

# Porous Carbons from Plastic Waste

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**Abstract** Thermoplastic polymers (such as polypropylene, polyethylene, polyvinyl chloride, polystyrene, etc.) are major constituents of municipal solid waste. Millions of tons of plastic waste are discarded each year, most of which is either incinerated or dumped in landfills. As an alternative, methods using these wastes as feeds for the production of value-added products such as fuels, carbon nanotubes, and porous carbons have been proposed by various researchers. In recent years there has been considerable research in the area of activated carbon production from plastic wastes and products with high surface areas and pore volumes have been produced. However, no literature survey has yet summarized the findings. Thus, herein, the studies pertaining to the production of porous carbon (such as activated carbon) from plastic wastes are reviewed for the first time. This review is organized on the basis of the type of plastic polymer used as the precursor. The first part covers various thermoplastics, whereas the second focuses more deeply on poly(ethylene terephthalate) (PET). This is because the majority of research in this area has used PET. The low carbon yield may make the production of porous carbons from plastic waste impractical. Hence, the authors suggest an alternative integrated approach for future studies so that porous carbons can be produced as a byproduct during the conversion of plastics to gaseous and liquid products.

**Keywords** Activation methods · Plastic wastes · Polymer pyrolysis · Porous carbon

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## Abbreviations

|      |                              |
|------|------------------------------|
| AC   | Activated carbon             |
| HDPE | High density polyethylene    |
| LDPE | Low density polyethylene     |
| PE   | Polyethylene                 |
| PET  | Poly(ethylene terephthalate) |
| PP   | Polypropylene                |
| PS   | Polystyrene                  |
| PVC  | Polyvinyl chloride           |

## 1 Introduction

Plastic polymers form a considerable portion of the volume of waste produced across the world. Although around 5–15% by weight of municipal solid waste is composed of plastics, this waste stream corresponds to 20–30% of the volume [1]. Around 1.45 million people work in Europe's plastic industry, which generates an estimated 300 billion euros in the EU-27 countries each year. Nonetheless, more than 25 million tons of plastic waste is annually generated in this region [2]. For years, researchers have been looking for various ways to overcome the problems of such large quantities of waste polymers. Currently, the use of landfills and incineration are the two most widespread solutions [3]. However, the increase in cost, environmental concerns, and the decreasing space for landfills make alternative treatment options desirable [4]. Various alternative routes have been proposed in order to process the plastic wastes [5–7].

One area of intense research is plastic pyrolysis, with the goal of obtaining oily products that could be later modified and treated to produce fuels [8]. The issue of plastic waste feedstock recycling has been so popular that from 1999 until now, the “International Symposium on Feedstock Recycling of Polymeric Materials (ISFR)” has been held in Japan (1999), Belgium (2002), Germany (2005), Korea (2007), China (2009), Spain (2011), and India (2013). The issues considered include mechanical and

chemical recycling, life cycle assessment, dehalogenation of plastics containing chlorine and bromine, various reactor designs such as rotary kilns and fluidized beds, and various heating methods such as microwave heating, molten baths and so on. Unfortunately, there is no golden rule that can be employed for optimizing the pyrolysis of all plastic species in a mixture because the optimal temperature for the degradation of one plastic polymer might be too low for another [9].

Catalysts (mostly zeolites) have been employed in order to improve the conditions of the pyrolysis to yield more useful products and lower the operation temperatures. Nevertheless, the produced oils require further processing in order to meet standard fuel qualities [10]. Various problems such as blockages caused by the production of unwanted products such as coke, waxes, and organic acids have been encountered. Another problematic issue is the thermal conductivity of plastics, which is low. Values as low as 0.17 and 0.33 Wm<sup>-1</sup> K<sup>-1</sup> have been reported for the thermal conductivity of polypropylene (PP) and polyethylene (PE), respectively [11, 12]. Although most of these problems have been overcome one way or another and some industrial-scale units are operational in the world today, in general, the scale of production is too small to make these processes economically viable. Political and environmental pressure obliges the continuation of such endeavors [13].

The ultimate/elemental analysis of mixed plastics has shown a carbon content of about 80% mass [14, 15]. Hence, another option for plastic waste treatment could be to target the production of solid and gaseous products instead of liquids. In recent years, there have been many studies that have aimed to do this. The authors have discussed the various methods of obtaining carbon nanotubes from plastic waste polymers in a detailed review elsewhere [16].

The present article will aim to give a literature survey of the studies pertaining to the production of porous carbons (in particular activated carbon) from plastic polymers. As far as the authors are aware, this is the first such review article. Activated carbons (ACs) are porous solids with desirable properties that include high thermal stability, high surface area, and high chemical resistance. The high surface area is produced by the numerous pore networks inside the material. It should be noted that the current IUPAC classification of pores is as follows [17]:

1. Micropore: pore width smaller than 2 nm
2. Mesopore: pore width between 2 and 50 nm
3. Macropore: pore width greater than 50 nm

The pore sizes and volumes are a function of various parameters including the precursor material, the pretreatment of the precursor prior to carbonization, the carbonization process itself, and the activation process carried out after or simultaneously with the carbonization. To date, a variety of materials have been used for AC production, including coals [18], bio and agricultural products [19–23], polymeric materials [24], tires [25], etc. [26]. At the moment, the use of coals and agricultural byproducts seem to be the most widespread industrial production paths [27]. Often, porous carbons investigated in research function better than the commercially available carbons [28, 29]. The economic analyses of AC plants are very sensitive to production yield and the activation route. In addition to plant capacity, another

important parameter in the cost of AC production is the availability and cost of its precursor [30].

This review will be organized on the basis of the plastic polymer used as the precursor for porous carbon production. Section 2 will include studies using various thermoplastics as precursors, whereas Sect. 3 will focus more deeply on poly(ethylene terephthalate) (PET) due to its popularity.

## 2 Porous Carbons from Various Plastic Precursors

### 2.1 *Steam Activation*

Activation with steam, also known as physical activation, has been employed for activated carbon production. Qiao et al. have used hot steam for the activation of PVC, which was prepared in the form of spinnable pitch [31]. The virgin plastics were first held at 260°C for 2 h and at 410°C for 1–2 h. The temperature of the second stage is not increased further because higher temperatures resulted in pitches with poor spinnability. A three-stage heat treatment (260, 360, and 410°C) was also tested but no particular difference was found. In the two-stage process, a weight loss of 58% is seen in the first significant step (200–320°C), which is attributed to the removal of HCl. It is interesting to note that this amount of recovered HCl is almost the same as the theoretical maximum amount of recoverable HCl from PVC (58.4%). The carbon content of PVC is approximately 43%, and the weight loss of the second step is approximately 23.2%, leaving only about 18.4% of the PVC as carbon to be used for AC synthesis. The pitch is spun and in turn stabilized in air without preoxidation treatment. The sample is carbonized at 900°C in the presence of air and finally activated with steam at 900°C for 30–90 min. The obtained activated carbons were predominantly microporous and had surface areas of 1,000–2,000 m<sup>2</sup>/g. In relation to the various activation times, the final yields varied from 4 to 8% of the initial PVC mass. This value corresponds to a yield of 9–18% with respect to the actual carbon content of PVC. Finally, it should be noted that the PVC used in the study was virgin resin material rather than waste. The additives and inorganic substances present in PVC waste might make pitch spinning difficult.

