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Chemical recycling of waste polystyrene by thermo-catalytic pyrolysis: A description for different feedstocks, catalysts and operation modes

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Abstract

Chemical recycling by thermo-catalytic pyrolysis/degradation offers the possibility of converting waste plastics into their original monomers or other valuable chemicals which can be used as feedstocks in chemical and petrochemical industries. Plastic wastes of polystyrene (PS) based materials can be a good source of styrene as well as mono-aromatic (BTEx: benzene, toluene, ethylbenzene, xylenes) compounds. The selectivity of pyrolysis products can be tuned by choosing the right catalyst as well as appropriate operating conditions/operation modes. In this regard, the focus of the present work was to perform thermo-catalytic pyrolysis of different waste polystyrene (WPS) feedstocks over acid and base catalysts employed in *ex-situ* and *in-situ* modes. The main goal was to compare the compositions of pyrolysis products obtained by changing feedstocks, catalysts and operation modes. A further goal was to discuss the suitability of the catalysts employed for the enhanced recovery of desired products from WPS pyrolysis. It was demonstrated that

expanded polystyrene gives very similar product distribution as compared to virgin PS, both giving high styrene content. Likewise, hard PS-based random packing materials produce similar results as compared to high impact polystyrene (HIPS). Moreover, it was shown that solid base catalysts influence the composition of the pyrolysis products only slightly as compared to thermolysis. Solid acid catalyst however, showed significant impact on the composition of the pyrolysis products as compared to non-catalytic pyrolysis. These results may provide new insights for the chemical recycling of plastic wastes.

Keywords: Chemical recycling, pyrolysis, polymer degradation, thermo-catalytic process, plastic recycling

1. Introduction

Waste polymeric substrates are potential sources of important raw materials that can be used as feedstocks for the production of new/virgin polymers, fuels and/or other valuable chemicals. Chemical recycling offers the possibility of transforming waste plastics into useful chemicals, and hence it is considered as a promising approach towards resource conservation and waste minimization (Ignatyev et al., 2014; Lee et al., 2021). During chemical recycling process of waste plastics, the type or nature of the polymeric material can play a major role in defining the product distribution. For example, one can expect different types of products during pyrolysis of condensation and addition polymers. The condensation polymers *e.g.* PLA (Polylactic acid) and PET (Polyethylene terephthalate) have an appreciable tendency to depolymerize and give original monomers as a major product. Whereas, addition polymers *e.g.* PE (Polyethylene) and PP (Polypropylene) tend to give diverse products during pyrolysis process, where respective monomers are not the major ones (Brems et al., 2012; Ignatyev et al., 2014). In contrast to most addition polymers

however, polystyrene (PS) shows a different behavior during pyrolysis by giving styrene monomers as major product. The other products include BTEX (benzene, toluene, ethylbenzene, xylenes) compounds (Achilias et al., 2007; Jaafar et al., 2022; Mo et al., 2014; Verma et al., 2021; Zayoud et al., 2022). Thus, polystyrene-based plastic wastes are a good source of styrene monomers as well as BTEX compounds. In literature, there have been several investigations on the thermal and thermo-catalytic pyrolysis of virgin polystyrene (VPS) and waste polystyrene (WPS). The authors used different catalysts (including solid acids and solid bases) and reactor configuration in order to tune the product selectivity. Solid acid catalysts (*e.g.* zeolites) have been employed by several authors for the thermo-catalytic pyrolysis of both polyolefin-based (Gaurh and Pramanik, 2018; Ratnasari et al., 2017; Santos et al., 2019) and PS-based (Ma et al., 2017b, 2017a; Sul Jung et al., 2021; Xue et al., 2017) plastics. Whereas, solid base catalysts (*e.g.* MgO) were mainly used for the PS-based plastics (Antonakou et al., 2014; Shah et al., 2014; Ukei et al., 2000). The details of reaction mechanism for acid and base catalysis can be found in (Marczewski et al., 2013; Ojha and Vinu, 2015; Ukei et al., 2000).

A recent study of the literature on the pyrolysis of PS-based materials reveals that despite some comprehensive reports that have been presented, systematic studies showing the influence of process parameters (in conjunction with different WPS materials and catalysts) are rather scarce. A brief overview of literature studies is given in Table 1. From Table 1, it can be observed that the data of product yields are somewhat scattered and lacking a correlation. Moreover, most authors have used only one type of feedstock. When dealing with PS-based plastic wastes, however, one must confront different types of materials *e.g.* expanded PS, high impact polystyrene (HIPS) or hard PS-based random packing materials.

Table 1. An overview of literature studies on the pyrolysis of PS-based feedstocks.

