



Review on the preparation of carbon membranes derived from phenolic resins for gas separation

D. Torres, S. Pérez-Rodríguez, L. Cesari, C. Castel, E. Favre, V. Fierro, A. Celzard

► To cite this version:

D. Torres, S. Pérez-Rodríguez, L. Cesari, C. Castel, E. Favre, et al.. Review on the preparation of carbon membranes derived from phenolic resins for gas separation. Carbon, 2021, 183, pp.12-33. 10.1016/j.carbon.2021.06.087 . hal-03450086

HAL Id: hal-03450086

<https://hal.univ-lorraine.fr/hal-03450086v1>

Submitted on 25 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Review on the preparation of carbon membranes derived from phenolic resins for gas separation: from petrochemical precursors to bioresources

D. Torres^{1*}, S. Pérez-Rodríguez², L. Cesari¹,
C. Castel¹, E. Favre¹, V. Fierro², A. Celzard^{2*}

¹ Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

² Université de Lorraine, CNRS, IJL, F-88000 Epinal, France

***Corresponding Authors:**

Tel: +34 6 60 63 16 68. E-mail: daniel.torres-gamarra@univ-lorraine.fr (Daniel Torres)

Tel: +33 3 72 74 96 14. E-mail: alain.celzard@univ-lorraine.fr (Alain Celzard)

Abstract

Membrane processes, whose low energy and operating costs make them competitive for gas separation compared to other conventional methods such as pressure swing adsorption, cryogenic distillation or amine absorption, allows high-purity gas to be obtained in a sustainable and continuous manner. Similarly, resin-derived carbon membranes with molecular sieving properties have improved the selectivity and permeability of conventional dense membranes, as well as having high chemical and thermal resistance. In this review, an overview of the preparation of phenolic resin-based carbon membranes and their performance in gas separation is presented, particularly in processes involving permanent gases such as hydrogen purification, air separation, natural gas/biogas sweetening or carbon dioxide capture. Moreover, bioresources already proven for the synthesis of “greener” phenolic resins and the separation performance of some carbon membranes based on bioresource-derived phenolic resin are also reported and discussed in this work. This review will summarise the development and gas separation performance of phenolic resin-based carbon membranes and will provide a clear future direction in “green” carbon membranes research.

Keywords: carbon membranes, carbon molecular sieves, phenolic resin-based carbon membranes, bio-based phenolic resins, gas separation processes.

1 INTRODUCTION

Since the separation of hydrogen boosted the large-scale industrial application of membrane processes in the 1980s, industrial interest has increased in biogas/natural gas sweetening, N₂ and O₂ enrichment, or volatile organic compounds removal [1, 2]. Although polymeric membranes have played a major role in this development, they are no longer conquering new fields of application due to problems related to their lack of resistance in strong or corrosive operating conditions [3-5]. Feedstock gas volume, physicochemical stability, plasticisation, or swelling by CO₂ are issues that are still being addressed today, and which have favoured the appearance and development of inorganic membranes [6]. Inorganic membranes minimise or eliminate these problems but present new challenges such as those related to brittleness or high processing costs. In this context, carbon membranes address these deficiencies by combining excellent permeation and selectivity with relatively easy fabrication. Carbon membranes may have better sieving effect compared to polymeric membranes. Some previous critical reviews on the advantages of carbon membranes for gas separation can be found elsewhere [7-14]. Regarding the cost per unit area of carbon membranes, it was estimated to be 1 to 3 orders of magnitude higher than that of polymeric membranes [15]. However, this difference has narrowed considerably in recent years [16]. Carbon membranes have been applied in processes where the dimensional cost of the membrane is not a limiting factor.

Although there is a wide range of carbon-based membranes, those that include carbon nanotubes [17-20], graphene and graphene oxide [20-27], or carbon molecular sieves (CMSs) [11, 14] have been the most studied in the literature with applications as diverse as water treatment (purification, filtration, desalination, biological treatment and pervaporation), air cleaning, energy storage and conversion (fuel cells and batteries) and gas and liquid separation. Carbon membranes have shown exceptional performance in the separation of

gases with molecular sizes similar to those of the membrane pores (separation by molecular sieving mechanism). Their thermal and chemical resistance is entirely related to the stability and strength of their highly aromatic structure based on a sp^2 carbon network [28, 29]. Due to the turbostratic packing of tiny crystalline domains in the carbon material, their porosity is composed of ultramicropores connected by larger micropores, which are responsible for molecular sieving and high permeability, respectively [29].