### 2.2 *Chemical Activation*

To obtain high BET specific surface areas ( $S_{\text{BET}}$ , i.e., surface area divided by mass, as measured using the Brunauer–Emmett Teller method) for activated carbons from plastic polymers, chemicals such KOH and NaOH have been used either alongside [32] or after the carbonization step.

In a recent example, the syntheses of activated carbons from different synthetic waste polymers were tested [33]. PVC pellets of 1–3 mm were bought from a

Chinese supplier and PET was obtained from cutting water bottles into small pieces. A 50% solid yield of carbonized residue was claimed after the raw material was carbonized at 600°C in nitrogen. Then, the residue was activated by ground KOH (1:2 plastic to KOH mass ratio) in a nitrogen stream at 850°C. After 90 min of activation, a further burn-off of about 50% occurred. Then the products were washed and dried. These conversions would amount to a final yield of approximately 25%. If these numbers are accurate, they are exceptionally high. Unfortunately, the explanation of the AC preparation procedures published in the study is quite short. Most of the study was centered on the characterization and application of the products with maximum BET surface areas of 2,831 and 2,666 m<sup>2</sup>/g for PET and PVC, respectively. It was speculated that this extremely high surface area is due to the uniform structure of the polymers as well as their small ash content. The adsorption capacities of the products for the remediation of wastewater were tested and it was concluded that in some cases they were more than twice that of the commercial F400 activated carbon. Table 1 contains information regarding the various samples in this study. Figure 1 shows the adsorption isotherms of methylene blue for these polymer-based activated carbons compared to commercial F400. Activated PET and activated PVC showed maximum removals higher than 2 mmol of pollutant per gram of adsorbent. Unfortunately regeneration studies have not been performed yet. The uptake of other liquid pollutants has been tested by the same group elsewhere [34].

PVC is a widely used plastic with a net calorific value of 22 MJ/kg and is used in long-life products such as window frames, flooring, fittings, door frames, and piping, which might not enter the waste stream for decades. PVC composed a little less than 7% of the municipal plastic waste collected in Western Europe in the year 2000 [1]. As an advantage in waste separation, the pieces of PVC are typically big, so their sorting is simple. Polystyrene (PS) and PVC both have an advantage when it comes to separation due to the difference in their densities compared to other plastics [35].

Various studies show that a two-stage heat treatment of PVC can be utilized in order to recover the chlorine content in the form of HCl. The remaining residue can then be used for other purposes such as porous carbon production and/or further volatilization [36]. As an example, the production of activated carbon from carbon residues has been investigated in conjunction with the removal of Cl from PVC containing plasticizer and inorganic filler [37]. After a heat treatment to remove the chlorine, the carbon residues were pre-oxidized at 300°C for 3 h under a flow of air. This was followed by a carbonization of 2 h at various temperatures under a flow of nitrogen. About 40–55% of the solid remained as carbonized residue (the difference in yield depends on the amount of plasticizer and inorganic filler used in the experiments). The material was then impregnated with KOH at various ratios, dried, and activated at 750°C in the presence of nitrogen for 1 h. The final yields after the activation were unfortunately not reported. When comparing the different samples, although the presence of the plasticizer and inorganic filler prolonged and hindered the evolution of HCl, they also improved the final AC product surface area.

**Table 1** Properties of the waste polymers and produced activated carbons (elemental composition on a dry mass basis)

|                                                           |                                 | Sample name |                       |      |               |      |               |
|-----------------------------------------------------------|---------------------------------|-------------|-----------------------|------|---------------|------|---------------|
|                                                           |                                 | Tire rubber | Activated tire rubber | PVC  | Activated PVC | PET  | Activated PET |
| Elemental composition % (results from elemental analysis) | C                               | 62.1        | 82.9                  | 40   | 86.7          | 62   | 80            |
|                                                           | H                               | 6.7         | 2.01                  | 5.36 | 1.31          | 5.2  | 1.76          |
|                                                           | N                               | 0.47        | 0.43                  | n/d  | 0.5           | n/d  | 0.52          |
|                                                           | O                               | 5.4         | 2.66                  | 17   | 6.12          | 32.8 | 16.6          |
|                                                           | S                               | 1.53        | 1.5                   | n/d  | n/d           | n/d  | n/d           |
|                                                           | Cl                              | n/d         | n/d                   | 21.4 | n/d           | n/d  | n/d           |
| Surface atomic composition % (results from XPS analysis)  | C                               | –           | 87.5                  | –    | 95.4          | –    | 77.6          |
|                                                           | O                               | –           | 10.3                  | –    | 3.7           | –    | 21.7          |
|                                                           | Si                              | –           | 2.15                  | –    | 0.44          | –    | 0.55          |
|                                                           | Cl                              | –           | 0.07                  | –    | 0.05          | –    | 0.12          |
|                                                           | Sb                              | –           | n/d                   | –    | 0.37          | –    | n/d           |
|                                                           | Pb                              | –           | n/d                   | –    | 0.06          | –    | n/d           |
| Ash content (%)                                           | –                               | 23.8        | 10.5                  | 16.2 | 5.37          | 0.12 | 1.17          |
| Pore structure of the materials                           | $S_{\text{BET}}$                | –           | 398.5                 | –    | 2,666         | –    | 2831          |
|                                                           | ( $\text{m}^2/\text{g}$ )       |             |                       |      |               |      |               |
|                                                           | $D_{\text{p}}$ (nm)             | –           | 3.81                  | –    | 2.16          | –    | 2.37          |
|                                                           | $V_{\text{tot}}$                | –           | 0.38                  | –    | 1.44          | –    | 1.68          |
|                                                           | ( $\text{cm}^3/\text{g}$ )      |             |                       |      |               |      |               |
|                                                           | $V_{\text{micro}}$              | –           | 0.11                  | –    | 0.25          | –    | 0.25          |
|                                                           | ( $\text{cm}^3/\text{g}$ )      |             |                       |      |               |      |               |
|                                                           | $V_{\text{mes}}$                | –           | 0.27                  | –    | 1.19          | –    | 1.43          |
|                                                           | ( $\text{cm}^3/\text{g}$ )      |             |                       |      |               |      |               |
|                                                           | $V_{\text{mes}}/V_{\text{tot}}$ | –           | 71.1                  | –    | 82.6          | –    | 85.1          |
|                                                           | (%)                             |             |                       |      |               |      |               |

