.6.3. and a database developed by Said et al. [31]. The chosen input data for the calculations are:

- Feedstock: 10 g of 30 wt% PVC/PW, with its composition of organic and inorganic elements displayed in Table 7.
- Reactor temperature range: 150–750 °C.
- Reactor pressure: 1 atm

Figs. 6a and b display the equilibrium mass percentages of inorganic and organic chloride species with respect to the total mass of chloride species and as a function of temperature, respectively. Fig. 6a shows that above 200 °C, 95 wt% of chloride species is released into the gas phase as HCl. In addition, Cl is mainly trapped in the inorganic solid phase as $CaCl_2$ (4 wt%). It is interesting to observe in Fig. 6b that organic chloride species are formed in trace amounts, the most abundant of which is dimethyl phosphinic chloride (C_2H_6ClOP), which forms a pinkish-white crystal at room temperature.

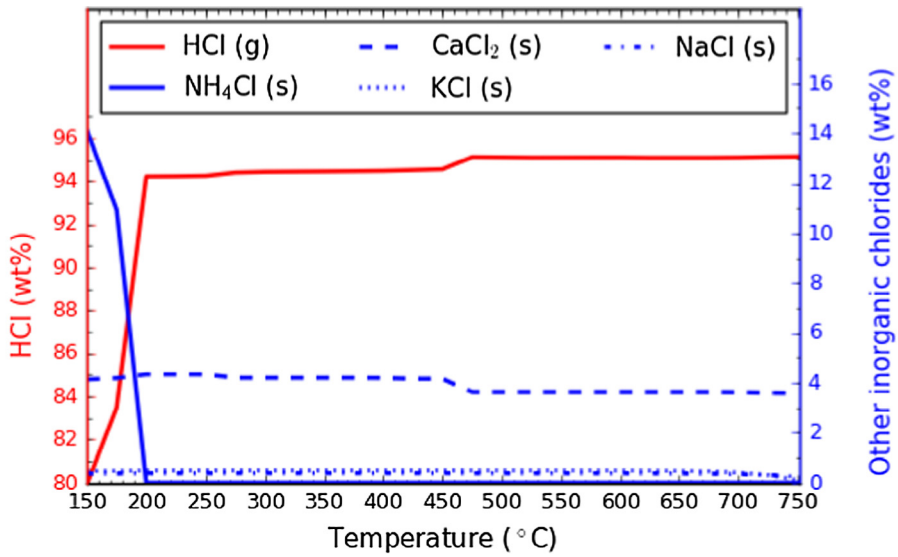
By comparing the predicted yields of chloride species from the thermodynamic equilibrium calculations, with those obtained experimentally from the pyrolysis of 30 wt% PVC/PW (Fig. 5), we can first conclude that chlorinated hydrocarbons are only in trace amounts in the condensed oil phase (a mixture of bio-tar, oil, wax and water), which contradicts the proposal by Zhou et al. [24]. Secondly, we propose that the high chlorine content observed in the oil phase is mainly due to HCl gas dissolved in the water fraction of the oil upon condensation. This statement is supported by our observation in Fig. 5 that HCl yield in the gas phase has a similar but opposite trend to the chloride species yield in the oil phase with respect to the initial PVC content in the sample. Future work should be done on the analysis of organic chlorinated compounds in the oil phase, using for example GC-MSMS technique.

Table 7
Elementary composition of 30 wt% PVC/PW.

