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# Advancing $CO_2$ Separation through Polyphenylene Sulphide-Based Fillers: A Preliminary Review

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**ABSTRACT**

Efficient removal of Carbon dioxide from biogas, which is consist of methane ($CH_4$) and $CO_2$, is essential to achieve the biomethane standard of ≥95% $CH_4$. Conventional separation methods, such as cryogenic distillation, pressure swing adsorption and amine-based absorption, face significant challenges in terms of energy consumption, complexity and scalability. Membrane-based separation has emerged as a promising alternative, with polymeric membranes offering specific advantages for $CO_2$ removal. However, traditional polymeric membranes encounter issues such as limited selectivity and compatibility, often requiring modifications or the incorporation of fillers. This review explores the innovative application of polyphenylene sulphide (PPS) including porous carbon materials derived from PPS (PCs) and nitrogen-sulphur co-doped (NSPCs) modifications, as organic fillers in polymers that focus on polysulfone membranes to enhance $CO_2$ separation. This review presents state-of-the-art advancements in biogas separation membranes. PPS-based fillers offer the potential to overcome limitations associated with traditional inorganic fillers, providing improved separation efficiency, compatibility and sustainability. This review also discusses the broader implications of enhanced biogas utilization, emphasizing its relevance to sustainable energy goals and environmental policy. The integration of PPS-based fillers addresses limitations associated with conventional fillers, offering enhanced compatibility, increased separation efficiency and improved scalability. By supporting sustainable energy objectives and aligning with environmental policies, this approach offers a pathway toward next-generation membrane technologies for efficient, scalable and sustainable biogas purification.

## 1. Introduction

A good source of energy is biogas, a mixture of gases comprised chiefly of $CH_4$ and $CO_2$ with a range of 55-75% and 25-45%, respectively. The processes of achieving significant upgrading of biogas

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into biomethane gas demand that the $CH_4$ concentration is between 95% and 100% pure [1,2]. In order to use biomethane in heating, generation of electricity or as a natural gas substitute, the biomethane gas needs to be of that high purity due to policy guidelines. Hence, $CO_2$ removal is among the most crucial steps in the biogas process. Amine-based absorption, pressure swing adsorption (PSA) and cryogenic distillation are mostly used as the most common procedures for $CO_2$ separation, but these techniques have some drawbacks [3]. Cryogenic distillation is an energy-intensive process that requires significant chilling and heating to separate gases according to their boiling points [4]. Pressure swing adsorption uses a lot of energy and is expensive because it requires complicated equipment and needs high pressures [5]. Amine-based absorption needs a lot of chemicals and produces waste [6]. These conventional methods require high energy, complex operation and have a bad effect on the environment.

However, polymeric membrane technology is a more effective and environmentally friendly method for $CO_2$ separation than conventional methods mentioned above [7]. The utilization of membrane separation results in decreased energy usage and simple operation based on selective gas permeation through a membrane matrix. Polymeric membranes have selective characteristics; thus, they can successfully separate $CO_2$ from $CH_4$ [8]. The Robeson limit states that the intrinsic trade-offs between permeability and selectivity result in high separation efficiency and selectivity [9].

Recent advancements in membrane technology have focused on incorporating various fillers to enhance the performance of polymeric membranes [10]. Among these, polyphenylene sulphide (PPS) and its derivatives have emerged as promising fillers due to their unique properties, including thermal stability, $CO_2$ chemisorption and compatibility with polymer matrices [11,12]. Additionally, porous carbon materials, including nitrogen-sulphur-doped porous carbons, have shown potential for improving gas separation performance by providing high surface area and tailored pore structures [13,14]. Despite these advancements, no studies have systematically explored the use of PPS-based porous carbon fillers for biogas purification. This presents a significant gap in the development of mixed matrix membranes (MMMs) tailored for efficient and sustainable $CO_2$ separation.

The limitations of conventional $CO_2$ separation methods necessitate the development of cost-effective and environmentally sustainable alternatives. While polymeric membranes show promise, their performance must be further enhanced to achieve high separation efficiency. PPS-based fillers offer potential solutions by improving the thermal stability, permeability and selectivity of polymeric membranes. However, the absence of targeted research on PPS-based fillers for biogas upgrading highlights a critical knowledge gap. Addressing this gap could lead to the development of scalable and efficient membrane technologies for industrial biogas purification, promoting cleaner energy production and sustainability.