While the synthesis of some carbon materials may be costly and difficult to standardise, the use of polymeric precursors (as in the case of CMSs) avoids this and also favours its support on a porous substrate that improves the permeability and the physical strength of the resulting membrane [30]. CMS membranes (CMSMs) have a specific structure and gas separation performance due to the selected polymeric precursor used [8]. Typically, CMSMs have pore sizes of less than 0.5 nm and are capable of separating mixtures of permanent gases such as CO_2/N_2 , O_2/N_2 or CO_2/CH_4 by a molecular sieving mechanism [11, 14]. In fact, CMSMs have shown higher selectivity for these gas pairs than purely polymeric membranes [31]. The precursors determine both the cost of the final membranes and the conditions of their production. Carbon membranes are obtained after pyrolysis of a carbon precursor such as thermosetting resins or biomass materials in an inert atmosphere or under vacuum. Among the polymeric precursors used for the manufacture of CMSMs, polyimide [32-35], phenolic resin [36, 37], polyetherimide [38, 39], polyacrylonitrile (PAN) [40, 41], cellulose [42] and polyfurfuryl alcohol (PFA) [43] have been reported.

Despite the advantages demonstrated by CMSMs, some drawbacks such as brittleness, the high cost of carbon membrane synthesis or the difficulty of manufacturing inexpensive and efficient membrane modules, have so far prevented their global use on an industrial scale. Due to this fragility, a CMSM must be carefully handled, which has made its practical application and the sealing of modules difficult when the objective of the latter is their use in

processes in harsh chemical environments. In this sense, although there are some commercial carbon membranes (generally in tubular form), only a couple of producers have been able to manufacture fibre modules for very specific applications. Scaling up this type of membrane remains a challenge today, and the next step towards its solution would be the manufacture of inexpensive hollow fibre tubular modules, where the cost of the carbon precursor and the resulting carbon production play a crucial role.

Phenolic resins, with mature industrial development and highly developed production, are presented as inexpensive and well-known polymers for many common applications such as adhesives, moulded products, composites or coatings [44]. These precursors have the advantages of easily allowing the synthesis of CMS films [45], offering a high carbon yield after pyrolysis [36, 46], being readily available and withstanding high temperatures without deformation. Phenolic resins are stable in handling and ensure a flawless structure due to their high glass transition temperature [47].

As far as membrane configurations are concerned, phenolic resin-based carbon membranes (PRCMs) have mostly been synthesised as very thin selective layers or films to improve their permeation properties. To this end, macroporous supports, including flat and tubular configurations, have been used to solve the associated mechanical issues [13]. At this stage, efforts were made to improve the film characteristics to avoid defects, cracks or pinholes, such as repeating the coating/drying/pyrolysis cycle or manufacturing asymmetrical supports. Alternatively, the incorporation of fillers in the phenolic resin, such as boehmite (ceramic filler widely used in the literature), makes it possible to obtain a defect-free carbon mixed matrix membranes (MMMs) in a single preparation cycle [48]. Moreover, it has been found that oxidation treatments can result in adsorption-selective carbon membranes (ASCMs) presenting slightly wider pores (0.5-0.7 nm), which are effective for the recovery of hydrocarbons from mixtures with weakly adsorbable gases (He, H₂, N₂, O₂, CH₄, air, etc.)

[49-51]. In addition to post-oxidation treatments to produce ASCMs, oxidation of the carbon membrane surface produces oxygenated groups that promote water vapour adsorption and water obstruction effect [51, 52]. CMSMs are more susceptible to pore blocking by humidity or oxidation, which reduces the permeability to the gas to be separated [8]. As the pore size distribution is important for molecular sieving applications, the possibility to modify it by varying the synthesis conditions or by including post-treatments during synthesis (both are possible for those obtained from phenolic resins) makes CMSMs adjustable for different gas sizes or increases their permeation [50, 53].