Reference	Feedstock	T (°C)	Catalyst	Catalyst placement	Operation	Styrene Yield (wt%)	BTEX Yield (wt%)
(Ukei et al., 2000)	Virgin PS	600	None	-	Semi-batch	56.10	7.50
		350	Powder MgO	Above the feedstock	in-situ gas phase/ Semi-batch	62.96	4.60
		350	Powder HZSM-5			50.36	11.50
(Kijeński and Kaczorek, 2005)	Virgin PS	400	None	-	Semi-batch	57.90	3.10
		375	MgO (particle size: 1.25 mm)	Mixed with feedstock	in-situ liquid phase/ semi-batch	59.60	4.50
		400				57.80	3.80
(Mo et al., 2014)	Container PS + Expanded PS	470-505	None	-	Semi-batch	64.52	Not given
(Artetxe et al., 2015)	Virgin PS	450	None	-	Continuous/ Conical spouted bed reactor	55.86	3.06
		500				70.57	5.26
		550				67.10	8.29
		600				66.80	7.88
(Verma et al., 2021)	Expanded PS	650	None	-	Semi-batch	84.74	11.38
		600	HZSM-5	Mixed with feedstock	in-situ liquid phase/ Semi-batch	55.78	18.98
		550		Above the feedstock	in-situ gas phase/ Semi-batch	46.42	24.27
		550		Above and mixed with the feedstock	in-situ multiphase/ Semi-batch	46.30	28.12
(Zayoud et al., 2022)	Expanded PS:	450	None	-	Continuous stirred tank reactor (CSTR) at 1 bar	35.70	16.70
	94.20%	550				41.20	15.10
		600				43.20	15.30

Due to differences in the overall compositions, these materials are expected to give different product distributions during pyrolysis process. Furthermore, the use of different operating conditions, catalysts, as well as operation modes can also affect the yields and compositions of the pyrolysis products to a great extent.

Considering the facts described in the above paragraphs, it becomes clear that systematic studies on thermal and thermo-catalytic pyrolysis are essential with regard to providing the data which in turn are required for designing efficient and selective pyrolysis processes. Therefore, the focus of the present investigation was to perform thermo-catalytic pyrolysis of different WPS feedstocks over acid and base catalysts employed in *in-situ* and *ex-situ* modus. The aim was to compare the compositions of pyrolysis oils obtained and to discuss the suitability of employed catalysts as well as operation modes in order to tune the product selectivity during pyrolysis of different PS-based plastic wastes.

2. Materials and Methods

2.1 Feedstocks and catalysts

Three types of WPS materials along with VPS were used as feedstocks (Fig. 1). VPS (3–4 mm diameter spheres) with an average molecular weight of 192000 g.mol⁻¹ was purchased from the company Sigma-Aldrich, Germany. The sample WPS-1 (HIPS, produced by recycling of cups used for dairy products) was purchased from the company SOLLAU, Czech Republic. The samples WPS-2 (hard PS-based material used in the packing of KONICA toner cartridge) and WPS-3 (expanded PS) were random packing materials.

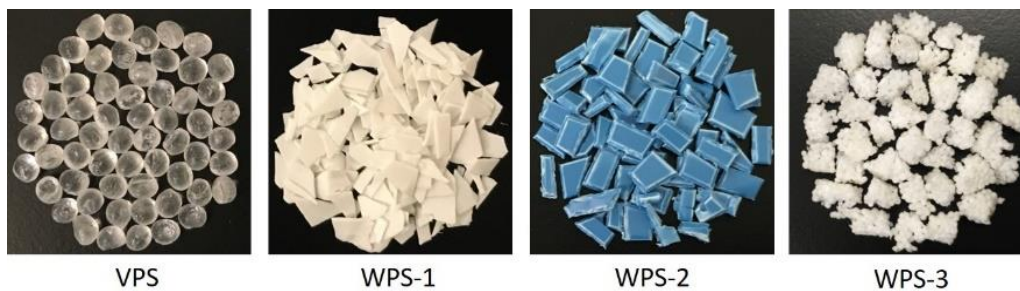


Fig. 1 Polystyrene samples used as feedstocks.

In order to obtain a comparable pellet size with VPS and WPS-1, WPS-2 was cut into small pieces. The volume of expanded polystyrene *i.e.* WPS-3 was reduced by simple heat treatment. For this purpose, 10 mm x 10 mm pieces of the original sample were treated at 120 °C for 30 minutes. Thermogravimetric analysis (TGA) of all feedstock samples was performed on a LECO TGA 701 (LECO Co., USA) thermogravimetric analyzer. For the experiments, 0.5 g of each sample was heated to 800 °C at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