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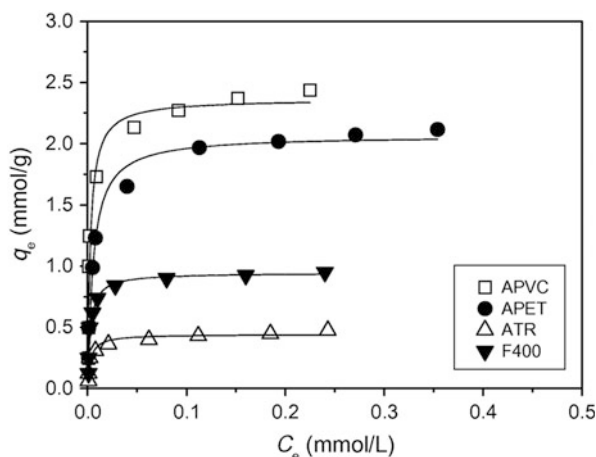
 $S_{\text{BET}}$  BET surface area,  $D_{\text{p}}$  pore size distribution,  $V_{\text{tot}}$  total pore volume,  $V_{\text{micro}}$  micropore volume,  $V_{\text{mes}}$  mesopore volume, n/d not detected

The presence of  $\text{CaCO}_3$  as inorganic filler was particularly effective because it resulted in activated carbons with maximum surface areas above  $1,700 \text{ m}^2/\text{g}$  [37].

Polyurethane foam has also been used as a precursor for AC production by chemical activation with  $\text{K}_2\text{CO}_3$ , and a maximum BET surface area of about  $2,800 \text{ m}^2/\text{g}$  has been obtained. It is speculated that  $\text{K}_2\text{CO}_3$  plays a large role in creating the high obtained surface area [38]. The use of  $\text{K}_2\text{CO}_3$  seems particularly attractive because it does not pose a hazard. The role of  $\text{K}_2\text{CO}_3$  in chemical activation using KOH has been recently studied elsewhere [39].

Refuse paper and plastic fuel (which is a mixture of old paper and plastic with a ratio in the range of 3:7 to 7:3) has also been used to produce porous materials consisting of activated carbon and amorphous  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  [40]. Both physical activation with wet  $\text{N}_2$  (20 mol% steam) and chemical activation with  $\text{K}_2\text{CO}_3$  were tested. Chemical activation resulted in higher BET surface areas (as high as

**Fig. 1** Isotherms and Langmuir model fitting of methylene blue adsorption for various adsorbents [33]. The pollution uptake capacity ( $q_e$ ) is plotted versus the equilibrium pollution concentration ( $C_e$ ). APVC, APET, ATR, and F400 are activated PVC, activated PET, activated tire rubber, and standard F400 activated carbon, respectively. Reproduced with permission from Lian et al. [33] Elsevier



1,330 m<sup>2</sup>/g) and lower ash content ( $\leq 28$  mass%). Physical activation resulted in BET surface areas of approximately 500 m<sup>2</sup>/g with a higher ash content ( $\leq 45$  mass%). Although the samples created by both activation methods showed potential multisorption properties for heavy metals, the chemically activated samples showed higher sorption capacity for organic dye, while the physically activated samples were favorable for removal of heavy metals and oxyanions. The pore sizes of both samples were relatively small as compared to the size of the methylene blue (MB) molecule [41].

### 3 Porous Carbons from PET

Poly(ethylene terephthalate) (PET) is used for bottles, carpets, and food packaging and is a very common waste polymer. It comprises 11.7% of the municipal waste plastic in Western Europe. Due to the fact that over 90% of all PET is used in packaging (in particular drink bottles because of its gas barrier characteristics) the majority of PET becomes waste within less than a year of production [1]. This plastic is commonly seen in studies attempting to derive porous carbons from plastic wastes due to the relatively higher residue that remains after its pyrolysis. A complete section in the review is allocated to PET due to its relative popularity for AC production.

The production of porous carbons is certainly not the only way of treating PET waste. Other recycling methods such as alcoholysis, hydrolysis, and glycolysis have been considered. Glycolysis is the oldest and simplest chemical recycling method for PET. With this technique, glycols are inserted into PET chains in order to obtain bis(hydroxyethyl) terephthalate (BHET), which is itself a substrate for the synthesis of various oligomers including PET. The main drawback of this method is the formation of various products along with BHET of higher oligomers, which are difficult to purify. Alcoholysis (which usually employs methanol) has the

noticeable disadvantage of methanol volatilization; and hydrolysis (which is done under acidic or alkali conditions) results in corrosion and pollution problems [41].

There are a wide range of studies that investigate the production and utilization of activated carbons derived from PET [42–47]. The production of activated carbons from blends such as coal/pitch and PET [48, 49], as well as the preparation of porous polyester fiber by using supercritical carbon dioxide, have also been studied [50].

In contrast to the studies mentioned previously, there has also been an investigation of the use of PET in conjunction with fly ash [51]. Although fly ash has the potential of being used in wastewater treatment its adsorption capacities are limited. Furthermore, the heavy metals within the ash might leach out and cause additional problems. By melting and blending waste PET bottles with fly ash, followed by subsequent thermal treatment, various adsorbents were produced that favorably restricted metal leaching. These were tested for removal of methylene blue and heavy metals from solution. It was speculated that after acid treatment, these adsorbents could ultimately be used for treatment of wastewater from dye processes, steel mills, mine factories, and electroplating plants. The BET surface area of these low-cost adsorbents was no more than  $485 \text{ m}^2/\text{g}$  [51].

Due to the use of heavy metals as catalysts during the synthesis of PET bottles, there are concerns regarding human exposure (in particular by the leaching of antimony into drinking water) [52]. Nonetheless, if plastic bottle manufacturers consider the contamination during the manufacturing process and wash the bottles before their first use, the degree of exposure to these contaminants will be reduced [53]. The presence of small amounts of antimony oxides has been detected in PET pyrolysis studies. The presence of antimony can also slightly decrease the decomposition temperature [54].

