



Pyrolysis of mixed plastic waste: Predicting the product yields

Homer C. Genuino^a, M. Pilar Ruiz^a, Hero J. Heeres^b, Sascha R.A. Kersten^{a,*}

^a Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Drienerlolaan 5, 7522 NB Enschede, the Netherlands

^b Engineering and Technology Institute Groningen, Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

ARTICLE INFO

Keywords:

Pyrolysis
Mixed plastic waste
DKR-350
Chemical recycling

ABSTRACT

The predictability of pyrolysis yields and product composition of mixed plastics has been studied. To do so, pyrolysis of virgin polymers (HDPE, LDPE, PP, PS and PET) and eight individual sorting categories from a real waste DKR-350 stream (PE rigid/film, PP rigid/film, PET, PS, multilayer flexibles, and clogged materials) was performed in a batch reactor at 500 °C at laboratory scale. The obtained oil/wax, gas, and solid yields and the composition of oil/wax of those individual feedstocks were used as input of a superposition model to predict the corresponding pyrolysis yields and oil/wax composition of mixed feeds, which were later compared with the experimentally measured product yields from the pyrolysis of those mixed streams. This linear model predicts the oil/wax yield of the mixed streams to a reasonable extent, with a maximum yield deviation (overestimation) of 8 percentage points. However, the presence of significant amounts of PET (above 33 wt%) in the mixed plastic streams negatively impacts the production of the condensable product and promotes the formation of solid products beyond the expected predicted values. Quantification of the type of carbon (aliphatic, aromatic and carbonyl) present in all the oil/wax products was done using ¹³C NMR spectroscopy. A linear model could also predict the aliphatic carbon yield in the condensable product from plastic waste streams with high accuracy (maximum yield difference of 6 percentage points). However, the aromatic carbon yield could not be predicted, probably due to the observed behavior of PET, which interacts with other polymers to promote solid product formation.

1. Introduction

Pyrolysis is being extensively investigated as a chemical recycling technology for processing plastic waste streams (Dogu et al., 2020, Kusenberget al., 2022a, Kusenberget al., 2022b, Lange, 2021, Roosen et al., 2020). Recently, we have reported the first pyrolysis study on the largest post-consumer plastic packaging waste stream in Europe, namely DKR-350, which is the mix of plastics that remains after the easily reusable plastics have been sorted out. In that study, the feedstock was characterized in detail, and the effect of pre-treatment in the form of washing on pyrolysis performance and the fate of contaminants was performed (Genuino et al., 2022).

DKR-350 is a complex mixture of different plastic categories, mainly polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC), together with multilayer flexibles (i.e., originated from different plastic-based aluminium and paper layers) and clogged materials (i.e., plastic items inside or tied up with others). In our previous study (Genuino et al.,

2022), we reported a DKR-350 stream mainly consisting of the categories PE film (16.6 wt%), PE rigid (18.5 wt%), PP film (2.7 wt%), PP rigid (11.4 wt%), PS (3.4 wt%), PET (20.1 wt%), clogged materials (12.1 wt%) and multilayer flexibles (10.4 wt%). However, the composition of DKR-350 is highly variable and among others differs per season and location, e.g., depending on sorting systems, customs, and lifestyles (Ates et al., 2013, Brouwer et al., 2018, Genuino et al., 2022, Lopez et al., 2010).

Considering the variability and complexity of this plastic waste feedstock, it is important to develop a tool to predict the pyrolysis behaviour of a mixed plastic waste stream in terms of product yields and composition, based on the mixture's composition. To do that, we have first run an experimental study on the pyrolysis of different individual virgin polymers (e.g., PE, PP, PS, PET) and mixtures of those. Secondly, experiments have been performed with real plastic waste mixed streams (DKR-350) and sorted categories of these streams. Thirdly, based on the feedstock composition and the individual components/categories pyrolysis performance, a simple linear (superposition) model, assuming

* Corresponding author.

E-mail addresses: h.c.genuino@utwente.nl (H.C. Genuino), m.p.ruizramiro@utwente.nl (M. Pilar Ruiz), h.j.heeres@rug.nl (H.J. Heeres), s.r.a.kersten@utwente.nl (S.R.A. Kersten).

<https://doi.org/10.1016/j.wasman.2022.11.040>

Received 26 September 2022; Received in revised form 25 November 2022; Accepted 29 November 2022

Available online 6 December 2022

0956-053X/© 2022 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

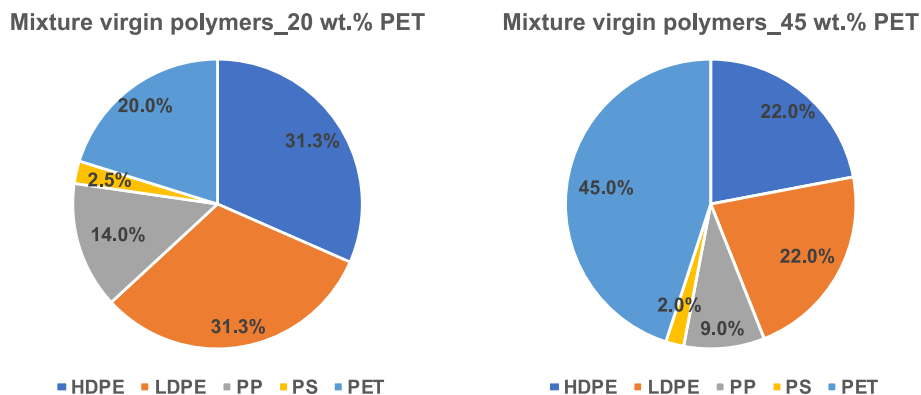


Fig. 1. Composition (wt.%) of the feedstocks used based on mixtures of virgin polymers. Left) 20 wt% PET in the mixture; Right) 45 wt% PET in the mixture.