This review aims to explore the present condition of PPS and its derivatives as fillers in polymeric membranes for $CO_2$ separation applications. The study addresses the utilization of porous carbon materials obtained from PPS, including possible enhancements via nitrogen-sulphur co-doping, to improve gas separation efficiency, as depicted in Figure 1. The article evaluates the potential of PPS to overcome substantial drawbacks of existing membrane technologies by highlighting the distinct chemical and physical interactions between PPS-based fillers and $CO_2$. The recognized advantages encompass enhanced membrane efficacy, decreased energy usage and streamlined processing, thus facilitating the scalability of PPS-based MMMs for industrial biogas purification.

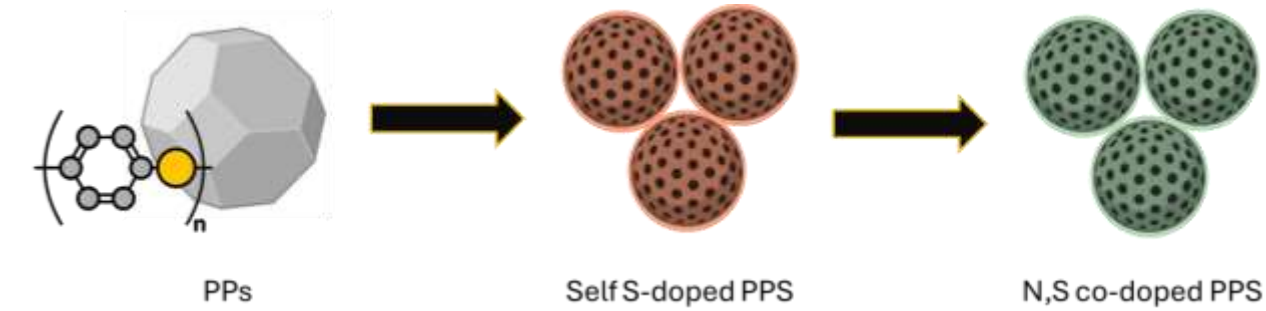


**Fig. 1.** Polyphenylene sulphide-based fillers

## 2. Methodology of $CO_2$ Separation

There are several methodologies that have been used to improve the quality of biogas. This gas separation technology can be categorized into cryogenic distillation, pressure swing adsorption (PSA), amine scrubbing and membrane separation [15-17]. Each of these strategies addresses biogas purification through separate mechanisms, providing an understanding of the various tactics used to increase the energy content and quality of biogas. Through an in-depth examination of these technologies, this part aims to provide insights into their principles and contributions to advancing the efficacy of biogas as a sustainable and versatile energy resource.

### *2.1 Cryogenic Distillation*

Cryogenic distillation is known as a low-temperature separation process used for biogas purification. This technique utilizes the differences in boiling temperatures of various components in the gas mixture [18]. The schematic of cryogenic distillation can be seen in Figure 1. The operational principle involves cooling the gas mixture to temperatures below -150 °C; this method facilitates the condensation of impurity gases such as hydrocarbons in the flue gas [19].

Considering the context of biogas purification, cryogenic distillation has emerged as a highly effective technique for obtaining biomethane of remarkable purity [20]. Cryogenic distillation can achieve purities within the range of 90–95%, with corresponding recovery rates [21]. The performance of cryogenic distillation is significantly enhanced when conducted under low pressure and in the presence of a high concentration of highly condensable components. However, it is crucial to acknowledge the substantial operating costs associated with this process [17]. The high energy demand arises from the need for extreme gas cooling processes and operational pressure.

### *2.2 Pressure Swing Adsorption (PSA)*

Biogas is purified using a physicochemical approach called PSA [22]. This process separates gases, especially $CO_2$, according to how they physically interact with adsorbent materials. Usually made of porous solid materials with high specific areas, these adsorbents maximize the interaction between the adsorbent and the gas. Zeolites, activated carbon, carbon molecular sieves and membrane are often used as adsorbents [23-25].