For the thermo-catalytic pyrolysis, powder samples of acid (zeolite) and base (MgO) catalysts were employed. The zeolite sample (HZSM-5 type) was produced by the company Süd-Chemie AG, Germany. The data on the structural, textural and acidic properties of the zeolite sample can be found elsewhere (Inayat et al., 2022). As base catalysts, two types of magnesium oxide samples *i.e.* of low and high BET surface area were employed. The low BET surface area sample (MgO-1) was obtained by the thermal decomposition of MgCO₃. The details of the preparation methods can be found elsewhere (Inayat et al., 2021). The MgO sample with high surface area (MgO-2) was prepared by the calcination of hydroxide precursor Mg(OH)₂. The hydroxide precursor was synthesized by the coprecipitation method using aqueous solutions of sodium carbonate decahydrate (2.60 g sample dissolved in 25 g distilled water) and magnesium nitrate hexahydrate (16.05 g sample dissolved in 25

g distilled water). The aqueous solution of magnesium nitrate was added drop wise to sodium carbonate solution under constant stirring at 60 °C while maintaining the pH of the mixture at 10.5 by adding 3M NaOH solution. The resulting precipitates were further stirred at 60 °C for 45 min then filtered, washed with distilled water and dried overnight at 70 °C. Finally, the sample was calcined at 400 °C (heating rate 2 °C) for 5 hours.

2.2 Experimental setup and procedure

The experiments on thermal and thermo-catalytic pyrolysis of VPS and WPS samples were carried out in a lab-scale test rig at 400 and 500 °C. For all experiments, a heating rate of 10 °C/min was used to reach the target temperature and nitrogen with a flowrate of 50 mL/min was used as carrier gas. The schematic diagram of the experimental setup is given in Fig. 2. The operating conditions such as temperature, heating rate, nitrogen flow rate etc. were adopted from our previous work (Inayat et al., 2021).

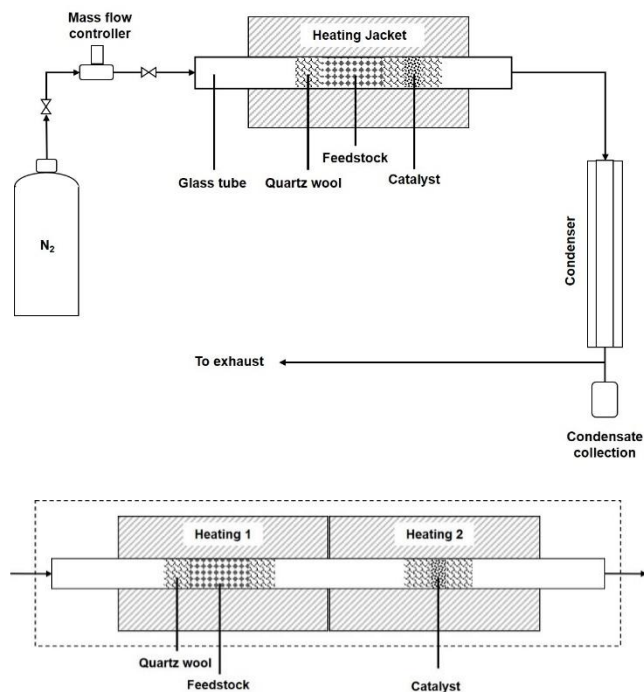


Fig. 2. Experimental setup: in-situ gas phase (top); ex-situ gas phase (bottom)

The main experimental campaign for the catalytic pyrolysis was carried out by applying the *in-situ* gas phase pyrolysis in which the feedstock and catalyst samples (separated by a thin layer of quartz wool) were heated using a single heating source. For the *in-situ* process, a glass tube of 300 mm in length and 20 mm in diameter was used as pyrolysis reactor.

In order to investigate the influence of preheating the catalyst to a desired temperature, selected experiments were repeated using the *ex-situ* gas pyrolysis. For this purpose, the feedstock and catalyst samples were packed separately in the reactor tube and were heated using independent heating sources. In this case, a longer reactor tube (500 mm in length) was used and the catalyst sample was preheated to the target temperature before heating of the feedstock was started.

2.3 Product analysis

The amounts of condensate oil, wax and residue were determined gravimetrically. The amount of gas was obtained by subtracting the total mass of oil, wax and residue from the mass of the feedstock used. The yields of all products were determined using the following Eqs. (1) – (3):

$$\text{Oil (wt. \%)} = \frac{\text{Mass of oil}}{\text{Mass of feedstock}} \times 100 \quad (1)$$

$$\text{Wax + Residue (wt. \%)} = \frac{\text{Mass of (wax + Residue)}}{\text{Mass of feedstock}} \times 100 \quad (2)$$

$$\text{Gas (wt. \%)} = \frac{\text{Mass of feedstock} - \text{Mass of (oil + wax + Residue)}}{\text{Mass of feedstock}} \times 100 \quad (3)$$

In order to identify the individual oil components, gas chromatography–mass spectrometry (GC-MS) analysis was performed. For this purpose, an Agilent 8890 GC-MS system equipped with a single quad detector 5977B and a HP-5 column was used. The yields of individual components *i.e.* styrene, BTE and alpha-methylstyrene as well as of oligomers

were determined by gas chromatography. For this purpose, a YL 6100 GC, equipped with a HP-5 column and a flame ionization detector was used.