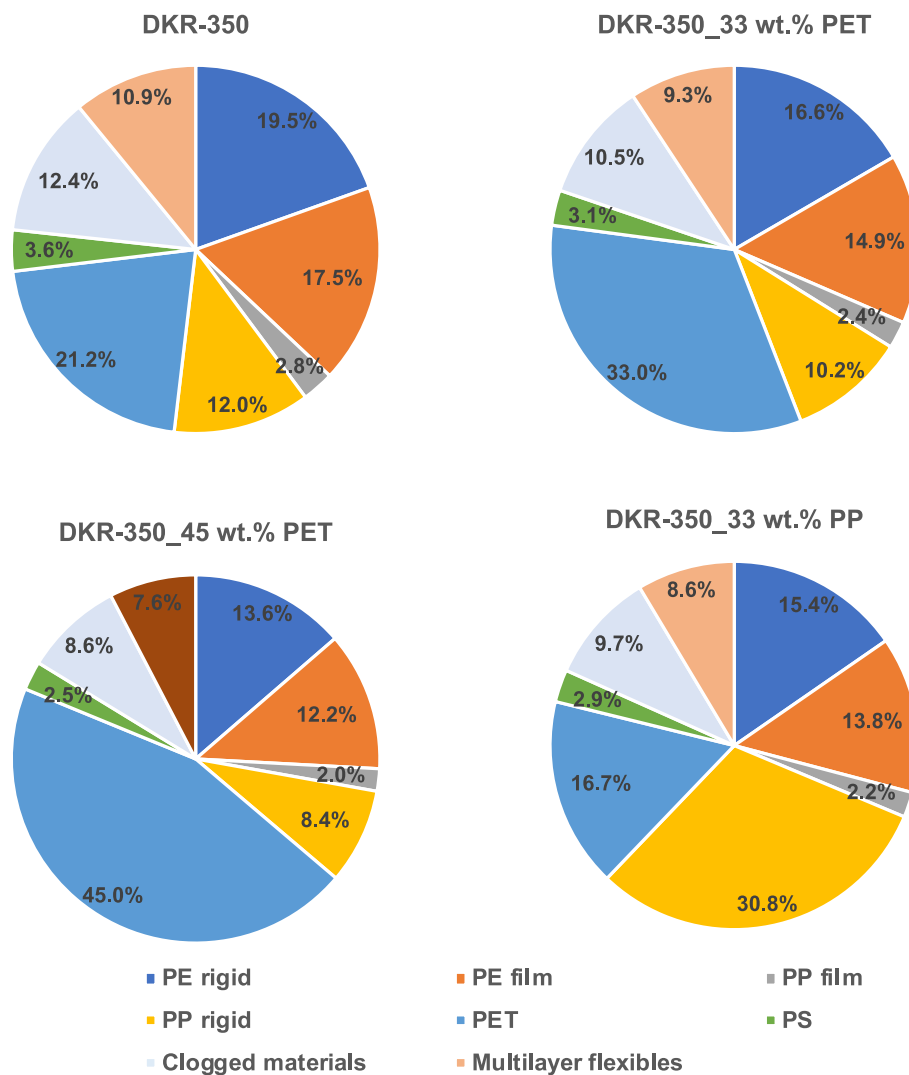


Fig. 2. Composition (wt.%) of the feedstocks used based on DKR-350.

absence of interaction between the constituents, has been used to calculate the pyrolysis product yields of mixed streams, which were then compared with the corresponding experimental values. In this way, possible discrepancies between the real and calculated yields allow us to investigate potential interactions between the polymers present in DKR-350 and synthetic mixtures during pyrolysis. We believe that we can neglect the potential catalytic effect of the minerals present in the waste,

as we previously observed that by washing pretreatment the ash content decreased considerably (from 7.5 to 1.9 wt%) while the yield and composition of the pyrolysis condensable products were not affected (Genuino et al. 2022).

Table 1

Product yields (wt.% relative to dry feed intake) from fixed-bed pyrolysis of different plastic feedstocks, and %C content (%C of all carbon in each spectrum) of the oil/wax products determined by ^{13}C NMR. Pyrolysis conditions: 125 g of virgin polymers and 60 g of DKR-350 categories, 17 °C/min, 500 °C for 60 min, 5 mL min $^{-1}$ N $_2$, average of three trials.

Feedstock	Product yields [wt. %] ± standard deviation			%C in oil/wax product determined by ^{13}C NMR		
	Gas	Oil/wax	Solid	Aliphatic C	Aromatic C	Carbonyl C
Virgin polymers						
HDPE	4 ± 1	94 ± 3	0 ± 0	100.0	0.0	0.0
LDPE	4 ± 0	96 ± 2	0 ± 0	100.0	0.0	0.0
PP	4 ± 1	96 ± 3	0 ± 0	98.9	1.1	0.0
PS	2 ± 0	94 ± 2	4 ± 1	5.9	94.1	0.0
PET	9 ± 5	54 ± 3	32 ± 9	23.4	68.9	7.7
DKR-350 categories						
PE rigid	4 ± 2	91 ± 1	0 ± 0	98.7	1.3	0.0
PE film	5 ± 0	80 ± 5	0 ± 0	97.9	2.1	0.0
PP rigid	7 ± 2	89 ± 1	0 ± 0	97.6	2.5	0.0
PP film	5 ± 0	88 ± 1	0 ± 0	97.5	2.5	0.0
PET	18 ± 0	54 ± 5	23 ± 6	23.9	69.6	6.4
PS	5 ± 1	81 ± 4	8 ± 0	7.2	92.8	0.0
Clogged materials	8 ± 1	54 ± 3	32 ± 2	78.6	19.5	1.9
Multilayer flexibles	9 ± 1	46 ± 3	39 ± 1	80.5	19.5	0.0
Mixtures						
Mixed virgin polymers_20 wt% PET	3 ± 1	84 ± 4	8 ± 1	80.1	18.2	1.6
Mixed virgin polymers_45 wt% PET	5 ± 1	72 ± 3	19 ± 1	71.2	27.0	1.8
DKR-350	9 ± 1	77 ± 2	8 ± 0	–	–	–
DKR-350_33 wt% PET	5 ± 0	70 ± 3	19 ± 3	69.1	27.4	3.5
DKR-350_45 wt% PET	4.1	61.0	28.7	74.5	20.1	5.4
DKR-350_33 wt% PP	3.6	83.0	8.5	73.8	24.0	2.2

2. Materials and methods

2.1. Feedstocks

Individual virgin polymers, synthetic mixtures of virgin polymers, a real plastic waste mixed stream (DKR-350) and mixtures of this stream with virgin polymers were used as feedstock for the pyrolysis experiments.