According to Mustafi *et al.,* [26], the PSA method incorporates multiple columns in order to provide a continuous cycle of separation. The main goal is to get the biogas to its optimum purity, which is typically between 4 and 10 bar. Notably, PSA has a remarkable capability to reduce undesired impurities to minimal levels, reaching parts per million (ppm). As a result, exceptional purity levels—often measured at 99.99%—are obtained and an outstanding 98% of the biogas is recovered. Despite

its effectiveness, the PSA method does have its challenges. One significant drawback is associated with the considerable cost involved in compressing the inlet gas [27]. The compression step is crucial for achieving the pressure conditions necessary for the separation process. Additionally, at full-scale operation, the PSA process demands a substantial footprint, posing logistical and space-related challenges.

### *2.3 Amine-Based Absorption*

The amine scrubbing system employs two stages for enhancing the quality of biogas: adsorption and desorption. According to Awe *et al.,* [28], the amine scrubbing unit features a packed bed (random or structured) and desorption (gas separator 1 and 2) unit with a reboiler for simplified process configuration. Biogas is adsorbate in a packed tower reactor with a cleaning solvent, usually mono-di-ethanol amine (MDEA). The amine in the solvent chemically reacts with biogas $CO_2$ to keep it in solution. The reactor recovers natural gas with high methane purity, frequently surpassing 99.9% [29]. This method effectively operates at lower pressures of about 0.5 to 3 psig. In the second step, the scrubbing solution is heated to boiling to reverse the chemical reaction. This high temperature reverses the chemical reaction, separating $CO_2$ from the cleaning solution [30]. Amine-impacting equipment is corrosive, requires periodic replenishment, requires high energy consumption for desorption, has environmental concerns with amine production and disposal, complex system requirements that cause downtime and has a large physical footprint [28-31].

### *2.4 Membrane Separation*

Membranes can be categorized into two distinct categories: inorganic membranes and polymers, which are differentiated depending on their primary composition. The choice of membrane materials is determined by their higher permeability, selectivity and chemical stability, all of which significantly enhance the efficiency of gas separation [32-34]. Table 1 presents a comprehensive summary of the various characteristics exhibited by different types of membranes, including polymeric, inorganic and mixed matrix membranes. This table highlights the wide range of features that these membranes possess [10,35-38].

**Table 1**
Characteristics of membrane types

| Properties | Polymeric membrane | Inorganic membrane | Mixed-matrix membrane |
|---|---|---|---|
| Material | Organic material (polysulfone, polyimide and cellulose acetate) | Inorganic materials (glass, silica and palladium alloys) | Combination |
| Characteristics | Hard and rigid in the glassy state | High resistance | Combination |
| Separation performance | Low to moderate | Moderate to high | Exceed Robeson's upper boundary |
| Separation mechanism | Solution diffusion | Knudsen diffusion (> 10 Å)<br>Surface diffusion (> 50 Å)<br>Capillary condensation (> 30 Å) | Combination of polymer matrix and dispersed filler materials. |
| Chemical and thermal stability | Moderate | Excellent | Excellent |
| Mechanical strength | Excellent | Poor | Good |
| Handling | Robust | Brittle | Robust |
| Production cost | Low | High | Moderate |

The process of selecting the most suitable polymeric membrane for the separation of $CO_2$ and $CH_4$ involves the careful evaluation of various important aspects. One of the primary considerations is the membrane's selectivity, which refers to its ability to preferentially adsorb $CO_2$ over $CH_4$ in order to produce efficient gas separation [39,40]. Furthermore, the factor of permeability assumes a crucial significance, requiring a careful equilibrium to uphold a high level of $CO_2$ permeability while simultaneously safeguarding the permeability of $CH_4$ [41,42]. The selected polymer must demonstrate chemical stability when exposed to gases and any potential contaminants present in the gas stream, hence guaranteeing long-term performance. Thermal stability is of equal importance in order to endure fluctuating temperature conditions, particularly inside industrial environments [43-45]. Mechanical strength is crucial for enduring the natural pressure differentials encountered during gas separation processes [46]. This is crucial, as it helps to prevent any potential damage to the membrane and ensures its long-lasting durability. The preservation of stable performance necessitates the ability to withstand plasticization under high-pressure circumstances.