Industrial producers of phenolic resins have devoted great efforts to modifying their production process, not only for economic reasons but also to reduce the health and environmental impacts of their petrochemical raw materials, which are often carcinogenic [54]. Phenol and formaldehyde, which are mainly obtained industrially from highly toxic petroleum-derived feedstocks by the cumene process and by catalytic oxidation of methanol, respectively, have been replaced partially or completely by other less harmful petrochemical compounds in the production of phenolic resins. For instance, cresols, xlenols, resorcinol and bisphenol A have been used as co-monomers replacing phenol in the production of specialty phenolic resins [54]. However, the source of these phenolic compounds is still far from sustainable. In the case of formaldehyde substitutes, special resins comprising acetaldehyde, glyoxal, butyraldehyde, furfural, or benzaldehyde have been produced [54]. Among these conventional formulations, phenol-formaldehyde and resorcinol-formaldehyde formulations were widely used to prepare CMSMs offering remarkable permeation and selectivity in permanent gas separation.

In recent decades, the growing interest in the incorporation of renewable resources, as well as bio-based and non-toxic materials for the development of phenolic resins has led to the publication of numerous works in this regard [55-57]. Thus, successful approaches

involving raw materials derived from plants (tannins, glyoxylic acid or phloroglucinol), lignin and thermochemically processed liquid biomass products (liquefied biomass, polyphenolic extracts or pyrolysis bio-oils), or even proteins (casein, canola and soy) have been developed. Most of these potential substitutes are natural polyphenolic compounds, although in some cases they may contain aldehyde groups, such as the neutral fraction resulting from the pyrolysis of biomass or glyoxylic acid, allowing them to replace formaldehyde [58]. Similarly, lignin is the most abundant natural aromatic polymer on earth and is a widely available by-product of the paper industry. This advantage has made it one of the most popular materials for greening the phenolic resin synthesis process [59, 60]. On the other hand, plant-derived compounds such as tannins, furfural or glyoxylic acid are among the most interesting alternatives in the adhesive industry, the former replacing phenol or resorcinol, and the latter two formaldehyde [61-65]. While glyoxylic acid has a catalytic effect in resin preparation [62], tannins offer a similar reactivity to phenol or resorcinol with formaldehyde [59].

Although there are many reviews on carbon membranes for gas separation, including those focused on CMSs, a thorough evaluation of carbon membranes produced using phenolic resins provides the basis for the development of new membranes with substitutes of sustainable origin. The versatility of the original phenol-formaldehyde recipe, which has been effectively and industrially adapted for the synthesis of “greener” phenolic resins, and its scarce but promising use in the synthesis of carbon membranes for gas separation, are now discussed.

2 DEFINITIONS AND OTHER IMPORTANT CONSIDERATIONS

As will be discussed throughout the review, microporous carbon provides molecular size restrictions to the passage of gas, allowing the sieving of small molecules such as permanent gases. This gas transport mechanism, known as molecular sieving, is the dominant phenomenon in ultramicroporous membranes (pore width < 0.7 nm), although it can be replaced by the Knudsen diffusion mechanism when the pore size is larger than the size of the gas molecule that must permeate through it. Thus, the separation properties of a CMSM change dramatically depending on the shape and kinetic diameter of the gases attempting to penetrate it. In this sense, gas pairs of industrial interest would be mainly O₂/N₂, CO₂/CH₄, H₂/N₂, He/N₂, CO₂/N₂, N₂/CH₄, H₂/CH₄, He/CH₄, He/H₂, H₂/CO₂ and He/CO₂, involved in a wide variety of upstream separation processes such as CO₂ capture, air separation, H₂ purification, or natural gas sweetening [66-69].