Virgin polymers: Five high-purity polymers, namely high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET). HDPE, LDPE and PP were purchased from Sabic, whereas PS and PET were purchased from Sigma Aldrich.

Mixtures of virgin polymers. A simulated DKR-350 stream was

prepared by mixing virgin polymers to obtain the following composition: HDPE (31.25 wt%), LDPE (31.25 wt%), PP (14 wt%), PS (3.5 wt%), and PET (20 wt%). Additionally, another stream was prepared with higher amount of PET: HDPE (22 wt%), LDPE (22 wt%), PP (9 wt%), PS (2 wt%), and PET (45 wt%). Fig. 1 shows the detailed composition of the two feedstocks used based on mixtures of virgin polymers.

Categories from DKR-350: the individual sorting categories (i.e., PE rigid, PE film, PP rigid, PP film, PET, PS, multilayer flexibles and clogged materials) from the DKR-350 stream used in our previous work (Genuino et al., 2022), treated with a cold-water pre-wash and hot water plus detergent and caustic soda.

Mixtures based on real DKR-350. A washed DKR-350 stream from our previous work (Genuino et al., 2022) with 20 wt% PET was used and spiked with virgin PET to increase the final PET concentration to 33 wt% and 45 wt%, and with PP to a final PP concentration of 33 wt%. Fig. 2 shows the detailed composition of the four feedstocks used based on DKR-350.

2.2. Pyrolysis experiments

Pyrolysis experiments were performed in a laboratory-scale batch reactor, heated at a heating rate of 17 °C min $^{-1}$ to 500 °C (see Supplementary Information). The sample (~60 g) was held at 500 °C for 60 min to completion. Nitrogen was used as the carrier gas at a fixed flow rate of 5 NmL min $^{-1}$. Details on the set-up, the procedures used for determining the products yields and the analysis techniques for characterizing the condensable products are described elsewhere (Genuino et al., 2022). Description of the ^{13}C NMR technique used can be found in the Supplementary Information.

2.3. Modelling

A simple linear model was used to predict the oil/wax, gas, and solid yields from the pyrolysis of mixed plastic streams, using as input the composition of the stream and the pyrolysis performance (i.e., experimentally measured pyrolysis product yields) of the individual components/categories (Equations 1–3). Thus, this model does not consider any interaction between the components of the mixture. Obviously, the yields of the components/categories are dependent on the specific experimental set-up and operating conditions used to perform the pyrolysis experiments. Thus, the parametrized model is dependent on the specific set-up and operating conditions used.

$$\text{Calculated gas yield of mixture} = \sum_i x_i \times \text{gas yield}_i \quad (1)$$

$$\text{Calculated oil/wax yield of mixture} = \sum_i x_i \times \text{oil/wax yield}_i \quad (2)$$

$$\text{Calculated solid yield of mixture} = \sum_i x_i \times \text{solid yield}_i \quad (3)$$

where

x_i is the mass fraction of component i in the plastic mixed stream

gas yield_i is the yield of gas obtained from the pyrolysis of component i

oil/wax yield_i is the yield of oil/wax obtained from the pyrolysis of component i

solid yield_i is the yield of solid obtained from the pyrolysis of component i

Additionally, the yield to aliphatic and aromatic carbons in the oil/wax product of mixed plastic streams was also calculated using a linear model (Equations (4) and (5)):

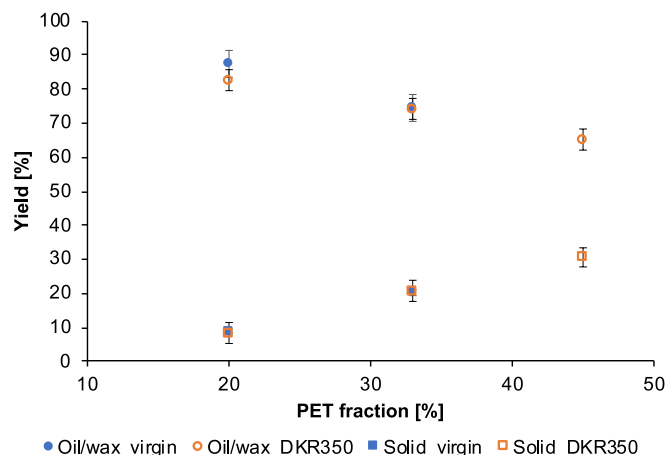


Fig. 3. Oil/wax and solid yields vs PET fraction in mixtures of virgin polymers and DKR-350.

Calculated aliphatic C yield_{oil/wax} of mixture

$$= \sum_i x_i \times \text{oil/wax yield}_i \times f_{\text{aliphatic C, oil/wax } i} \quad (4)$$

Calculated aromatic C yield_{oil/wax} of mixture

$$= \sum_i x_i \times \text{oil/wax yield}_i \times f_{\text{aromatic C, oil/wax } i} \quad (5)$$

where

oil/wax yield_i is the yield of oil/wax obtained from the pyrolysis of component *i*

$f_{\text{aliphatic C, oil/wax } i}$ is the mass fraction of aliphatic carbon in the oil/wax obtained from the pyrolysis of component *i*, measured by ¹³C NMR

$f_{\text{aromatic C, oil/wax } i}$ is the mass fraction of aromatic carbon in the oil/wax obtained from the pyrolysis of component *i*, measured by ¹³C NMR.