## 3. Development of Membrane Separation

### *3.1 Overview of Polymeric Membranes*

Polymeric membranes are regarded as a cutting-edge technology in gas separation, particularly in the purification of biogas composition to meet specific standards. Polymer membranes are favoured due to their ease of production, cost-effectiveness and efficient separation capabilities, as stated in the material [47]. Among these membranes, those composed of polysulfone (PSf) have emerged as particularly effective tools for the separation of $CO_2$ and $CH_4$ within the complex matrix of biogas [48-52]. In polymer membranes, separation performance depends on permeability and selectivity. Gas permeation refers to the process of penetration of molecules through a membrane involving sorption and diffusion processes [53,54], while selectivity refers to its ability to separate gas mixtures into purer forms.

The use of polymer materials can be an alternative to inorganic membranes because the fabrication process is simple and most membranes have a more economical price [55]. Nevertheless, the inherent trade-off between permeability and selectivity observed in polymer membranes poses a significant obstacle to their practical utilization [56]. The establishment of compatibility between fillers or additives and the polymer is vital, as it is crucial to ensure a robust and harmonious link between these substances in order to prevent any potential performance-related complications [64-66]. The issues of cost-effectiveness, membrane thickness and ease of manufacture are crucial factors that underscore the practicality of large-scale industrial applications. In brief, the best polymeric membrane for the separation of $CO_2$ and $CH_4$ incorporates these elements to provide optimal performance in certain applications.

### *3.2 Recent Developments in Mixed Matrix Membrane*

The concept of mixed matrix membranes (MMMs) develops as a potential solution to address the limitations associated with polymeric membranes, as discussed before. A key factor in the development of MMMs is the choice of fillers, which has a significant impact on the MMMs' properties and performance. Fillers are essential for improving the characteristics of the membrane matrix, which raises the effectiveness of gas separation and improves the membrane's overall performance [57]. When choosing a filler, it's important that characteristics like large surface area, pore size adjustability and targeted interactions with target gases enhance gas separation capabilities while also increasing permeability and selectivity [58,59]. Fillers have a crucial role in maintaining the

stability and mechanical strength of the MMM, thereby preventing any potential deformation or collapse during its operational usage [60]. Achieving an ideal morphology characterized by a uniform dispersion of fillers within the polymer matrix is crucial for minimizing agglomeration and maintaining the desired membrane structure, hence enhancing the efficiency of gas separation. Certain fillers also possess the advantageous characteristic of thermal stability, rendering them valuable in scenarios where temperature variations occur.

In order to mitigate adverse effects on the integrity of the membrane and its ability to separate gases, it is imperative to establish compatibility between the filler material and the polymer matrix [58-61]. The profitability of MMMs is contingent upon a meticulous evaluation of filler availability and cost, prioritizing the attainment of desired enhancements while minimizing any significant increase in production expenses. The process of selecting fillers is intricate and encompasses various aspects, contributing to the progress of gas separation technology by offering potential enhancements in efficiency, durability and cost-effectiveness.

## 4. Polyphenylene Sulphide for Mixed Matrix Membrane

Organic materials like polyphenylene sulphide (PPS) have promising potential as fillers for membranes, offering a potential solution to address compatibility challenges. The presence of sulphur functional groups facilitates the enhancement of $CO_2$ solubility in the membrane by means of polar interactions. Furthermore, the presence of sulphur within an aromatic framework can greatly enhance the affinity of $CO_2$ through acid-base interactions [62]. PPS has exceptional mechanical capabilities, remarkable resistance to elevated temperatures, impressive stability across diverse environmental conditions and notable resilience to extremely alkaline and acidic environments, owing to its unique structural arrangement [63].

### *4.1 Properties and Synthesize Method of PPS*

PPS is a thermoplastic polymer characterized by a distinctive molecular structure consisting of sulphur atoms and interconnected benzene rings. PPS is classified as a semi-crystalline polymer and possesses an enduring and flexible character that is highly attractive [64]. PPS is known for its high thermal stability due to its density of 1.34 g/cm$^3$, glass transition temperature of 85 °C and melting temperature of 285 °C [65,66]. Its high thermal stability, withstanding decomposition temperatures over 450 °C in normal atmospheric conditions and maintaining operational temperatures around 200 °C, makes it essential in various industrial sectors.