### 3.1 Steam Activation

In the 1990s, several studies attempting to produce ACs from PET emerged. ACs produced from PET and cellulose sheets with BET surface areas of 1,190 and  $780 \text{ m}^2/\text{g}$ , respectively, were compared and contrasted [55]. First, the materials were carbonized at  $700^\circ\text{C}$  in the presence of nitrogen. Although unfortunately the carbon yield was not reported, judging from other similar studies by the same authors it can be predicted to be about 20% [56]. The carbonized chars were subsequently activated with steam diluted with nitrogen (1:1 ratio) at  $900^\circ\text{C}$  until a burn-off of 50% related to the mass of the char was obtained. Based on other studies, the final yield compared to the initial amount of PET was 9–12%. The details of the yields can be seen in Table 2. The researchers went on to investigate the adsorption of a binary benzene–methanol liquid mixture and concluded that morphological differences exist in the ACs that correspond to the different links between their crystallites [55].

László and coworkers conducted more studies regarding the production of porous adsorbents from PET in the following years [57]. The samples were first



**Table 2** Yields after treatment, relative to initial carbonaceous precursors

| Precursor         | Carbonization (wt%) | Activation (wt%) |
|-------------------|---------------------|------------------|
| Polyacrylonitrile | 48–52               | 26–31            |
| PET               | 17–21               | 9–12             |
| Cellulose         | 17–22               | 11–14            |

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carbonized under nitrogen flow at 750°C for 30 min, and then activated at 900°C under steam and nitrogen flow (1:1 molar ratio) for 90 min [58]. Microporous carbons were produced with BET surface areas of 1,170 m<sup>2</sup>/g, a total pore volume of 0.625 cm<sup>3</sup>/g, an amphoteric surface (due to oxygen functionalities), and with a majority of basic functional groups. The adsorption of phenol and 2,3,4-trichlorophenol were studied at various pH values. It was found that both the pH and pK of the phenols affect the adsorption mechanism. The final yield was 9–12%. The researchers proposed that these carbons could be used for wastewater treatment because, although the majority of their pores were micropores, a sufficient amount of mesopores were also available, which play a vital role for the diffusion of the pollutants into the sample [59]. The same preparation and activation method for PET was used by the researchers in a later study [60]. The researchers concluded that the surface properties and morphologies of the carbonaceous products are dependent on the heat treatment method as well as the temperature applied for their preparation. Surprisingly, the porosity and surface areas were found to decrease as the temperature and heat treatment increased. This is because the pore structure showed a gate effect and the open pores closed during heat treatment. As temperatures rises, however, the carbon skeleton becomes much more ordered.

In a later study, additional treatment was carried out on the porous products from PET [61]. The samples were treated with nitric acid to obtain various degrees of surface functionalization. Additional heat treatment was also sometimes incorporated for modification and distribution of some surface functional groups. Overall, various porous carbons with BET surface areas of 1,200–1,500 m<sup>2</sup>/g were obtained. Buffered aqueous phenol and aniline solutions were used to assess the waste removal capacity of the products. It was seen that the concentration of the pollutant molecule was always more than that of the functional groups, meaning that “the major contribution to the adsorption came from the dispersion effect” and that “the enhancement of the interactions was obtained only through attractive electrostatic forces” [61]. Various differences were seen between phenol and aniline. For example, phenol adsorption showed a maximum peak, whereas aniline adsorption strongly increased monotonically with pH. The maximum uptake of phenol was higher than that of aniline. In addition, the lower solubility of aniline in water did not lead to increased adsorption capacity. Complementary techniques and analysis of the porous carbons was carried out elsewhere [62]. Surface oxygen content was not greatly increased due to acid treatment at room temperature and the adsorption properties and structural parameters remained unchanged. Nevertheless, treatment with boiling acid resulted in significant differences in morphology, leading to approximately 75% loss of BET surface area.

Further examination of phenol adsorption by such porous carbons was carried out [63]. Both adsorption and desorption of phenol were seen to be influenced by not only the pH of the solution, but also by the method of pH setting. The thermal regeneration of the carbon adsorbents was studied and it was found that with unbuffered solutions, only a part of the surface area could be regenerated. If NaOH is used for regeneration, the surface area of the carbons will significantly increase; and when physisorption is dominant no substantial variation in the surface area is observable. It is noteworthy that surface oxidation lessens the adsorption capacity for phenol and favors physisorption. Carbon deposition and subsequent pore blocking during thermal regeneration are also reduced when high concentrations of surface acidic groups are present.

### 3.2 Chemical Activation

The combination of chemical activation (heat treatment by sulfuric acid) and physical activation (by steam) has been investigated [64]. The impregnation coefficient of 28% was found to be particularly important. An increase in the activation temperature enhanced the surface area and pore volume in addition to increasing burn-off. With a yield of 15%, a maximum BET surface area of approximately 1,000 m<sup>2</sup>/g was obtained. The adsorption of methylene blue and iodine were also examined. The effects of soaking the PET precursors with chemicals (in particular sulfuric acid) have also been investigated elsewhere [65, 66].

In studies by other researchers, compounds such as Ca(OH)<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> together with HNO<sub>3</sub> treatment have been used to produce better quality ACs [67]. Nakagawa et al. used a mixture of several metal salts (5 wt%) and acid pretreatment (HCl for 24 h) prior to steam activation and discussed the effects of the various mixtures on the pore properties [68]. The samples showed a larger mesoporosity than carbons with no such pretreatment. Although the mesopores were dependent on the kind of metal salt used, the microporous structure was not influenced by this factor. Compared with commercial carbon, these samples show better adsorption capacity for C<sub>4</sub>H<sub>10</sub>. The details of the various prepared samples can be seen in Table 3. It should be noted that the values reported for “burn-off” are relative to the chars produced from prior pyrolysis of the PET at 773 K for 1 h under nitrogen flow. So, in fact, the final yields compared to the initial waste material are much less [68]. In addition to PET, the researchers applied their method to waste tires, refuse-derived fuel, and waste generated during lactic acid fermentation from garbage [69]. The surface of PET-derived adsorbents had a fairly strong hydrophobic nature. Phenol and Black5 adsorption were tested and it was concluded that the adsorption capacities of the samples are comparable to commercially available activated carbon and that these porous carbons are suitable for the adsorption of bulky molecules in aqueous solutions.