3. Results and discussion

3.1. Pyrolysis of individual components

The yields of oil/wax, gas, and solid products obtained from the pyrolysis of virgin polymers and individual sorting categories of DKR-350 are summarized in Table 1. HDPE, LDPE, PP, and PS pyrolysis resulted in similar product yields, with high yields of oil or oil/wax between 94 and 96 wt%, whereas PET only produced 54 wt% of condensable product, with significant amount of solid residue (32 wt%).

The high oil/wax yields obtained in this work have also been reported by other researchers investigating the recycling of waste plastics by pyrolyzing individual polymers and plastics. For example, Bagri and Williams investigated LDPE pyrolysis in a fixed-bed reactor, obtaining 95 wt% oil/wax yield at 10 °C/min at 500 °C (Bagri and Williams, 2002). A high oil/wax yield of 93.1 wt% was also obtained by Marcilla et al. (2009) in batch at 550 °C at 5 °C/min. Scott et al. (1990) pyrolyzed PS in a fluidized-bed reactor at 532 °C and reported high yields to oil, which consisted mainly of styrene. Onwudili et al. (2009) pyrolyzed PS in a batch pressurized autoclave reactor at 300–500 °C, producing a very high amount of oil at 97 wt% at 425 °C. Williams and Williams (1999) pyrolyzed PS in a fixed bed reactor and also showed that styrene was the main product of pyrolysis.

Aside from virgin plastics, six real individual categories from DKR-350 (i.e., PE film and rigid, PP film and rigid, PET including plastic bottles, and PS) (Genuino et al., 2022) were also pyrolyzed. The results of products yields and the composition of the condensable fraction are also summarized in Table 1. The product yields from the pyrolysis of these feedstocks are similar to the yields of the high-purity polymer they dominantly consist of, albeit mass balance closures are slightly worse. For example, the yield of oil/wax from virgin HDPE is 94 wt%, and the PE rigid category gives an oil/wax yield of 91 wt%. 54–58 wt% oil/wax yields were obtained for PET, both for the virgin polymers as for the PET categories in DKR350. These comparable product yields from the individual virgin polymers and individual waste categories suggest that a low amount of residual components are present in the last, probably due to a high degree of sorting or efficient washing applied. Additionally, this result implies that pyrolysis of polyolefins is not adversely affected by the presence of such residual components (i.e., additive or blend formulations in the parent material) with respect to yield.

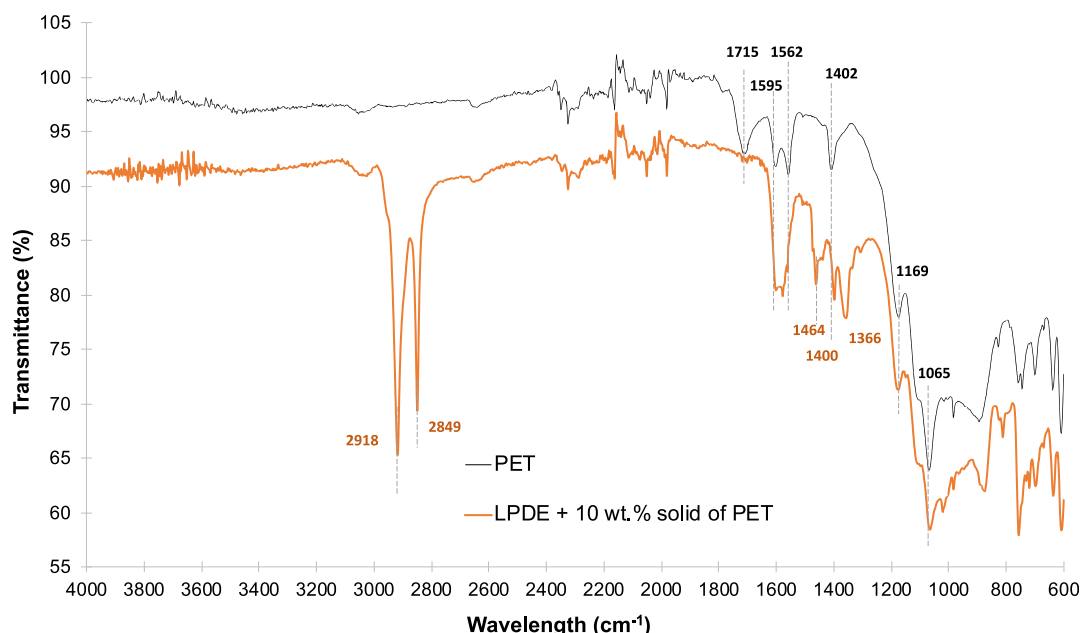


Fig. 4. FTIR spectra of the solid products obtained from the pyrolysis of PET and LDPE + solid of PET (10 wt%).