Polyphenylene sulphides are synthesized through the chemical interaction between 1,4-dichlorobenzene and sodium sulphide in the presence of an NMP solvent. The resulting polymer is subjected to filtration, purification and drying processes. PPS can be synthesized in several structural configurations, including linear, branching or cross-linked forms. The linear polymer, characterized by minimal branching, is commonly employed in applications involving injection moulding and extrusion [67].

### *4.2 Development of PPS as Porous Carbon*

Porous carbons offer significant advantages, characterized by their cost-effectiveness and easy production from a variety of natural and synthetic sources. Widely acknowledged for substantial surface areas and pore volumes, as well as favourable thermal, chemical and mechanical stability, porous carbon-based adsorbents are gaining attention for $CO_2$ capture. Their abundant availability,

physicochemical stability, affordability and the ability to tailor their porosity make them ideal additives for membrane gas separation applications. These materials are frequently synthesized using different synthesis techniques, such as physical activation, chemical activation or a mix of both processes. Prior studies have effectively utilized KOH as a chemical activating agent, leading to the production of highly porous carbons [68,69].

The potential of PPS and its derivatives for $CO_2$ separation technologies is increasingly acknowledged owing to their exceptional stability, cost efficiency and adjustable properties, making them highly appealing for diverse industrial applications. A promising area is biogas purification, wherein PPS-derived porous carbons, especially those doped with sulphur, have demonstrated efficacy in $CO_2/CH_4$ separation, facilitating the generation of high-purity methane appropriate for utilization as a renewable energy source. Moreover, flue gas treatment presents another significant application. PPS-based materials, such as membranes or fillers, are ideal for $CO_2$ capture from flue gases in power plants and industrial facilities due to their resilience to elevated temperatures and corrosive chemical conditions.

The scalability of these materials is a crucial consideration, with techniques such as KOH activation and co-doping offering avenues for increased production capacity. Optimizing activation parameters to attain elevated porosity without sacrificing the material's structural integrity can lower production costs while preserving high performance. Additionally, PPS-derived materials can be incorporated into existing systems, such as MMMs, which amalgamate the benefits of porous fillers and polymeric matrices. These hybrid systems are optimal for gas separation, enhancing both efficiency and cost-effectiveness, thereby rendering them appropriate for extensive $CO_2$ capture applications.

## 5. Exploring the Methodology to Synthesized Porous Carbon Materials

Porous carbon and activated carbon (AC) are carbon-based materials distinguished by their high surface area and intricate internal pore structures, which make them highly valuable across various applications. Porous carbon features a network of pores that can be classified by size into micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm). This pore network provides a significant internal surface area, critical for its functional performance. Activated carbon, a specialized form of porous carbon, undergoes additional processing to enhance its adsorptive properties. It is typically produced by carbonizing organic materials like wood, coal or coconut shells, followed by physical or chemical activation to develop a highly porous structure, often exceeding 1000 $m^2/g$ in surface area.

Porous carbons offer significant advantages, characterized by their cost-effectiveness and easy production from a variety of natural and synthetic sources [68]. Widely acknowledged for substantial surface areas and pore volumes, as well as favourable thermal, chemical and mechanical stability [69], porous carbon-based adsorbents are gaining attention for $CO_2$ capture. Their abundant availability, physicochemical stability, affordability and the ability to tailor their porosity make them ideal additives for membrane gas separation applications. These materials are frequently synthesized using different synthesis techniques, such as physical activation, chemical activation or a mix of both processes. Prior studies have effectively utilized KOH as a chemical activating agent, leading to the production of highly porous carbons [70]. The carbonization reaction is commonly represented by this reaction below [71]. The carbonization reaction, as depicted in Eq. (1), is a crucial process in the production of porous carbon materials. It involves the reaction between carbon and KOH. The subsequent reactions involving the volatile groups from the precursor, as described in Eq. (2), lead to the production of $K_2CO_3$. The metallic potassium, obtained from the reaction between $K_2CO_3$ and

carbon as described in Eq. (3), significantly contributes to the development of porosity in the carbon structure [63].