Increasing the hydroxide content in the treatment often increases the micropore volume and the formation of mesopores, while an increase in nitrogen flow enhances ultramicropore volume and homogenous porosity, yielding molecular

**Table 3** Properties of prepared porous carbons from the mixing of PET pellets with 5% metal compounds, followed by acid treatment and subsequent steam activation

| Chemical                                                  | Activation time (min) | Burn-off (wt%) | $S_{\text{BET}}$ ( $\text{cm}^2/\text{g}$ ) | $V_{\text{mic}}$ ( $\text{cm}^3/\text{g}$ ) | $V_{\text{mes}}$ ( $\text{cm}^3/\text{g}$ ) |
|-----------------------------------------------------------|-----------------------|----------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| None                                                      | 0                     | 12.5           | 394                                         | 0.21                                        | 0.04                                        |
|                                                           | 5                     | 12.7           | 456                                         | 0.24                                        | 0.06                                        |
|                                                           | 120                   | 68.7           | 1,450                                       | 0.72                                        | 0.13                                        |
|                                                           | 240                   | 77.8           | 1,740                                       | 0.93                                        | 0.15                                        |
| $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$      | 0                     | 13.2           | 396                                         | 0.20                                        | 0.04                                        |
|                                                           | 5                     | 18.0           | 521                                         | 0.25                                        | 0.08                                        |
|                                                           | 150                   | 63.7           | 1,460                                       | 0.66                                        | 0.27                                        |
|                                                           | 180                   | 85.7           | 2,190                                       | 0.81                                        | 0.90                                        |
| $\text{Ca}(\text{OH})_2$                                  | 0                     | 25.0           | 419                                         | 0.21                                        | 0.07                                        |
|                                                           | 5                     | 29.4           | 495                                         | 0.23                                        | 0.08                                        |
|                                                           | 150                   | 60.6           | 1,200                                       | 0.55                                        | 0.19                                        |
|                                                           | 180                   | 81.0           | 1,960                                       | 0.86                                        | 0.50                                        |
| $\text{CaCO}_3$                                           | 0                     | 14.4           | 421                                         | 0.22                                        | 0.09                                        |
|                                                           | 5                     | 20.7           | 446                                         | 0.23                                        | 0.05                                        |
|                                                           | 150                   | 57.1           | 1,170                                       | 0.59                                        | 0.14                                        |
|                                                           | 240                   | 87.5           | 2,180                                       | 0.93                                        | 0.78                                        |
| $\text{ZnO}$                                              | 0                     | 13.9           | 416                                         | 0.20                                        | 0.09                                        |
|                                                           | 5                     | 20.5           | 459                                         | 0.25                                        | 0.05                                        |
|                                                           | 1,150                 | 61.6           | 1,240                                       | 0.66                                        | 0.16                                        |
|                                                           | 240                   | 85.9           | 2,240                                       | 1.10                                        | 0.87                                        |
| $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ | 0                     | 15.6           | 370                                         | 0.17                                        | 0.03                                        |
|                                                           | 5                     | 23.3           | 493                                         | 0.27                                        | 0.04                                        |
|                                                           | 150                   | 63.5           | 1,220                                       | 0.66                                        | 0.11                                        |
|                                                           | 240                   | 85.1           | 2,080                                       | 0.82                                        | 0.61                                        |

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$S_{\text{BET}}$  BET surface area,  $V_{\text{mic}}$  micropore volume,  $V_{\text{mes}}$  mesopore volume

sieves. An increase in the pyrolysis temperature while other parameters remain constant increases the micropore volume [70]. Plasma pretreatment of PET with a microwave apparatus prior to carbonization showed positive results, which could help reduce the need for a subsequent activation step [71]. The use of these carbons as electrode material in supercapacitors has also been investigated by the group of researchers [72].

Parra and coworkers also focused on the production of porous carbons from PET [73, 74]. Sometimes, the surfaces of the produced activated carbons do not have enough strength for particular adsorbate–adsorbent interactions. When facing such a problem, it is possible to modify the chemistry by incorporating heteroatoms such as nitrogen on the AC. As an example, PET from soft-drink bottles was compounded with different functionalities, namely acridine, carbazole, and urea. PET and the N-compound were mixed and stirred (1:1 ratio) in a solution of water containing KOH. Then, the slurry mixture was vacuum-dried overnight followed by heating up to a 30-min carbonization at 500°C. Secondary interactions and

reactions occur during the carbonization, which incorporates nitrogen into the carbonized material. This alteration significantly influences pore structure and pore size. The researchers went on to examine how the adsorption of CO<sub>2</sub> is affected by this nitrogen enrichment. Results showed moderate effectiveness, and indicated that in addition to the surface area and the nitrogen content, the nature of the N-functionalities is important [75]. Modification of activated carbon from PET by urea impregnation and pyrolysis has shown an increase in the mean pore size, total pore volume, and the point zero charge. By contrast, sodium hydroxide treatment reduced the total pore volume and mean pore size of PET-based activated carbons. This was not the case for cork-based or other activated carbons [76].

### 3.3 Carbon Dioxide Activation

Almazán-Almazán et al. attempted to change the textural properties of activated carbons from PET by controlling various variables and showed that these carbons can be tailored to range from molecular sieves to samples with variant pore sizes and high adsorption volume [70]. Chars were obtained after pyrolysis at 800 and 950°C with 19% yield. Subsequent activation under CO<sub>2</sub> flow took place for 4 or 8 h. The activation resulted in further burn-offs of 81–87%. In the carbonization process at 800°C under carbon dioxide, the amorphous carbon is eliminated but the micropore system is not affected. These porous samples show molecular sieve behavior for cyclohexane/benzene as well as 2,2-DMB/benzene pairs. At 950°C, however, micropore textural characteristics are changed and the samples do not exhibit molecular sieve behavior due to constrictions at the entrance of the micropores [77].

Porous materials with high capacities have been proposed for the storage of gases such as hydrogen, methane, and carbon dioxide. In gas storage, the gaseous molecules accumulate in the pores of the sorbent material. Various adsorbents have been developed and tested. Studies show high dependence on the surface area, porosity, and pore-size distribution. Regardless of which type of adsorbent is used, the following characteristics are favorable [78]:

1. The adsorbent should be composed of light elements
2. The adsorbent should have high stability under working conditions
3. The adsorbent should be chemical inert – especially towards the adsorbed gas
4. The density of the material should be high as to avoid undesirable large volumes

High hydrogen uptake, equal to that of other high-technology carbon materials, is possible with the ACs produced from PET. In a particular study, PET waste was first pyrolyzed in a quartz tube reactor to yield around 20% char. Further activation was carried out under a CO<sub>2</sub> flow of 10 mL/min at 925°C [79]. Samples with different activation degrees were obtained and denoted as PC#, where # is a number showing the percentage of burn-off resulting from activation (PC12, PC35, PC58, and PC76). Although the samples were not highly ordered structures, XRD analysis showed that elongation of the activation process (and thus additional burn off) increased the