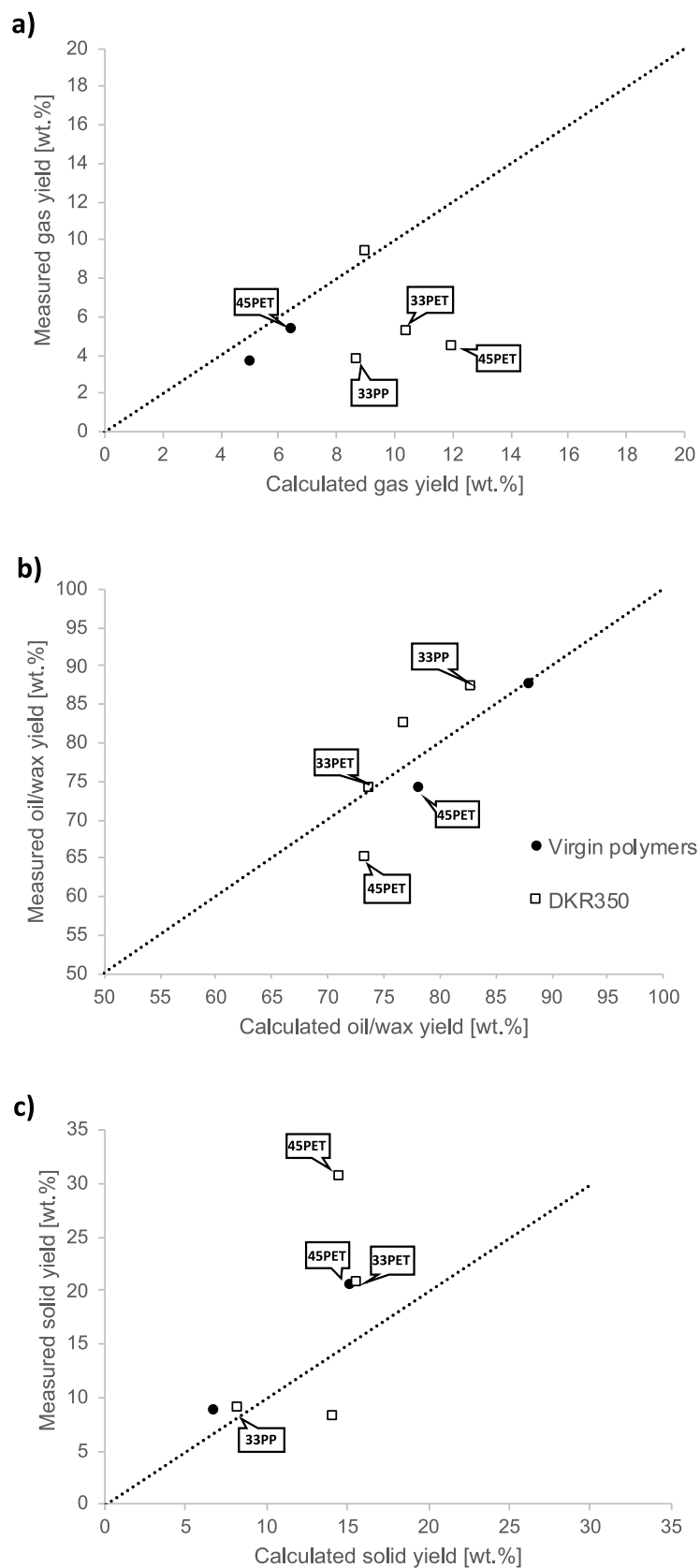


Fig. 5. Measured vs calculated gas (a), oil/wax (b), and solid (c) product yields (wt.%) in the pyrolysis of DKR-350 and synthetic mixtures.

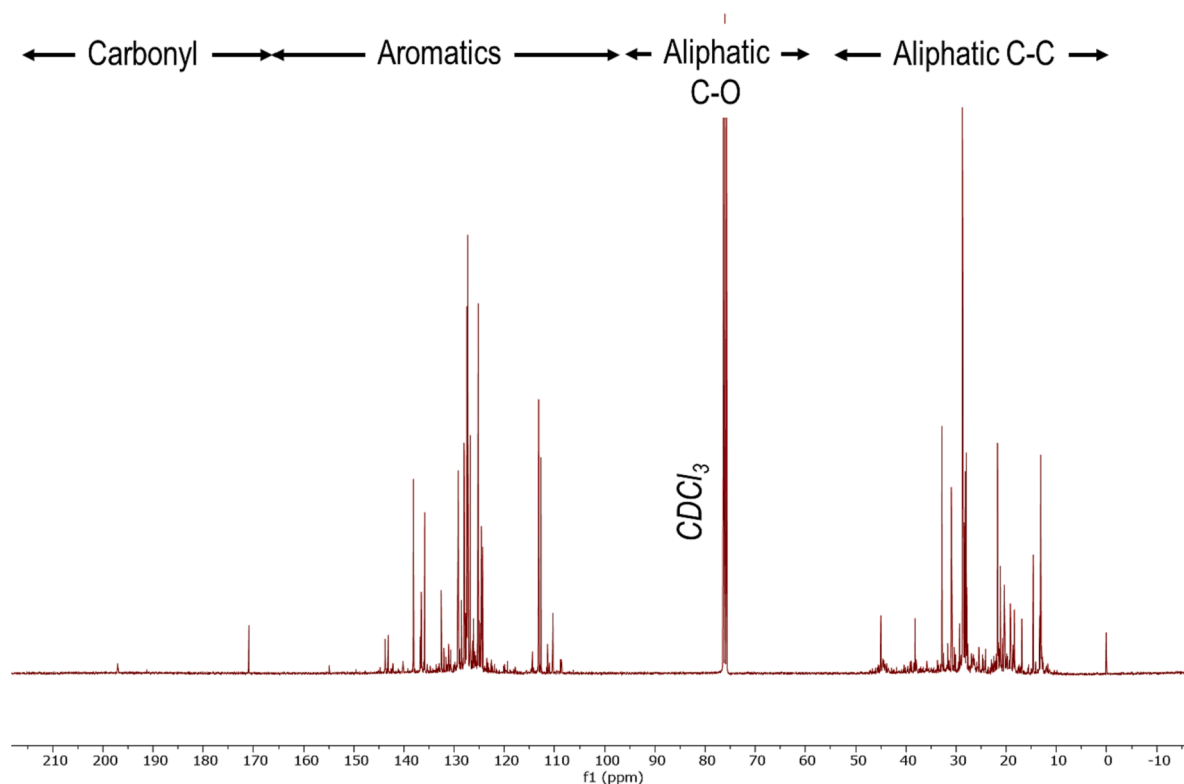


Fig. 6. Typical ^{13}C NMR spectrum of oil/wax obtained from DKR-350 pyrolysis.

Two other real individual categories from DKR-350 (clogged materials and multilayer flexibles) were also pyrolyzed under the same operating conditions. The multilayer flexibles are mostly composed by paper and Al laminates, while the clogged materials are hard-to-separate plastic components (Genuino et al., 2022). They are very complex mixtures, with at least 70 % of polyolefins in their composition. Upon pyrolysis, both categories gave oil/wax, gas, and solid yields between 47 and 54 wt%, 8–9 wt%, and 30–40 wt%, respectively. This implies that the presence of clogged materials and multilayer flexibles in DKR-350 contributes to significant solid product formation.