$$2C + 6KOH \rightarrow 2K_2CO_3 + 2K^+ + 3H_2 \quad (1)$$

$$2KOH + CO_2 \rightarrow 2K_2CO_3 + H_2O \quad (2)$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \quad (3)$$

The synthesis of activated carbon through chemical methods entails either a one-step or a two-step activation process. A biomass precursor is impregnated with a chemical activator and subsequently carbonized at elevated temperatures to yield activated carbon in a single-step process. The two-step procedure initially transforms biomass into biochar *via* thermal treatment, subsequently followed by impregnation and activation to produce biochar-derived activated carbon.

### *5.1 One-Step Activation*

The one-step synthesis via direct pyrolysis is a straightforward and effective technique for generating porous carbon materials. The process entails the thermal decomposition of carbonaceous precursors, including polymers or biomass, at elevated temperatures (400–1000°C) in an inert atmosphere, such as nitrogen or argon, without additional chemical activation. This method involves fewer processing steps and predominantly depends on the intrinsic properties of the precursor to establish the porous structure [72].

The procedure commences with the selection and preparation of an appropriate carbon-rich precursor. Subsequent to drying and grinding the material for uniform heating, it is subjected to pyrolysis in a furnace with an inert gas flow. After carbonization, the material is allowed to cool either naturally or under regulated conditions, subsequently undergoing optional post-processing such as grinding or shaping to enhance its form.

The one-step synthesis provides numerous benefits, such as simplicity, cost efficiency and environmental sustainability, owing to the elimination of chemical activation agents. It is additionally more scalable for industrial manufacturing. This method has limitations, including diminished control over porosity, reduced surface areas relative to chemically activated carbons and reliance on the precursor's intrinsic properties. Notwithstanding these limitations, one-step synthesis continues to be an attractive method for generating porous carbon materials, especially when utilizing plentiful and cost-effective precursors for practical uses.

### *5.2 Two-Step Activation*

The two-step synthesis involves a combination of pyrolysis followed by activation to yield porous carbon materials with improved porosity and surface area. This method offers enhanced control over the pore structure of the final material in comparison to one-step synthesis [73,74].

The process commences with pyrolysis, wherein a carbon-based precursor is subjected to elevated temperatures (400–1000°C) in an inert environment, resulting in the formation of char. The second step, activation, enhances porosity via physical or chemical methods. Physical activation utilizes gases such as $CO_2$ or steam at elevated temperatures (800–1000°C) to generate pores through the selective gasification of carbon atoms. Chemical activation employs agents such as KOH, $ZnCl_2$ or $H_3PO_4$, utilized prior to or during pyrolysis, to facilitate pore development *via* chemical reactions.

The two-step synthesis provides considerable benefits, such as increased porosity, elevated surface areas and customized material characteristics for particular applications. These attributes enhance adsorption capacities and optimize performance in energy storage, catalysis and environmental remediation. Nonetheless, the method possesses limitations, including heightened process complexity, elevated energy consumption and the possible environmental repercussions of chemical reagents. Notwithstanding these challenges, two-step synthesis continues to be an exceptionally effective method for generating high-performance porous carbon materials with meticulous structural control.

### *5.3 Direct Comparison Result*

The comparison of single-stage and two-stage pyrolysis for the synthesis of chemically activated carbon from waste biomass demonstrates notable disparities in specific surface area (SBET), total pore volume (Vtot) and micropore surface area (Smicro). In the single-stage process, biomass is directly infused with a chemical activator (e.g., KOH) and carbonized in one step. This method yielded activated carbon with a reduced $S_{BET}$ of 204.3 $m^2/g$ and a Vtot of 0.134 $cm^3/g$, in contrast to the values of 677 $m^2/g$ and 0.360 $cm^3/g$ achieved through the two-stage process [73]. The two-stage procedure entails pre-carbonization to transform biomass into biochar, succeeded by chemical activation, which improves the porous architecture.