3. Results and Discussion

3.1 Characterization of feedstocks and catalysts

The TGA and DTG curves of all feedstocks used in the present study are shown in Fig. 3a and b respectively. For all samples, the main thermal degradation occurred in the temperature range of 400 to 500 °C. The sample WPS-3 (expanded polystyrene) showed very similar thermal behavior as compared to VPS which indicates high PS content in its composition.

The different thermal behavior of WPS-1 and 2 as compared to VPS can be attributed to the additives (*e.g.* butadiene rubber (Wang et al., 2010)) added to obtain high impact polystyrene-based materials. Further characterization data *i.e.* FTIR spectra, elemental analysis and density (determined by He pycnometry) of the feedstocks used can be found in the supplementary material.

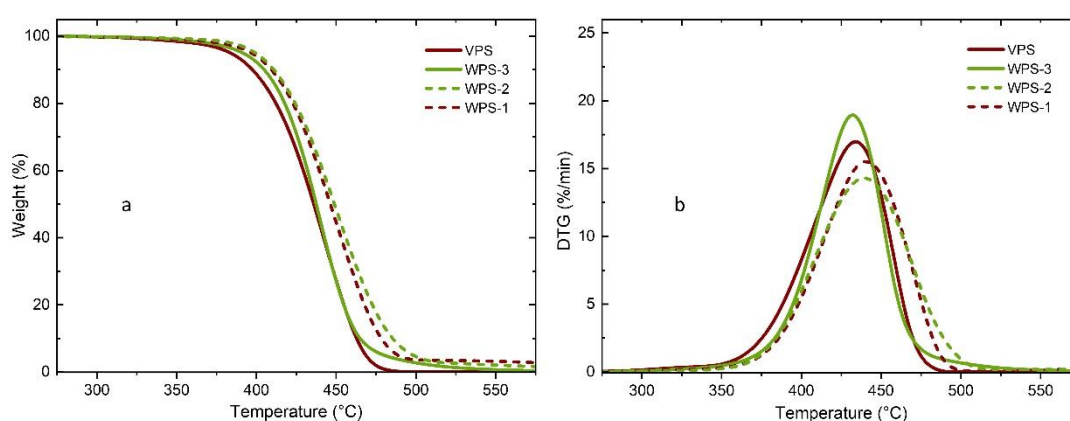


Fig. 3. TGA (a) and DTG (b) curves of the feedstocks used.

For all catalyst samples employed in this work, the textural properties were determined by physisorption of nitrogen. The values of S_{BET} for zeolite, MgO-1 and MgO-2 were found to be 411, 58 and 211 m^2g^{-1} respectively. The characterization data of the acidity of zeolite and basicity of MgO can be found in the supplementary material.

3.2 Thermal and thermo-catalytic pyrolysis

3.2.1 Thermal pyrolysis

The results of thermal pyrolysis performed on all feedstock samples are shown in Fig. 4. From these results it can be observed that samples WPS-1 (HIPS) and WPS-2 (hard packing material) produced very similar results. This is evident not only from the amounts of oil, gas and wax/residue but also from the composition of oil. A similar product distribution as well as a thermal behavior in TGA suggests that WPS-1 and 2 share comparable material composition. Likewise, VPS and expanded polystyrene (WPS-3) samples produced similar results in terms of yields of styrene monomer and other mono-aromatic compounds. The main difference was the higher amount wax for WPS-3 and consequently lower amount of oil.

This may be attributed to slightly different melting of pellets (in the very beginning of the pyrolysis) for both feedstocks and somewhat shorter residence time of the pyrolysis vapors in the case of expanded PS, possibly due to some retained gas pockets in the pellets. Although, the volume of the expanded polystyrene was reduced (section 2) before the experiments, it still had lower density as compared to VPS (see Supplementary material). In Fig. 4b, a comparison of the chromatograms obtained for VPS and WPS2 is shown. Here, formation of comparatively higher amounts of styrene monomer and oligomers in the case of VPS may be ascribed to its higher styrene content as compared to WPS-2.