3.2. Pyrolysis of mixed streams

Mixtures of virgin polymers, as well as samples of DKR-350 spiked with virgin polymers (PP and PET) were pyrolyzed under the same conditions to analyse the behaviour of these mixtures and identify interactions between the polymers.

Pyrolysis of mixed virgin polymers with a similar composition to DKR-350 (simulated DKR-350) gave an oil/wax yield of 84.4 wt% (Table 1), which is significantly higher than the one obtained with DKR-350 (77 wt%). The gas yield was considerably lower for the simulated feed (3.5 wt%) than for DKR-350 (8.7 wt%) while the solid yields were similar (i.e., 7.6 wt% vs 8.5 wt%, respectively). The lower oil/wax yield from real DKR-350 is expected considering clogged materials and multilayer flexibles.

As mentioned above, DKR-350 contains PE, PP, and low levels of PS (35.1 wt%, 14.1 wt%, and 3.4 wt%, respectively) which, when pyrolyzed, give high yields of oil/wax. However, it also contains PET, clogged materials, and multilayer flexibles (20.1 wt%, 11.7 wt%, and 10.4 wt%, respectively) which, when pyrolyzed, give high yields of solid product, and also gas (in the case of PET). It has been experimentally observed that there is no formation of solid product from the pyrolysis of virgin polyolefins, whereas pyrolysis of PET produces it to a considerable extent. As such, additional experiments were performed with higher amounts of PET in the simulated stream with virgin polymers, as

well as in DKR-350 (from 20 wt% to 45 wt%) to explore potential interactions between the polymers that could lead to different products' selectivity. It was observed that there is a direct relation between the amount of PET present in both streams and the solid yield produced (Fig. 3). Indeed, upon pyrolysis, PET forms heavy compounds or fragments that are precursors of solid (Holland and Hay, 2002, Williams and Williams, 1999, Yoshioka et al., 2004), which may interact with polyolefins during pyrolysis of mixed plastics, affecting the primary pyrolysis of latter negatively, thus giving less oil/wax.

To prove this hypothesis, a pure LDPE polymer (representative polyolefin in DKR-350) and the solid from PET pyrolysis at 10 wt% were co-pyrolyzed ("LDPE + solid of PET"). After pyrolysis, only 88 wt% oil/wax (on basis of LDPE fed) was obtained (compared to 96 wt% from pure LDPE, Table 1), but the solid yield was 4.4 wt% (wt.% solid is defined as the difference in the amount of solid before and after pyrolysis). When compared to the pyrolysis of LDPE alone, there is a significant decrease in the yield of oil/wax with a concomitant increase in solid.

The physicochemical properties of solid products were also examined. Fig. 4 shows the FTIR spectra of both solid materials. When comparing the two spectra, the intensities of several peaks typical for PET either decreased or disappeared in the second sample. Specifically, the peak at 1715 cm^{-1} for $\text{C}=\text{O}$ decreased, while aromatic ring vibrations (1595 and 1562 cm^{-1}) increased in intensity in the LDPE + solid of PET. New peaks appeared in LDPE + solid of PET at 1464 and 1400 cm^{-1} (aromatic $\text{C}-\text{H}$), and 2918 and 3000 cm^{-1} (aliphatic $\text{C}-\text{H}$). As the major difference, the characteristic symmetric and asymmetric stretching bands of $\text{C}-\text{H}$ bonds corresponding to $-\text{CH}_2-$ groups at 2918 and 2849 cm^{-1} were present. Therefore, the presence of solid of PET during pyrolysis of LDPE either led to the adsorption of hydrocarbon chains in the solid or led to chain scissions and fragmentations between different aromatic units in the solid of PET, which further reacted with LDPE.

To further investigate this phenomenon, we did a washing step of both solids with tetrahydrofuran (THF) at room temperature, to see if the new peaks observed in the solid from LDPE + solid of PET were due to adsorption of condensable species on the surface of the solid. The

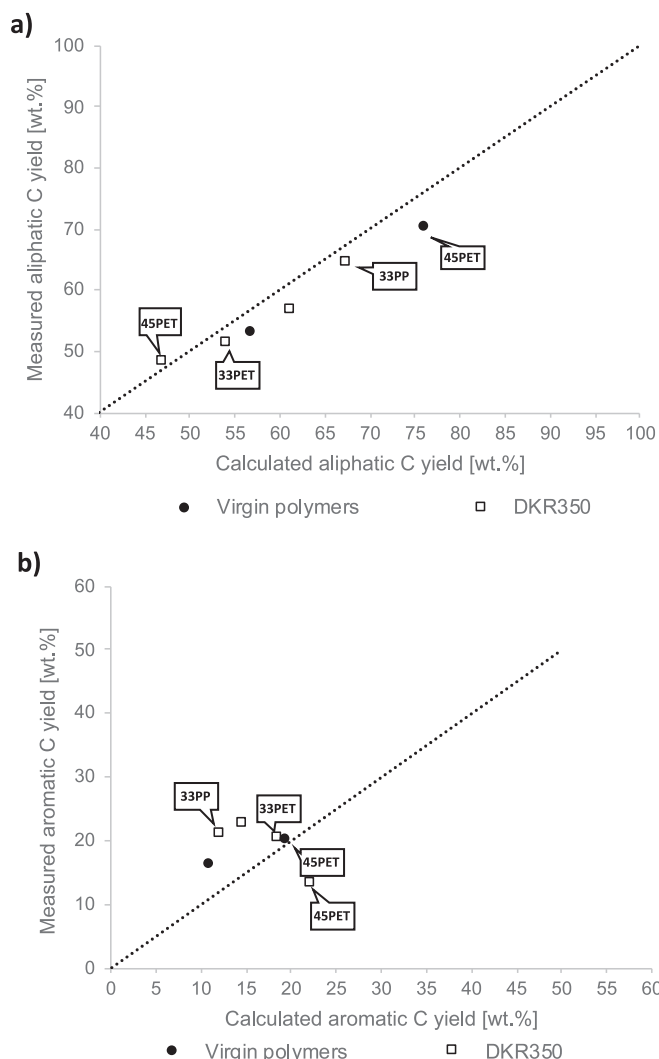


Fig. 7. Measured vs calculated yields of the aliphatic (a) and aromatic (b) carbon (wt.%) in the oil from pyrolysis of DKR-350 and mixtures of virgin polymers.