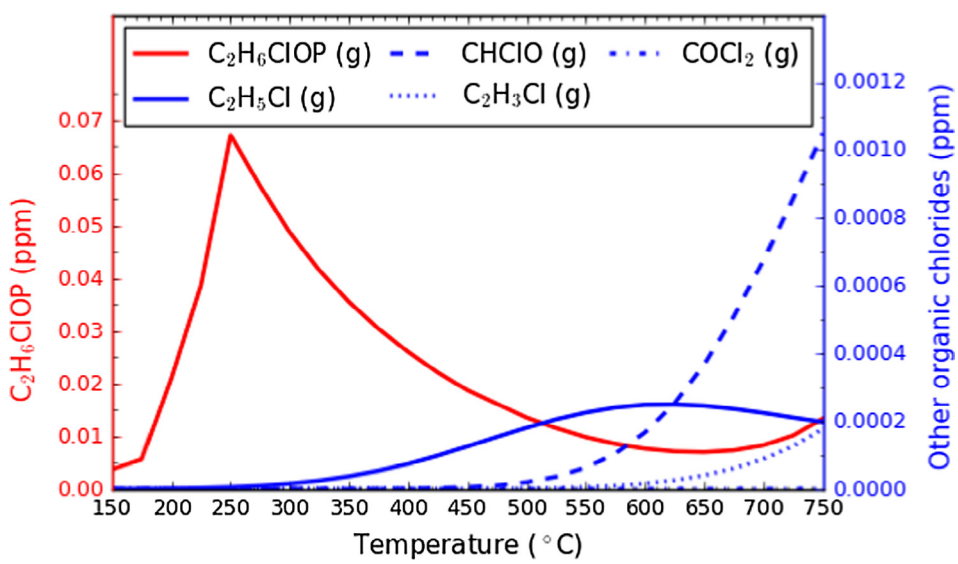
	30 wt% PVC/PW
Organic elements (wt.%)	
N	0.7
C	46.6
H	5.9
S	0.0
O	29.4
Cl	16.9
Inorganic elements (ppm)	
Al	131
As	52
B	27
Ba	20
Ca	2787
Cd	20
Co	23
Cr	24
Cu	77
Fe	56
Hg	10
K	459
Mg	269
Mn	32
Mo	28
Na	268
Ni	26
P	238
Pb	69
Sb	76
Se	91
Si	133
Sn	190
Sr	21
Ti	26
V	26
Zn	32
Zr	24

4. Conclusion

Experimental work on the co-pyrolysis of poplar wood (PW) and the plastics, PS and PVC, has been presented in this paper in which different synergistic effects of plastic type and content on product yield, gas specie yield and gas heating value were studied.



(a) Inorganic chloride species



(b) Organic chloride species

Fig. 6. Theoretical chloride species yield from the pyrolysis of 30 wt% PVC/PW between 150 °C and 750 °C, 1 atm.

Regarding char yield, PVC was found to provide a relatively large positive synergy with a maximum value of 8 wt% at 30 wt% PVC content, whereas PS only showed a slightly positive synergy (2.5 wt% maximum). The addition of PS generally increased oil yield and lowered gas yield relative to the pyrolysis of pure PW. However, for oil production, a small negative synergy was seen for PS, although the reverse effect on gas yield was observed. Interestingly, the presence of PVC had a significant positive synergy on oil yield with a maximum value of 11 wt% at 50 wt% PVC content. This was linked to a strong negative synergy in gas (mainly HCl) production, where a maximum synergy of 18 wt% was observed at 30 wt% PVC content.

With respect to the influence of plastic type and ratio on gas specie yield, the addition of PS resulted in positive synergies in the formation of H_2, CH_4, CO and CO_2, although insignificant interactions were seen for C_xH_y compounds. With regard to PVC, an increase in H_2 yield was observed accompanied by a positive synergistic effect. Furthermore, HCl gas yield was found to decrease by 53.6 wt% when PVC content was decreased from 100 to 30 wt%. A further analysis of the distribution of Cl molecules in the char, gas and oil products using thermodynamic equilibrium calculations, revealed that Cl was largely fixed in the condensed oil phase mainly as dissolved HCl gas in the water fraction, although some chlorine was also trapped in the solid residue in the form of metal chloride salts. Concerning the gas lower heating value (LHV), the addition of PS and PVC to the sample had an insignificant synergistic effect below 50 wt% plastic content.

Our work consolidates the understanding of the effect of synergy between wood, PVC and PS, on product yield, gas specie yield and gas heating value under operating conditions that favor gas production. Moreover, by comparing the results of our work with literature, we have identified the need for a better understanding of the interactions involving HCl during co-pyrolysis of biomass and PVC. Our future work will therefore focus on modelling the kinetics of interactions between poplar wood and PVC during co-pyrolysis.

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