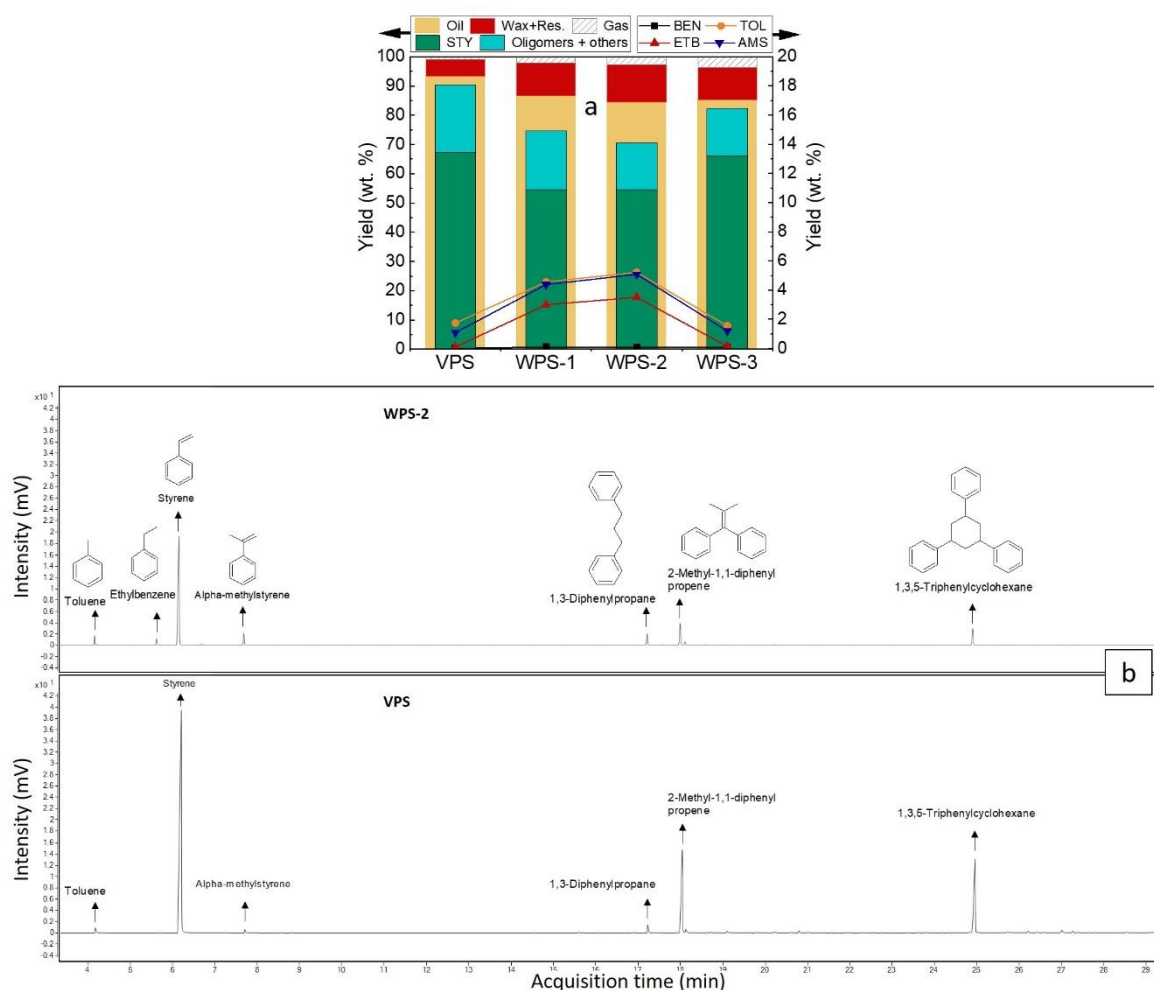


Fig. 4. Thermal pyrolysis at 400 °C: (a) composition of pyrolysis oil; (b) GC-MS chromatograms of the pyrolysis oils obtained from PS and WPS-2.

Mo et al (Mo et al., 2014) studied thermal pyrolysis of container PS and expanded PS (weight ratio of 1:1) and reported a styrene content of 64.54% in the pyrolysis oil. This is slightly higher than the average value (ca. 60%) calculated from the ones obtained for expanded PS (ca. 66%) and HIPS (ca. 54.5%) at 400 °C (with heating 10 °C/min and carrier gas flow rate 10 mL/min) in the present work. The dissimilarities with the results as reported by of Mo et al. may be ascribed to the different operating conditions used by them. *e.g.* higher temperature range (470-505 °C). Also, very recently Zayoud et al. (Zayoud et al., 2022) in their comprehensive study on the pyrolysis of end-of-life PS showed that by just

varying process temperature and/or pressure, it was possible to substantially alter the yield of styrene monomer and other mono-aromatic compounds.

3.2.2 Thermo-catalytic pyrolysis over base catalysts

In Fig. 5a and b the product distributions of thermo-catalytic pyrolysis over MgO-1 at 400 and 500°C are shown, respectively. In case of VPS, the increase in temperature did not affect the product distribution appreciably, as the amount and composition of oil fractions are essentially the same at both temperatures. The wax yield however, was decreased and the gas yield increased though, which can be ascribed to the higher temperature. A similar trend was observed for WPS-1 and 2, where the amount of wax was reduced at higher temperature. In this case however, the oil yield was increased, as more wax was converted at 500°C.