To evaluate the separation performance of a membrane for a certain gas pair, it is necessary to determine both gas permeance and selectivity. Permeance is defined as the amount of gas that passes through a membrane of known surface area per unit of time and per partial pressure difference. Frequently, permeability is reported instead of permeation in order to compare different membranes with each other, and this corresponds to the product of gas permeation and membrane thickness. Finally, selectivity (also called separation factor, α) provides a measure of separation efficiency by the ratio of the permeances (or permeabilities) of two gases passing through the membrane. Selectivity data are almost systematically calculated from the ratio of pure gases permeability (often referred to as an ideal separation factor, α^*), for the sake of simplicity. It is important to stress that different selectivity data can be obtained in some cases with gas mixtures [70]. Regarding the units used for permeance and permeability, gas permeation unit (GPU) and Barrer are conventionally used, respectively, whose conversion from SI units would be as follows:

$$GPU = 1 \times 10^{-6} \frac{cm^3 (STP)}{cm^2 \cdot s \cdot cm \text{ Hg}} = 3.35 \times 10^{-10} \frac{mol}{m^2 \cdot s \cdot Pa}$$

$$Barrer = 1 \times 10^{-10} \frac{cm^3 (STP) \cdot cm}{cm^2 \cdot s \cdot cm \text{ Hg}} = 3.35 \times 10^{-16} \frac{mol \cdot m}{m^2 \cdot s \cdot Pa}$$

There is a known upper bound for these gas pairs, which establishes a limit in membrane performance to achieve a high separation factor combined with a high gas permeability [71, 72]. This upper bound, established for polymeric membranes by Robeson [73], is derived from the representation of the logarithms of the two parameters. The gas permeability in a given gas pair and the separation factor are the key parameters of a membrane for gas separation, although one generally increases at the expense of the other. The following sections will focus on gas pairs of current industrial interest for which CMSMs have traditionally performed better than polymeric membranes. It is important to note that the breakthrough performances potentially offered by nanostructured materials in terms of permeance and/or selectivity, compared to current polymeric materials, are expected to have a major impact for industrial applications, especially for energy efficiency purposes [74, 75]. However, the relationship between increased selectivity and energy efficiency is complex and requires a dedicated engineering study for each case [76]. Moreover, depending on the target application, techno-economic analyses show that the key interest may be either an increased selectivity or an increased permeance. There is an interplay between materials properties (permeance, selectivity) and industrial application potential (i.e., overall cost compared to alternative processes) (Figure S1 of the Supplementary Information, [77]). Thus, depending on the case study and specification, a slight or major improvement in permeance and/or selectivity can be critical.

To better evaluate the performance improvements offered by PRCMs, the corresponding Robeson-type plots for each gas pair will be presented (Figures 8-12), including the upper

bound established for polymeric membranes and the permeability/selectivity pairs published in the works on PRCMs. Moreover, the gas permeability values of the latter membranes correspond to the selective carbon layer and are calculated when the cited work provides the permeation values and the thickness of this layer (the thickness of the support is not taken into account). The thickness of this selective layer is mainly measured by scanning electron microscopy (SEM) observations. For comparison purposes, the ideal gas permeability values obtained from the permeation of pure gases are offered instead of those of gas mixtures (the ideal selectivities or ideal separation factors were calculated from its quotient). It is also important to point out that the interactions between gases are generally not negligible, which would lead to a deviation between the mixture separation factor and the ideal selectivity.

3 SYNTHESIS AND CARBONISATION OF PHENOLIC RESINS

3.1 Conventional chemicals for the synthesis of phenolic resins

Despite the apparent simplicity of obtaining a phenolic resin from a mixture of formaldehyde and phenol, there is a wide variety of products available on the market and in the literature due to the different possible reaction conditions such as pH, temperature, time, catalyst and formaldehyde/phenol (F/P) molar ratio [44]. According to the latter, two main types of phenolic resins are obtained as phenol-formaldehyde condensation products: novolak and resole, whose main difference is the reactivity to temperature. A summary scheme of the formation pathways of resole and novolak resins is shown in Figure 1. Resoles are produced using F/P molar ratios ≥ 1 and a basic catalyst. Usually, polymerisation is carried out at 100 °C and is stopped at the gel point (corresponding to B-staging resin [78]) by cooling. The catalyst favours the formation of methylol ($-\text{CH}_2\text{OH}$) functional groups during synthesis, which promotes the self-curing of the resin. In this way, resole resins are therefore unstable