results of FTIR (Supplementary Information) showed similar spectra to the unwashed ones (Fig. 4), indicating that those peaks were thus probably a result of some reactions of the different fragments present during the co-pyrolysis. Additionally, a N_2 physisorption analysis indicated that the solid of PET is non-porous (surface area of $1.4 \text{ m}^2/\text{g}$), implying that capillary condensation of LDPE volatiles during pyrolysis could not occur. Co-pyrolysis with LDPE did not affect the surface properties of the solid product (surface area of $1.2 \text{ m}^2/\text{g}$). All these results support the hypothesis that some reactions happened between aromatic fragments from PET and LDPE, to favor solid formation. In any case, from a process point of view, either if this increase in solid yield is due to adsorption or reaction phenomena, the outcome is the same, an undesired loss in the oil/wax product.

A linear model was then used to calculate the product yields of the different mixtures of virgin polymers and DKR-350, based on the feedstock composition and the yields from the pyrolysis of different individual plastic components (both virgin and plastic waste categories). Fig. 5 shows the parity plots for the measured vs the calculated yields for the gas, oil/wax and solid products. For the model calculations, all the measured mass balances were normalized to 100 %, to avoid misperception of the results based on potential differences in mass balances.

Calculations reveal the oil/wax yield can be predicted to a reasonable extent, considering the high level of heterogeneity of the feedstock.

When a higher amount of PET is present, the oil/wax yield is overestimated, up to a maximum deviation of 8 percentage points when 45 wt% PET is present (Fig. 5b, DKR-350 sample).

Solid yields were underestimated in most cases (Fig. 5c), with differences of up to 16 percentage points from the actual yield (for the sample with 45 wt% PET), indicating a potential interaction between plastic components resulting in an increased solid product yield. That deviation was more pronounced with higher amounts of PET in the sample. It was previously reported in the literature that the pyrolysis kinetics of the polymers in a mixture of PE, PP and PS remains unaltered in comparison with the pyrolysis kinetics of the pure polymers (West-erhout et al., 1997), which supports our hypothesis that the presence of PET could be the main cause of the interaction among polymers during pyrolysis of complex mixtures.

An additional experiment was then performed wherein instead of PET, the proportion of PP was increased in DKR-350 (from 14 wt% to 33 wt%). As expected, the yield of oil/wax increased (from 77 to 83 wt%, Table 1), showing that by adding polyolefins to a real mixed plastic waste such as DKR-350, containing a significant amount of PET, an improvement in the yield of the desired oil/wax product can be achieved.

3.3. Characterization of the oil/wax products

The condensable (oil/wax) products were analyzed by ^{13}C NMR spectroscopy to get insights in their chemical composition. Table 1 summarizes the percentage of aromatic, aliphatic, and carbonyl carbons for each of the pyrolysis condensable products obtained. A typical spectrum of the oil/wax from the pyrolysis of DKR-350 from this technique is shown in Fig. 6. By integration of the spectrum, the contents of various functional groups (i.e., aromatic, aliphatic and carbonyl carbons) in the oil/wax can be obtained.

It can be observed that virgin polyolefins produce an oil/wax with mostly composed of aliphatic carbons (99–100 wt%). In the case of PS, the majority of the carbons are aromatic (94 wt%), and in PET, the ratio of aromatic/aliphatic carbon is ~ 3 , with 7 wt% of the carbon in carbonyl form. ^{13}C NMR analysis of the oil/wax derived from clogged materials and multilayer flexibles resulted in around 80 % of aliphatic carbons, indicating that they are mostly composed of polyolefins (i.e., PE and PP films and rigids).

In DKR-350 (Genuino et al., 2022), the aromatic/aliphatic ratio in the oil/wax (1/3) is comparable to the one present in the feedstock (from PET and PS, 24 wt%), indicating that aromatization products were not derived from the pyrolysis of PE and PP fractions.

With the carbon distribution data from ^{13}C NMR, we also applied a linear model to explore the predictability of the composition of the oil/wax obtained. Fig. 7 shows the parity plots for the measured versus the calculated yields of the aliphatic and aromatic carbon in the oil/wax samples from the mixtures (virgin polymers and DKR-350) with different amounts of PET and PP. Interestingly, the prediction of the aliphatic carbon yield is good in all the cases, always overpredicted, but with a maximum difference of 6 percentage points respect to the measured yield (70 wt% real vs 76 wt% calculated yield for the sample with 45 wt% PET). However, the aromatic yield cannot be predicted to such a good extent, most likely due to the behavior of PET above discussed (interaction with other polymers to produce more solid than expected), which is the main source of aromatic carbon in the feeds.

4. Conclusions

The predictability of the pyrolysis behavior of different mixed plastic streams from virgin polymers and real plastic waste (DKR-350) was evaluated by using a linear model based on their composition and the individual plastic components behavior. With the mixtures analyzed, the model allowed a good prediction of the pyrolysis oil/wax yield, with a maximum deviation of 8 percentage points when higher amounts of PET

(45 wt%) were present. Indeed, with high amounts of PET, the obtained oil/wax yields were always lower than the predicted ones. Consistently, increasing the proportion of PET (>33 wt%) favored the formation of solid product above the predicted values (up to 16 percentage points of yield difference), suggesting the interaction of plastic components. This work provides a first indication of the influence of PET on pyrolysis performance and its direct relation with the solid product formation.

Interestingly, the model was also capable to accurately predict the aliphatic carbon yield in the oil/wax product, with a maximum difference of 6 percentage points. However, that is not the case with the aromatic carbon yield, which supports the hypothesis that PET (the main source of aromatics in the feeds studied) interacts with other polymeric components present in the feed, favoring the solid formation and the decrease in oil/wax yield.