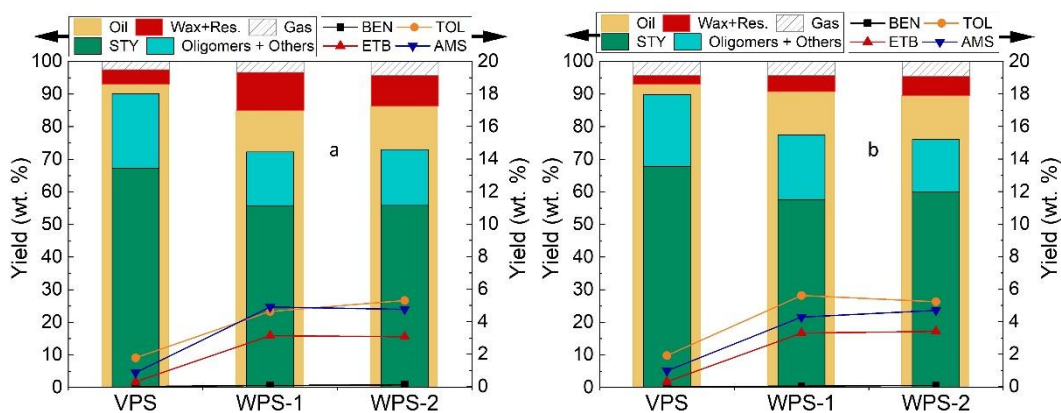


Fig. 5. Thermo-catalytic pyrolysis (*in-situ*) of different feedstocks over MgO-1 at 400 °C (a) and 500 °C (b) for a catalyst-to-feed ratio of 1:10

When the results of thermo-catalytic pyrolysis over MgO-1 catalyst were compared with those obtained from thermolysis, no significant difference was observed. Only a slight increase in the yields of oil and styrene for WPS-1 and 2 was recorded. This shows that the base catalysts did not influence the pyrolysis process significantly. Antonakou et al.

(Antonakou et al., 2014) studied catalytic pyrolysis of HIPS and reported slightly higher monomer yield over MgO, which may be due to the higher temperature (600 °C) they employed. Furthermore, they used relatively higher amount of catalyst that gave a catalyst-to-feed ratio of 1:2.

Among the MgO catalyst samples used in the present, MgO-1 (Fig. 5) featured lower specific surface area (S_{BET} : 58 m²g⁻¹). In order to study the effect of S_{BET} , experiments on MgO-2 (S_{BET} : 211 m²g⁻¹) sample were also carried out. In Fig. 6, a comparison of the product distributions obtained at 500 °C for MgO-1 and 2 is given.

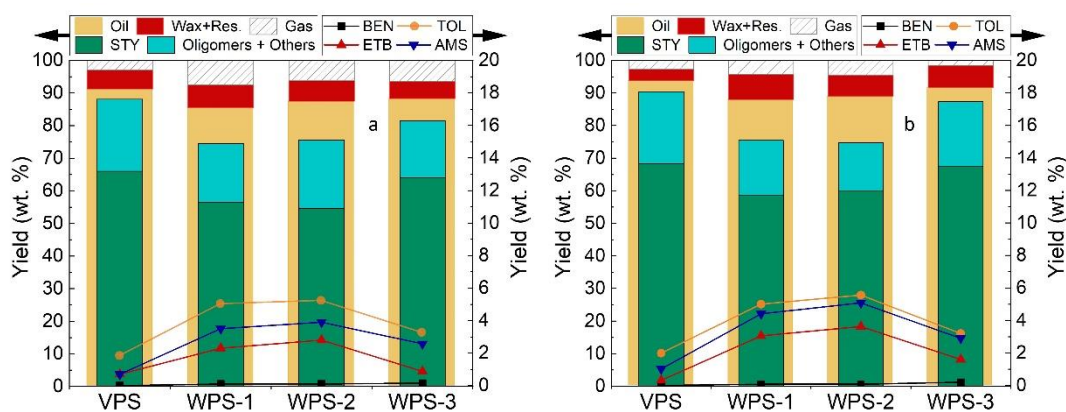


Fig. 6. Thermo-catalytic pyrolysis (*in-situ*) of different feedstocks at 500 °C over MgO-1 (a) and MgO-2 (b) for a catalyst-to-feed ratio of 1:20

The results as presented in Fig. 5 and 6 suggest that, at 500 °C, the specific surface area as well as the catalyst amount (catalyst to feed ratio of 1:10 and 1:20) do not affect the composition of the pyrolysis products significantly. Moreover, feedstocks of the group 1 (i.e. VPS and WPS-3) and of group two (WPS-1 and 2) continued showing similar behaviors as they showed in thermal and thermo-catalytic pyrolysis at 400 °C. These results show that the amount of styrene and that of the BTEX compounds produced during the pyrolysis of PS-based feedstocks depend mainly on the type (composition of the feedstock) and operating conditions (e.g. temperature). Thus, it appears that neither the basicity nor the

S_{BET} of the base catalyst plays a major role in the thermo-catalytic pyrolysis of PS as compared to thermolysis.