over time since they contain methylol groups that continue the polymerisation process. In the case of novolak resins, they are produced under acidic conditions and using an F/P ratio less than the equimolar value, thus generally between 0.75 and 0.85. Novolak resin is a pre-polymer that can be moulded and then cured by the action of heat and the addition of more formaldehyde or amine [44, 79]. Ideally, the system is entirely crosslinked in the equimolar reaction (or above the F/P ratio) or using the addition of a crosslinker. Theoretically, all phenols will be linked by methylene bridges in the fully crosslinked product. One of the most commonly used crosslinking agents is hexamethylenetetramine (HMTA), which generates formaldehyde and ammonia (a basic catalyst) when heated at around 165 °C. HMTA yields a cured material that is highly resistant to solvents and heat since a complex 3D polymer network is built up during polymerisation.

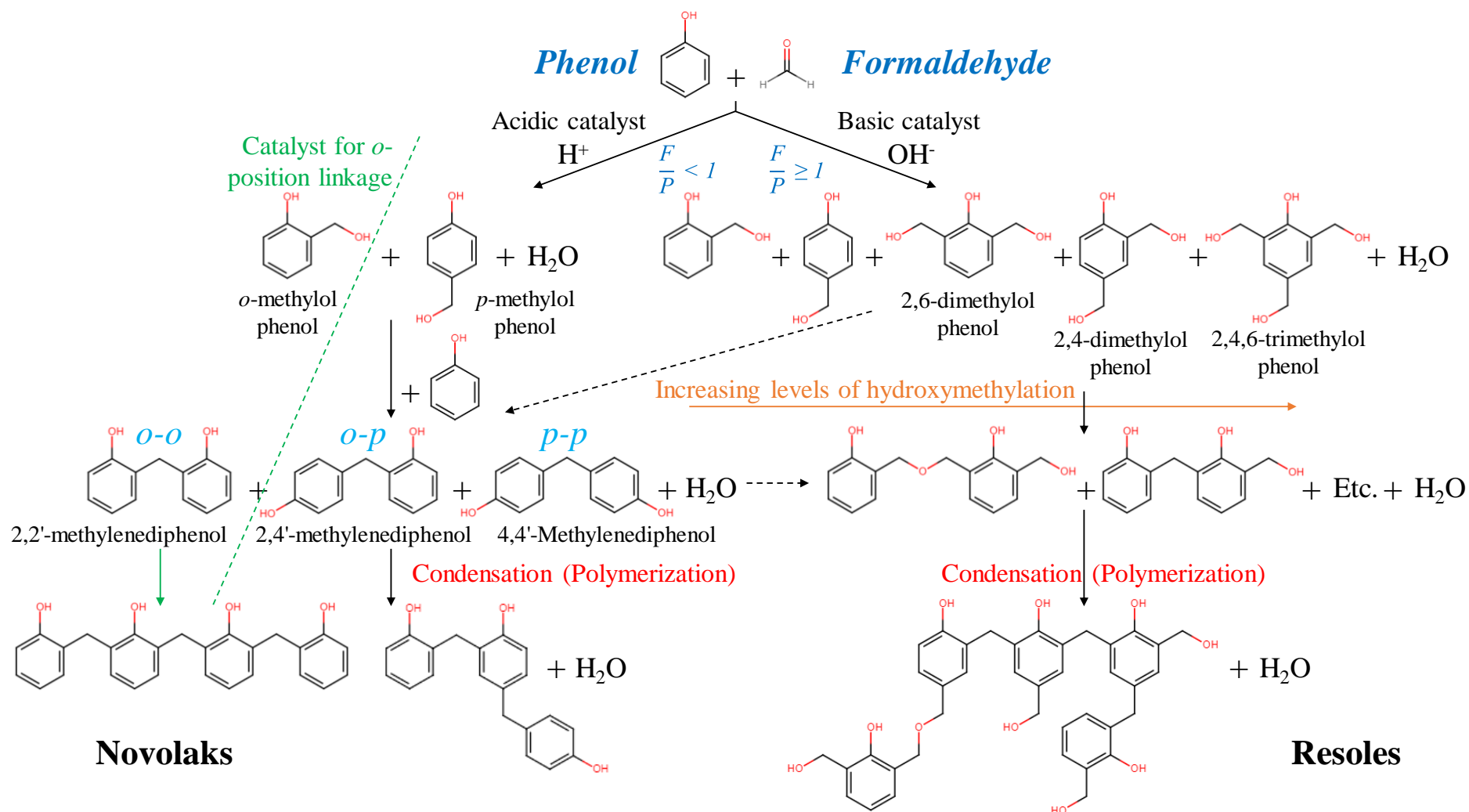


Figure 1. Synthesis pathways leading to phenol-formaldehyde resins in the form of novolaks or resoles.

As already mentioned, the reaction consists of the polymerisation of phenol with formaldehyde via a polycondensation reaction and the resulting formation of water. Regardless of the type of phenolic resin (resole or novolak), methylene glycol ($\text{HO}-\text{CH}_2-\text{OH}$), in equilibrium with formaldehyde in aqueous solution (generally 37 wt. % for commercial products), reacts with phenol to form methylolated phenol, with the methylol group in the *ortho* or *para* position, and water. This first step is called hydroxymethylation, and it may imply the participation of the phenolate ion formed from phenol using heat and NaOH as a catalyst in resole synthesis [54]. The methylolated phenol can react with more formaldehyde, resulting in dimethylol phenol and trimethylol phenol. During condensation, this substituted phenol reacts either with a new phenol (dashed lines in Figure 1) creating a methylene bridge between the two aromatic rings or with another methylol phenol via methylene or dimethyl ether ($-\text{CH}_2-\text{O}-\text{CH}_2-$) bonds. The latter case occurs during the formation of resole resins, phenol being the limiting reagent. In any case, the condensation of the phenolic compounds occurs randomly in the *o*- or *p*- position, allowing for further branching. At acidic pH, generally for novolak synthesis, the reaction using phenol and formaldehyde generates a linear polymer [80]. On the other hand, the use of high F/P ratios leads to higher hydroxymethylation, increasing the degrees of polymerisation and branching [81].