**Table 4** BET surface areas of various samples as well as adsorption capacities obtained from phenol and naphthalene breakthrough curves

| Sample <sup>a</sup> | BET surface area (m <sup>2</sup> /g) | Adsorption capacity (mg/g) |                          |
|---------------------|--------------------------------------|----------------------------|--------------------------|
|                     |                                      | Phenol <sup>b</sup>        | Naphthalene <sup>c</sup> |
| PC12                | 668                                  | 125                        | 24                       |
| PC35                | 1,405                                | 200                        | 26                       |
| PC58                | 1,920                                | 239                        | 27                       |
| PC76                | 2,468                                | 291                        | 28                       |
| Q                   | 1,149                                | 289                        | 30                       |
| CM                  | 849                                  | 263                        | 24                       |
| F400                | 1,164                                | 346                        | 33                       |

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<sup>a</sup>PC12, PC35, PC38, and PC58 are PET-derived porous carbons of increasing degree of activation (see text). Q, CM, and F400 are three commercially activated carbons

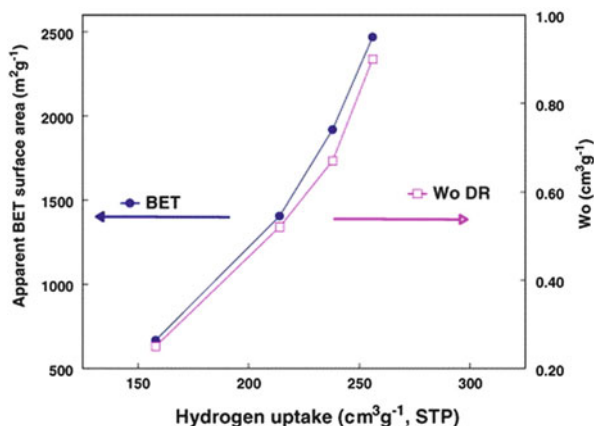
<sup>b</sup>Solution of phenol (2,000 ppm)

<sup>c</sup>Saturated solution of naphthalene (30 ppm)

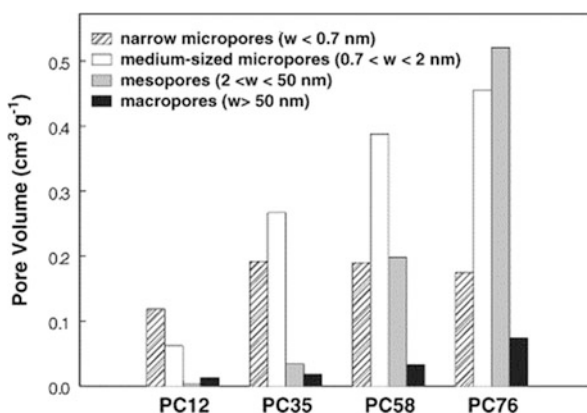
crystallographic parameters of the crystallites to some extent. This could be due to two reasons: first, the disordered fraction of the carbon is more liable to destruction during activation because it is more reactive; and second, the longer activation time may cause some ordering to take place. The hydrogen adsorption capacities of the samples were studied in the 0–1 bar pressure range and showed reversible physisorption in all samples. The maximum hydrogen uptake (2.3%) was by the PC76 sample at  $-196^{\circ}\text{C}$ . The adsorption seems non-dissociative since no hysteresis is seen in the uptake–release process. It is thought that higher hydrogen adsorption is observed in samples with more activation due to their increased volume of micropores [80]. The BET surface areas of various samples, as well as adsorption capacities obtained from phenol and naphthalene breakthrough curves, can be seen in Table 4 (Q, CM, and F400 are three commercially activated carbons). Figure 2 shows the correlation of  $\text{H}_2$  adsorption capacity with surface area and the volume of the micropores. Figure 3 is a depiction of the pore size distribution of the samples with an increase in heat treatment/burn-off [79].

Parra and coworkers also investigated the removal of the widely used drug ibuprofen using such activated carbons [81]. For adsorption of ibuprofen, the existence of mesopores is vital for accessibility to the inner porosity. In addition, the microporosity must be large enough for the compound molecule. The PET porous carbons outperformed the adsorption capacity of commercial activated carbons for the targeted drug. However, the adsorption kinetics were much slower due to the lack of enough mesopores to establish an internal transport network in the adsorbent (less than 10%). Nonetheless, high ibuprofen uptake was achieved over a longer pH range by the PET-derived carbons than by commercial adsorbents. This is linked to the basicity of the PET-derived carbons, due to the delocalized  $\pi$  electron density of their graphene layers, which may act as Lewis base sites for adsorbing protons [82].

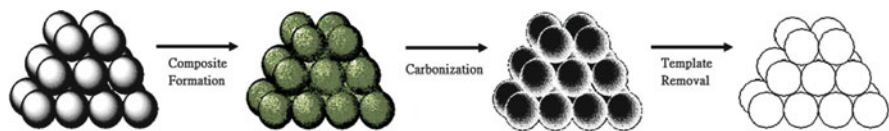
**Fig. 2** Correlation of  $H_2$  adsorption capacity with surface area and the volume of the micropores ( $W_0$ ). Reproduced with permission from Parra et al. [79] Elsevier



**Fig. 3** Pore size distribution of PET-derived porous carbon samples with the increase of heat treatment/burn-off. Sample number indicates the percentage of burn-off resulting from activation: PC12, PC35, PC58, and PC76 signifying 12, 35, 58 and 76% respectively;  $w$  pore width. Reproduced with permission from Parra et al. [79] Elsevier



The Iranian team of Esfandiari and coworkers has also investigated activated carbon production from PET [83]. Carbon dioxide activation was used and the effects of variables such as temperature, heating rate, flow rate, and duration of heat treatments were investigated. It was observed that the most influential parameters are the activation time, activation temperature, and carbonization time. At the expense of further burn-off, the iodine number of the sample was seen to increase with elongation of the activation time. The experimental values for the iodine number were in good agreement with those obtained by the Taguchi optimization model [84].



**Fig. 4** Illustration of hard template method for porous carbon production. Modified and adapted with permission from [86] Copyright 2011 American Chemical Society

## 4 Hard Template Method

Producing porous carbons from templates has a general three-step procedure. First, a composite is produced from the carbon precursor and the template. Then, the mixture is carbonized. Finally, the template is removed [85]. A schematic of the hard template method is provided in Fig. 4.