Furthermore, in order to study the effect of preheating the MgO catalyst, an experiment on VPS was carried out by using the MgO-2 sample in *ex-situ* catalysis and the results obtained (in comparison with the *in-situ* catalysis) are shown in Fig. S4. From the comparison, it can be observed that the *ex-situ* catalytic pyrolysis produced essentially similar results as compared to those obtained from the *in-situ* pyrolysis, both in terms of oil yield and composition. This suggests that preheating the base catalyst during thermo-catalytic pyrolysis of PS does not affect the product distribution appreciably.

3.2.3 Thermo-catalytic pyrolysis over acid catalyst

The results of the *in-situ* and *ex-situ* catalytic pyrolysis over acid (zeolite) catalyst are shown in Fig. 7a and b respectively. For all experiments performed on the *in-situ* catalytic pyrolysis in this work, interestingly, more residue (inside the reactor) and more wax (inside the condenser) were observed over zeolite (acid) catalyst as compared MgO or non-catalytic pyrolysis. The formation of higher amounts of wax and residue thus led to lower oil yields and consequently lower yields of styrene monomer.

A plausible explanation for the formation of high wax and low oil yields over zeolites can be the occurrence of cross-linking reactions that produce crosslinked polymers which need harsh cracking conditions. According to Serrano *et al.* (Serrano et al., 2000), at lower temperatures, the cross-linking reactions over acid catalysts might be favored as compared to cracking reactions. This can lead to the formation of cross-linked polymers which need harsh conditions for cracking and hence remain as waxes.