In addition to the monomers mentioned (phenol and formaldehyde), others have been used to replace them or as co-monomers in the synthesis of resins. Among the most commonly used by manufacturers are substituted phenols such as cresols, xylenols, resorcinol or bisphenol A, and other aldehydes such as furfural, acetaldehyde or glyoxal [54].

Novolak resins tend to form amorphous thermoplastics whereas the use of a catalyst does not lead the polymerisation. In this sense, catalysts can, for example, orient methylene bonds as far as they promote *ortho-ortho* linkages by preserving the *para*- positions, which

accelerates the curing of the resin. Regarding the catalyst, alkaline catalysts such as alkali or alkaline earth metal hydroxides (KOH, NaOH, LiOH, Ba(OH)₂, Mg(OH)₂), ammonia or sodium carbonate, or acidic catalysts such as hydrochloric, oxalic, sulphuric, formic and aromatic sulphonic acids have been used for the synthesis of resole and novolak resins, respectively [54, 82]. The industrial production of novolaks commonly uses sulphuric and oxalic acids [83].

3.2 “Greener” substitutes for phenol and formaldehyde

More and more publications, patents and industrial products that include more environment-friendly and/or less toxic reagents are increasingly found on phenolic resins. A selection of known green substitutes for phenolic resins is shown in Figure 2. Likewise, their origin and examples of phenolic resins reported in the literature can be found in Table S1 of the Supplementary Information. The most obvious and natural response to the need for “greener” feedstocks has been to turn to biomass, mainly lignocellulosic, an inexpensive and widely available resource to obtain phenolic compounds as the substitutes for phenol in resin synthesis [84, 85]. In addition to phenolic compounds, synthetic aldehydes have been also investigated for this purpose, the liquefied biomass obtained by thermal processes being the main resource for both types of substitutes [58, 86, 87]. Lignin, representing 40 wt. % of lignocellulose, has a phenolic structure from which a wide variety of phenols such as syringol or guaiacol can be obtained, which have already been widely explored and used as substitutes [64, 88]. Besides, phenol-formaldehyde resin formulations readily assimilate pyrolytic lignin [89]. Liquefaction, phenolysis or rapid vacuum pyrolysis of biomass, in addition to bio-oil fractionation methods, are the main routes for obtaining phenolic compounds [58]. Although the reactivity of biomass-derived phenols is lower than that of pure phenol, which is related to the lower average number of positions available for polymerisation, suitable thermal