The effect of integrating pre-carbonization with KOH activation is especially significant. The activated carbon produced by the two-step method attained an $S_{BET}$ of 2048 $m^2/g$ and a $V_{tot}$ of 1.32 $cm^3/g$, markedly exceeding the 1186 $m^2/g$ and 0.71 $cm^3/g$ obtained through the one-step method [74]. This enhancement is ascribed to pre-carbonization, which stabilizes biomass morphology and averts structural collapse during high-temperature activation. The intact structure of Lycopodium clavatum during pre-carbonization enhanced the exceptional porous characteristics noted in the two-step process [74].

The micropore contributions were greater in the two-step process, with the $S_{micro}/S_{BET}$ ratio attaining 39.14%, in contrast to 28.48% for one-step activated carbons [75]. The increased microporosity results from the elimination of tarry compounds during activation, which unblocks the pore networks in the biochar. The increased micropore volume (Vmicro = 0.360 $cm^3/g$) resulting from two-stage activation is demonstrated by the elevated position of the adsorption isotherm and the higher SBET value [73]. These factors demonstrate that two-step activation significantly enhances the proportion of micropores within the carbon structure.

Notably, certain studies indicate discrepancies in the identified trends. One study indicated that one-step synthesis resulted in an $S_{BET}$ of 1372.93 $m^2/g$ and a Vtot of 1.45 $cm^3/g$, whereas two-step synthesis produced inferior values of 697.96 $m^2/g$ and 0.55 $cm^3/g$, respectively [74]. These discrepancies may arise from variations in biomass type, activating agent concentration or activation conditions, underscoring the significance of process optimization in attaining desired properties.

At overall, the two-step pyrolysis process, which includes pre-carbonization and subsequent chemical activation, typically surpasses the single-step method in generating activated carbon with superior SBET, Vtot and microporosity. Pre-carbonization's structural stabilization is essential for improving pore development and adsorption characteristics. Nevertheless, discrepancies in findings among studies highlight the necessity for meticulous regulation of experimental parameters to optimize the activation process's efficiency.

## 6. Key Factor to Improve the Porous Carbon Properties

To gain an in-depth understanding of how carbon materials have evolved and how they affect important characteristics such as specific surface area ($S_{BET}$) and $CO_2$ uptake, refer to all of the data provided in Table 1. The data in this table is derived from multiple diverse studies. This study demonstrates the impact of various synthesis processes and activating agents on the production of porous carbon materials, as well as their efficacy in membrane gas separation applications.

The amount of precursor substances to activation agents is a key factor that determines the shape, mechanical properties and structure of the carbon products that are made [76]. An activating agent ratio of approximately 4 is ideal for enhancing porosity through the process of intercalating the carbon structure and enlarging the pores. Nevertheless, exceeding this ratio (more than 6) might result in an excessive increase in intensity, leading to the deterioration of pore walls and a decrease in overall porosity [77].

### *6.1 Activation Conditions*

Studies on KOH activation reveal that $S_{BET}$ is highly influenced by the KOH:sample ratio and carbonization temperature. Choi *et al*., [78] showed that when using a ratio of 3:1 (KOH:sample) and a carbonization temperature of 800°C, there was a significant rise in the $S_{BET}$ from 0.8 to 1460 $m^2/g$. Nevertheless, employing different ratios of 2:1 and 1:1 under the same temperature conditions resulted in reduced SBET values of 1214 and 937 $m^2/g$, respectively. Min *et al*., [79] observed a substantial rise in $S_{BET}$ from 2.94 to 2457 $m^2/g$ while using a KOH:sample ratio of 1:1 and carbonizing at a temperature of 700°C. By adjusting the temperature proportionally, the resulting $S_{BET}$ values were 1318 and 2680 $m^2/g$ at 600 and 800°C, respectively. However, $CO_2$ uptake was less impacted, suggesting a complex relationship between activation conditions, porosity and adsorption performance.