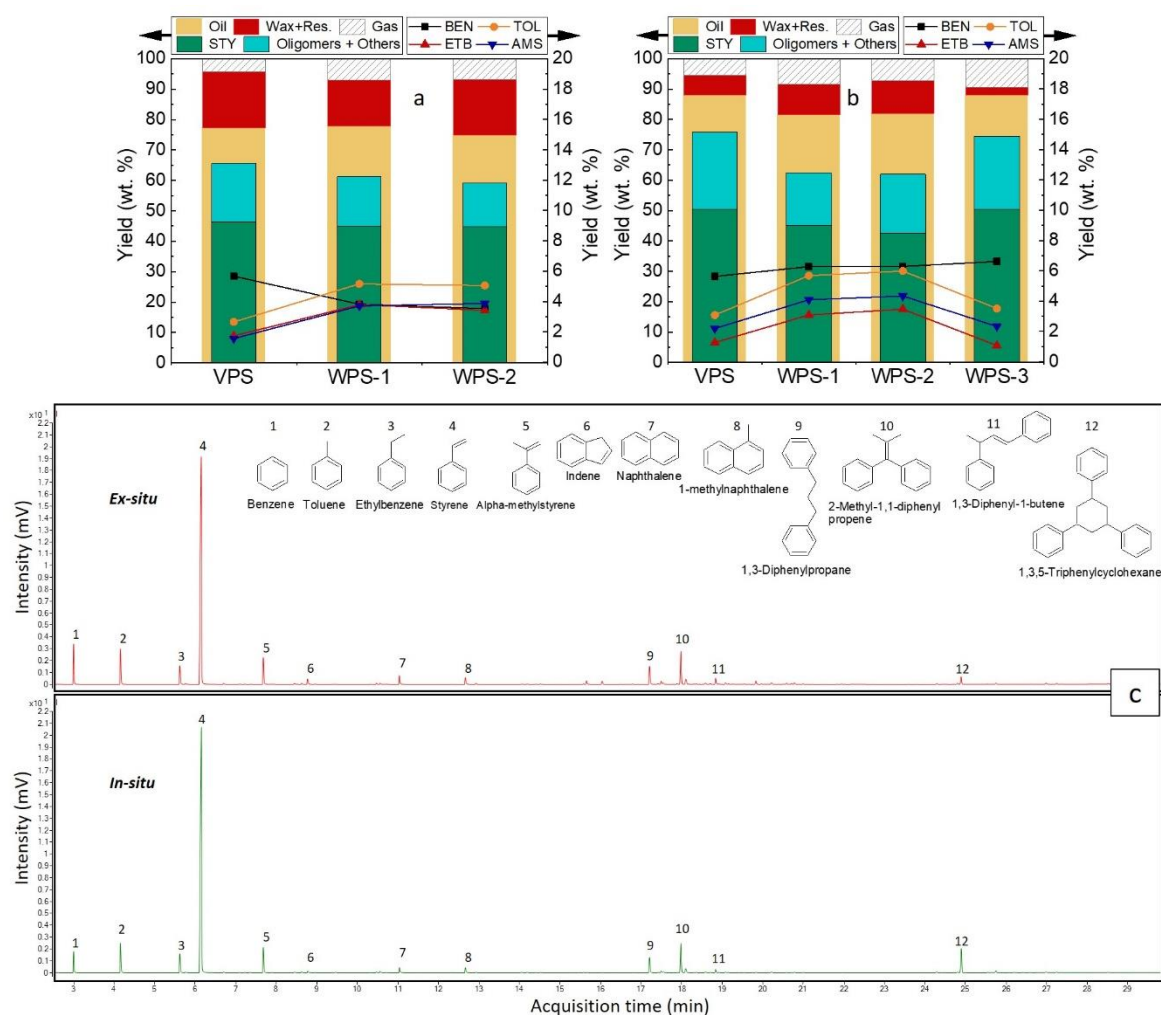


Fig. 7. Product distribution in thermo-catalytic pyrolysis performed at 500 °C over zeolite catalyst for a feed to catalyst ratio 1:20: (a) *in-situ* pyrolysis (b) *ex-situ* pyrolysis (c) chromatogram for the samples WPS 2

In contrast to the *in-situ* catalysis, the amount of wax was reduced in *ex-situ* catalysis over zeolites (Fig 7b). This is clearly due to enhanced cracking caused by the preheating of the catalyst bed during *ex-situ* process.

Note that, for the *in-situ* catalysis, the feedstock and catalyst were heated simultaneously. During heating up, the occurrence of cross-linking reaction might be favored over cracking when the temperature of the reaction zone was still in the low-temperature regime and had not reached the final temperature yet. On the other hand, during *ex-situ* catalysis, the catalyst bed was preheated to the target temperature before pyrolysis vapors (produced by thermal

treatment) came in contact with the catalyst particles. Therefore, in this case, the cracking reactions dominated and consequently less wax was produced as compared to the *in-situ* catalysis. This is also shown in Fig. 7c, where the concentration of the heavier molecules (*e.g.* peak no. 12) was reduced during the *ex-situ* catalysis. Moreover, the use of zeolite catalyst (employed in *in-situ* or *ex-situ*) increased the yield of benzene, toluene and ethylbenzene as compared to thermal and thermo-catalytic pyrolysis over MgO. This can be ascribed to the Bronsted acidity of the catalyst. Zeolite catalysts with Bronsted acid site are effective in depolymerizing styrene dimers to give styrene, toluene, ethylbenzene etc. (Wang et al., 2020).

4. Conclusion

Thermo-catalytic pyrolysis of PS-based plastic wastes was carried out. The influence of different feedstock materials, catalysts, and operation modes on the product distribution was studied. The main findings and concluding remarks are given as follows:

Regardless of the feedstock material (Virgin PS, expanded PS, hard PS-based packing material and HIPS), catalyst type (acid and base) and operation mode (*in-situ* and *ex-situ*), oil was obtained as the main pyrolysis product with styrene monomer as the major oil component.

Based on the similarity of their behavior in TGA as well as in thermal and thermo-catalytic pyrolysis, the feedstock materials can be divided into two groups. The first group contains virgin and expanded polystyrene, while the second includes hard PS-based packing material and HIPS.

A plausible explanation for the lower styrene production during pyrolysis of the feedstocks of second group can be the lower overall styrene content which is due to the presence of

additives (e.g. butadiene rubber). Also, in this case, comparatively enhanced formation of mono-aromatics can be attributed to the degradation of styrene butadiene rubber that produces more BTEX compounds.

Solid base catalyst influenced the composition of the pyrolysis products only slightly when compared with the one obtained from the non-catalytic pyrolysis. Also, the textural properties of the base catalyst showed no significant impact on the yield and composition of the pyrolysis oil as compared to thermal pyrolysis. Based on these results, it can be concluded that the product distribution (e.g. styrene and BTEX yields) depends more on the type (e.g. polystyrene content) of PS wastes than on the solid base catalyst and that the use of catalytic pyrolysis in this case may not be worthwhile.

Solid acid (zeolite) catalyst influenced the composition of the pyrolysis oils significantly as compared to the base catalyst and non-catalytic pyrolysis. The *in-situ* catalysis resulted in higher amount of wax which can be ascribed to the cross-linking reactions (occurred at lower temperature) during heating of the feedstock and catalyst mixture. Ex-situ catalysis reduced the amount of wax due to enhanced cracking over preheated acid zeolite catalyst. Moreover, zeolite catalysts (particularly in *ex-situ*) promote the formation mono-aromatics (*i.e.* BTEX) compounds, which can be attributed to their Bronsted acidity. These findings suggest that acid catalysts have the potential of transforming PS-based materials into more valuable compounds. However, in order to further explore the potential of acid catalysts, a detailed study using harsher conditions (e.g. higher temperature), improved textural properties of the catalyst (e.g. S_{BET} , mesoporosity etc.) and/or using two stage pyrolysis, would be of interest for future studies.

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Appendix A. Supplementary material

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