In summary, this model allows to predict to a good extent the yield and aliphatic carbon composition of the oil/wax pyrolysis product, which is the main target product of this technology. This work is of importance considering the variability and complexity of the feedstock, plastic waste streams, even though the input of the model is dependent on the experimental set-up and operating conditions used.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors gratefully acknowledge the Institute for Sustainable Process Technology (ISPT) of the Netherlands and the Dutch Polymer Institute (DPI) within the framework of the Circular Plastics Initiative Program (CP-50-02, *Towards improved circularity of polyolefin-based packaging*) and partners. The authors would also like to thank several additional partners involved in this work: Suster, B.V. for making the pyrolysis set-up available, Maria Del Mar Barreiro and Marcel van Eijk from the Nationaal Testcentrum Circulaire Plastics for sourcing the waste plastics used in this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2022.11.040>.

References

- Ates, F., Miskolczi, N., Borsodi, N., 2013. Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I. Product yields, gas and pyrolysis oil properties. *Bioresour. Technol.* 133, 443–454. <https://doi.org/10.1016/j.biortech.2013.01.112>.
- Bagri, R., Williams, P.T., 2002. Catalytic pyrolysis of polyethylene. *J. Anal. Appl. Pyrol.* 63, 29–41. [https://doi.org/10.1016/S0165-2370\(01\)00139-5](https://doi.org/10.1016/S0165-2370(01)00139-5).
- Brouwer, M.T., van Velzen, E.U.T., Augustinus, A., Soethoudt, H., De Meester, S., Ragaert, K., 2018. Predictive model for the Dutch post-consumer plastic packaging recycling system and implications for the circular economy. *Waste Manag.* 71, 62–85. <https://doi.org/10.1016/j.wasman.2017.10.034>.
- Dogu, O., Pelucchi, M., Van de Vijver, R., Van Steenberghe, P.H.M., D'hooge, D.R., Cuoci, A., Mehl, M., Frassoldati, A., Faravelli, T., Van Geem, K.M., 2021. The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: state-of-the-art, challenges, and future directions. *Prog. Energy Combust. Sci.* 84, 100901.
- Genuino, H.C., Ruiz, M.P., Heeres, H.J., Kersten, S.R.A., 2022. Pyrolysis of mixed plastic waste (DKR-350): Effect of washing pre-treatment and fate of chlorine. *Fuel Proc. Technol.* 233, 107304–107314. <https://doi.org/10.1016/j.fuproc.2022.107304>.
- Holland, B.J., Hay, J.N., 2002. The thermal degradation of PET and analogous polyesters measured by thermal analysis - Fourier transform infrared spectroscopy. *Polymer* 43, 1835–1847. [https://doi.org/10.1016/S0032-3861\(01\)00775-3](https://doi.org/10.1016/S0032-3861(01)00775-3).
- Kusenbergh, M., Eschenbacher, A., Djokic, M.R., Zayoud, A., Ragaert, K., De Meester, S., Van Geem, K., 2022a. Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? *Waste Manag.* 138, 83–115. <https://doi.org/10.1016/j.wasman.2021.11.009>.
- Kusenbergh, M., Zayoud, A., Roosen, M., Dao Thi, H., Seifali Abbas-Abadi, M., Eschenbacher, A., Kresovic, U., De Meester, S., Van Geem, K.M., 2022b. A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition. *Fuel Proc. Technol.* 227, 107090. <https://doi.org/10.1016/j.fuproc.2021.107090>.
- Lange, J.-P., 2021. Managing plastic waste: Sorting, recycling, disposal, and product redesign. *ACS Sust. Chem. Eng.* 9, 15722–15738. <https://doi.org/10.1021/acscuschemeng.1c05013>.
- Lopez, A., De Marco, I., Caballero, B.M., Laregoiti, M.F., Adrados, A., 2010. Pyrolysis of municipal wastes: Influence of raw material composition. *Waste Manag.* 30, 620–627. <https://doi.org/10.1016/j.wasman.2009.10.014>.
- Marcilla, A., Beltran, M.I., Navarro, R., 2009. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. *Appl. Catal.* 86, 78–86. <https://doi.org/10.1016/j.apcatb.2008.07.026>.
- Onwudili, J.A., Insura, N., Williams, P.T., 2009. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *J. Anal. Appl. Pyrol.* 86, 293–303. <https://doi.org/10.1016/j.jaap.2009.07.008>.
- Roosen, M., Mys, N., Kusenbergh, M., Billen, P., Dumoulin, A., Dewulf, J., Van Geem, K.M., Ragaert, K., De Meester, S., 2020. Detailed analysis of the composition of selected plastic packaging waste products and its implications for mechanical and thermochemical recycling. *Environ. Sci. Technol.* 54, 13282–13293. <https://doi.org/10.1021/acs.est.0c03371>.
- Scott, D.S., Czernik, S.R., Piskorz, J., Radlein, D.S., A. G., 1990. Fast pyrolysis of plastic wastes. *Energy Fuels* 4, 407–411. <https://doi.org/10.1021/ef00022a013>.
- Westerhout, R.W.J., Waanders, J., Kuipers, J.A.M., van Swaaij, W.P.M., 1997. Kinetics of the low-temperature pyrolysis of polyethylene, polypropylene, and polystyrene modeling, experimental determination, and comparison with literature models and data. *Ind. Eng. Chem. Res.* 36, 1955–1964. <https://doi.org/10.1021/ie960501m>.
- Williams, P.T., Williams, E.A., 1999. Interaction of plastics in mixed-plastics pyrolysis. *Energy Fuels* 13, 188–196. <https://doi.org/10.1021/ef980163x>.
- Yoshioka, T., Grause, G., Eger, C., Kaminsky, W., Okuwaki, A., 2004. Pyrolysis of poly (ethylene terephthalate) in a fluidised bed plant. *Polym. Degrad. Stab.* 86, 499–504. <https://doi.org/10.1016/j.polymdegradstab.2004.06.001>.