### *6.2 Heteroatom Doping Method*

Heteroatom doping (N, S) significantly improves $CO_2$ uptake in porous carbon materials. Studies have shown substantial increases, with N and S co-doping yielding the highest uptake. The study conducted by Ma *et al.,* [80] revealed a significant increase in $CO_2$ uptake, with levels increasing from 1.56 to 4.30 mmol/g. Shao *et al.,* [81] saw a significant increase in the value, going from 0.86 to 3.33 mmol/g. In addition, Cao *et al*., [82] examined the influence of $CO_2$ uptake in carbon materials using configurations that were doped with nitrogen, sulphur or both nitrogen and sulphur. However, higher KOH concentrations or activation temperatures can reduce dopant levels. For instance, increasing KOH concentration decreased N and S content by up to 22% and 15%, respectively [83], while higher temperatures reduced N by 30% and S by 41% [84]. The study emphasized the presence of simultaneous potassium intercalation, a process that could either fully or partially block micropores. The difference in findings highlights the complex dynamics of the activation process and indicates that the effect of KOH on the surface area depends on various elements, such as the activation temperature and the interaction between potassium and the carbon material. These findings underscore the critical need to balance KOH activation conditions with the preservation of N and S dopant levels in order to optimize the $CO_2$ uptake performance of porous carbon materials. By carefully selecting activation parameters such as KOH concentration and activation temperature, it may be possible to achieve an ideal trade-off between surface area, porosity and heteroatom content, thereby enhancing the overall efficacy of the materials.

## 7. Future Direction

Future research should focus on utilizing PPS as a precursor to synthesize self-S-doped porous carbon through carbonization. This method utilizes the intrinsic sulphur content in PPS, streamlining the doping process and improving $CO_2$ adsorption capabilities. Enhancing this concept through the inclusion of nitrogen dopants can further refined the material, resulting in nitrogen-sulphur co-doped porous carbons (NSPCs). These NSPCs possess the capacity to synergistically improve gas separation efficacy, especially in the context of $CO_2/CH_4$ separation.

Optimizing pyrolysis conditions for the synthesis of self-S-doped porous carbon is essential to achieve a balance between increasing porosity and preserving sulphur content. Moreover, investigating alternative activation techniques can enhance pore architecture without detracting from sulphur functionality. Nitrogen doping can be optimized by modifying dopant ratios and implementing structural alterations to enhance gas separation efficiency and selectivity.

Comprehensive kinetic and thermodynamic analyses are essential to clarify the mechanisms of $CO_2$ adsorption in NSPCs and assess their efficacy under diverse gas conditions. Integrating NSPCs into PSf membranes necessitates additional optimization to achieve uniform filler distribution, robust polymer compatibility and mechanical integrity. Evaluating these membranes under authentic operational conditions will be crucial to confirm their scalability and industrial feasibility.

In addition to $CO_2/CH_4$ separation, the capabilities of PPS-based materials should be explored for other separations, including $CO_2/N_2$ and $CO_2/H_2$, as well as their incorporation into hybrid systems such as mixed-matrix or composite membranes. These initiatives will facilitate the advancement of scalable, efficient and sustainable sulphur-based materials for sophisticated gas separation technologies.

## 8. Conclusions

This review highlights the potential of PPS in enhancing $CO_2$ separation technologies by serving as a polymeric filler in membranes and a precursor for self-S-doped porous carbon. PPS proficiently resolves compatibility challenges linked to conventional inorganic fillers in MMMs, providing an effective, scalable and energy-efficient method for gas separation. Optimizing activation parameters, including the KOH-to-precursor ratio and carbonization temperature, is essential for improving the porosity and specific surface area of PPS-derived carbon, which directly influences $CO_2$ adsorption capacity.

Moreover, the co-doping of nitrogen and sulphur enhances the $CO_2$ affinity of PPS-based materials, with the elevated sulphur content significantly augmenting their adsorption efficacy. PPS-based membranes exhibit considerable potential for improving $CO_2/CH_4$ selectivity, facilitating the generation of biomethane with over 95% purity, thereby satisfying industrial standards and decreasing operational expenses.

The advancement of PPS-based materials enhances biogas purification efficiency, thereby contributing to renewable energy objectives and aligning with global sustainability initiatives aimed at reducing greenhouse gas emissions and promoting clean energy sources. PPS is a highly promising material for sustainable gas separation applications, facilitating cleaner energy production. This progress bolsters global climate and energy policies, facilitating additional innovation in renewable energy technologies.

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