A good review has already been published on the production of porous carbons by mixing carbonaceous precursors with MgO precursors, subsequent carbonization, and the dissolution of the MgO substrate by a diluted acid [87]. The carbon precursors included (but were not limited to) thermoplastics such as poly(vinyl alcohol) and PET. Even though there is no classic “activation” method used in this process, BET surface areas as high as  $2,000 \text{ m}^2/\text{g}$  and large pore volumes as high as  $3 \text{ mL/g}$  are obtainable. Interestingly, as can be seen from Fig. 5, the ratio of MgO to precursor does not affect the yield when poly(vinyl alcohol) or hydroxyl propyl cellulose is used as the carbon source. Porous carbon yield from PET is dependent on the mixing ratio.

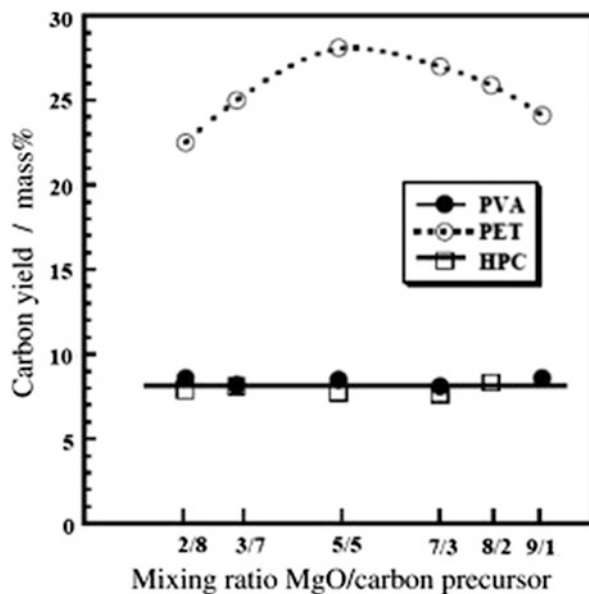
In addition to the fact that the resulting materials are obtained in powder form, the following four advantages have been distinctly mentioned for this method:

1. The MgO template is easily removable with a non-corrosive acid
2. The MgO is recyclable
3. Although the arrangement of mesopores in carbon is random, the size and volume of the mesopores in the porous carbon can be tuned by adjusting the MgO precursor
4. Various carbon precursors can be selected for tuning the size and volume of resulting micropores

These porous carbons, referred to as MgO-templated carbons, have been applied in various areas such as electrodes for electric double-layer capacitors [88], as absorbents for gasoline, and as anodes for lithium ion batteries. The application of these MgO-templated porous carbons has been reviewed elsewhere in Japanese [89].

The use of polystyrene-based materials has also been investigated for porous carbon formation with the hard template method using amorphous silica gel, mesoporous alumina, and microporous zeolites as inorganic templates [90].

**Fig. 5** Dependence of porous carbon yield on mixing ratios with MgO. PVA polyvinyl alcohol, PVC polyvinyl chloride, HPC hydroxypropyl cellulose .Reproduced with permission from Morishita et al. [87] Elsevier



## 5 Outlook and Future Prospects

Low production yields seem to be the main hindrance to the feasibility of producing porous carbons from plastics. Lower pyrolysis temperatures do give higher yields of solid amorphous products; however, these carbons require further high-temperature processing for activation, which would in turn cause additional burn-off [3] [31]. In addition, the residues from plastic waste pyrolysis often leave behind inorganic impurities and additives. Hence, using them to produce solid products such as activated carbons might incur further problems. With calorific values of about 20 MJ/kg, it has been suggested that these solid residues be used as fuels on a par with brown coal [91]. If the low yields of the process are not to cause concern, the justification would lie in looking at porous carbon products as “byproducts” alongside the simultaneous production of other gaseous and/or liquid products with heat. Only in such a condition would low solid porous carbon yields be economically attractive.

Another option would be to employ an alternative method for plastic carbonization that would overcome the problem of low yields posed by classic carbonization and activation methods. A possible route would be the employment of pressurized pyrolysis. For purposes other than activated carbon production, hydrocarbon precursors have been heated under pressure to produce solid carbon products with high yields and high purity [92–94]. As an example, exceptionally hard carbon microspheres have been produced from PET waste via the closed autoclave method. This autogenic method has been patented for the production of carbon spheres for use in batteries [95]. Pol et al. further explained their method in a more extensive article [96]. In order



to overcome the problems associated with the separation of various plastic types, Pol et al. evaluated the process for mixed polymers, namely low density polyethylene (LDPE), high density polyethylene (HDPE), poly(ethylene terephthalate) (PET), and polystyrene (PS). Most of the break down is presumed to occur between 600 and 700°C. The conversion of the plastics to solids in this study resulted in yields ranging from 30 to 55%, with 40% being characteristic. The plastic polymers in this particular study (which were processed together) account for more than three quarters of all plastics found in municipal solid waste. The high-pressure processing of combined plastics is particularly favorable because in plastic recycling it is difficult to obtain homogeneous streams from household waste due to their variety. One of the main obstacles is the existence of food contamination on lightweight plastics. Due to energy requirements, it is often not justifiable both economically and environmentally to clean and recycle such plastics. That is why almost all selective collection schemes in the EU for household waste plastics focus on bottles that are mostly composed of PET and HDPE [1]. Also, the obtained solid yields of high-pressure pyrolysis are particularly important because plastics such as LDPE and HDPE normally produce very minute amounts of solids under atmospheric carbonization. Furthermore, high pressure pumps/compressors are not required in the proposed high-pressure system. This is because the utilization of an autoclave can lead to high pressures just by containing the gases evolving during the break down of the polymers. The economic importance of this phenomenon should not be overlooked. Nonetheless, the main obstacle of such high pressure systems is the capital cost of high pressure equipment, including the alloy that the reactor must be constructed from.

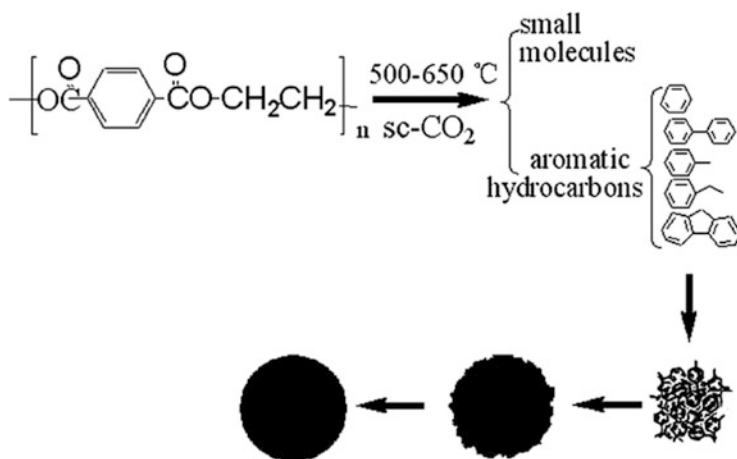
As early as the 1970s, Inagaki et al. considered the pressure pyrolysis of plastic products[97]. Generally, when pressures are applied to the evolved gases during the reaction of a precursor, the carbonization behavior changes and the carbon products are different from those obtained without pressure. The differences can be seen in the structure, properties, and even the morphology of the residue carbon particles. It is important to note that although the solid yield is increased for all carbonaceous precursors, the magnitude of the increase is dependent on the precursor material. Again, it was shown that although the atmospheric pyrolysis of PE does not leave behind significant residues under atmospheric heat treatment, considerable solid yields are obtained under pressure. When powder mixtures of PE with the addition of a smaller mass percentage of PVC (5–30%) were carbonized in a gold tube under a pressure of 10–30 MPa, solid yields as high as 45% were obtained [98–100]. The process is also applicable when polypropylene (PP) is used to replace PE. When a specially designed autoclave is used instead of a gold tube, the yield falls to about 30% [101]. The effects of some impurities on the residue product in a pressurized method have also been studied [102].

If the temperatures and pressures of the pressurized carbonization are not high enough, less solids will emerge and a high amount of liquid will be obtained [103]. With higher pressure, the carbon number distribution of products shifts to lower molecular weights. At lower temperatures, the co-pyrolysis of plastics has been shown to produce different products compared to when individual polymers

**Table 5** Solid carbon yields after treatment for various durations and temperatures

|                       | Treatment conditions |               |               |                 |               |               |               |               |
|-----------------------|----------------------|---------------|---------------|-----------------|---------------|---------------|---------------|---------------|
|                       | 500°C,<br>3 h        | 600°C,<br>3 h | 650°C,<br>0 h | 650°C,<br>0.5 h | 650°C,<br>1 h | 650°C,<br>2 h | 650°C,<br>3 h | 650°C,<br>9 h |
| Carbon yield<br>(wt%) | 23.8                 | 27.0          | 13.0          | 22.7            | 33.5          | 42.1          | 45.4          | 47.5          |

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**Fig. 6** Solid carbon yields after treatment for various durations and temperatures. Reconstructed from Wei et al. [105]. Copyright 2011 American Chemical Society

are used. Aromatic compounds are speculated to have a role in increased char formation due to the condensation of the aromatic ring structure [104].

Adding CO<sub>2</sub> into an autoclave system to create supercritical conditions has also been considered. Soft-drink PET bottles were used as precursors and 1.5 g of the PET cut foil was placed inside a 25-mL stainless steel autoclave alongside 12 g of solid CO<sub>2</sub>. The mixture was kept at 350–650°C for 3 h under autogenic pressures, prior to being naturally cooled to room temperature, washed, filtered, and dried. As can be seen in Table 5, the yield increased with reaction time and temperature. At a temperature of 650°C, the carbon yield increased from 22.7 to 45.4 as reaction times increased from 30 min to 3 h. At a temperature of 500°C, the yield stood at 23.8 after 3 h. Elemental analysis showed that the PET sample (61.73% carbon prior to reaction) contains 93.15% carbon after 3 h reaction at 650°C. Figure 6 shows the formation mechanism. When no dry ice was used (1 g PET/16.67 cm<sup>3</sup>), a coke cake rather than carbon spheres was obtained. Increasing the amount of PET (g PET/cm<sup>3</sup>) resulted in formation of carbon spheres. The researchers indicated that when the PET precursor is smashed into a powder (and not used as a foil), then multiple conglomerates of irregular carbon spherules appear with larger BET

surface areas (values not reported). Unfortunately, obtaining a larger BET surface area is only passingly mentioned by the researchers but not fully explored [105].

The hopes of generating pores in solid carbon spheres formed under pressure seems to be a valid supposition because other non-porous carbon spheres have been successfully activated previously, showing large increases in specific surface areas [106, 107]. As an example, Yuan et al. [108] were able to activate hard carbon spheres with initially low surface areas in molten KOH at 600°C for 1–2.5 h. Measurements showed that depending on the KOH/carbon ratio, the specific surface areas could increase to more than 1,100 m<sup>2</sup>/g. Elsewhere, solid carbon spheres derived from glucose have been activated with KOH, resulting in a 100-fold increase of their surface area from 13.9 to 1,283 m<sup>2</sup>/g [109]. Meanwhile, although some other researchers have failed to increase the BET surface area from low surface area carbon spheres, they were nevertheless able to achieve satisfactory adsorption of compounds during experimentation [110].

The use of various pretreatments of the plastic wastes such as chemical soaking, heat treatments, microwave, and plasma treatments, etc. in conjunction with the pressurized method might be attractive areas for future research. Co-pyrolysis with other wastes such as food wastes is also plausible. Much work has been carried out on other pressurized carbonization methods such as biomass hydrothermal carbonization [111, 112]. If an industrial process is to emerge from the research, the combined use of various carbon sources would be attractive for economy-of-scale purposes. Producing porous carbons for further applications from plastic wastes would not only yield useful products from cheap precursors, but it would also help reduce the problems associated with the ever-growing plastic waste stream.

Overall, not many studies utilizing the pressurized method for treating plastic wastes have exclusively focused on the production of porous carbons with high surface areas [113, 114]. Recently, one research group has reported the production of porous carbons and porous carbon composites using a high temperature, high pressure system [115]. The only other study that has addressed the issue of porous carbon production via a high pressure system is in the Chinese language [116]. In the study, SBA-15 was used alongside a surfactant that acted both as a soft template and carbon source. A carbon/silica composite was produced under high pressure, followed by the removal of the silica using H<sub>2</sub>O, ethanol, and NaOH. The final product was highly mesoporous with a narrow pore size distribution.

## 6 Conclusion

Activated porous carbon can be created from plastic wastes by using various activation routes. The ACs can have high BET surface areas, pore volumes, and good adsorption capacities. However, the carbon yields are rather low (usually around 10%). Large volatilization and burn-off under vacuum, atmospheric, and moderate pressure pyrolysis conditions makes the production of AC from plastics less attractive. Nonetheless, coupling AC production from plastic wastes with other processes such as the production of liquid fuels and high calorific value gases could

be helpful in achieving better economic feasibility. Such research is greatly in line with the goals of waste reduction and sustainability.

On the other hand, if only solid carbon products are sought, high pressure pyrolysis could potentially be used. Although hard non-porous spheres have been repeatedly produced by this method, further research is needed to assess the possibility of obtaining porous carbons. The lack of diverse literature regarding the use of plastic wastes as precursors of autogenic methods leaves the door open for further investigations.

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