processes make it possible to obtain phenolic compounds with equivalent reactivity and the associated benefits in terms of cost and environmental impact [58]. The properties of the resulting phenolic resins using these substitutes remain as good as those of conventional resins as long as they do not exceed 50% substitution, except possibly when phenolic fractions are used that allow higher substitutions [58].

In addition to thermal processes of lignin-rich biomass resources, there are other natural substances extracted from plants (tannins, glyoxylic acid, or phloroglucinol) that have been investigated for decades as substitutes for phenol or formaldehyde. Tannins comprise three groups of phenolic compounds: condensed tannins, hydrolysable tannins and complex tannins, the latter combining the characteristics of the first two types. However, it is mainly the first group, based on flavonoids with different condensation degrees, which has been extensively studied for wood adhesive formulations [65]. In contrast, hydrolysable tannin have limited reactivity with formaldehyde and lesser moisture-resistant bonds between phenolic units [55, 90]. Tannin-formaldehyde resins present *a priori* a low condensation degree and were therefore initially modified by blending or by copolymerisation with additives and small amounts of phenol-resorcinol-formaldehyde or phenol-formaldehyde polymers of low molecular weight [91]. However, the reactivity and crosslinking chemistry of tannins are similar to those of phenol-formaldehyde and resorcinol-formaldehyde resins [59]. Thus, there are two reaction approaches to prepare a phenolic resin from tannins depending on whether or not a curing agent is used: polycondensation or autocondensation reactions, respectively.

Polycondensation of tannins requires aldehydes or other types of crosslinkers such as HMTA, furfuryl alcohol or glyoxal to obtain resins with very low formaldehyde emission [55, 92]. In the case of HMTA, which is already used in industrial application and commercial tannin-HMTA adhesives [93, 94], its decomposition into formaldehyde and ammonia is

prevented by condensed tannins, which explains the low formaldehyde emission [95]. On the other hand, tannins can auto-condense under acidic or alkaline conditions without crosslinkers [96]. The autocondensation of tannins occurs after the opening of the pyran rings, which promotes self-polymerisation, and the rate at which it occurs depends strongly on the origin of the tannins [97]. The autocondensation of tannins is induced by contact with the surface of lignocellulose [96] or by Lewis acids such as silica, boric acid, silicates or aluminium chloride [98]. The latter can accelerate the autocondensation of slow reacting tannins (e.g. quebracho or mimosa) [96, 99, 100].

Glyoxylic acid, which is found in bacteria, plants and fungi, has been used in the preparation of phenolic resins as formaldehyde substitute, as crosslinker and as catalyst due to the presence of aldehyde and carboxylic groups in its structure. Recently, Matei-Ghimbeu *et al.* took advantage of this characteristic to react it with phloroglucinol without the need for catalysts [62]. Phloroglucinol is also a phenolic compound that can be produced from natural resources [101] and has been used in the reaction with formaldehyde for phenolic resins [102-104]. Additionally, Liang and Dai indicated that phloroglucinol polymerises with formaldehyde faster than resorcinol or phenol [103].

Finally, proteins of plant or animal origin such as casein, canola or soy, among others, have been widely explored to produce biosourced phenolic resins [105-110]. These proteins, or their fragments, have been chemically crosslinked with a phenol-formaldehyde prepolymer to obtain adhesives with similar performance to wood adhesives based on urea-formaldehyde or phenol-formaldehyde. Although as a result of these formulations, commercial wood products have been successfully developed using isolated soy protein, the high cost of production of the latter has prevented further industrial implementation of this process, which has been oriented towards investigating the use of waste animal proteins such as casein [107].

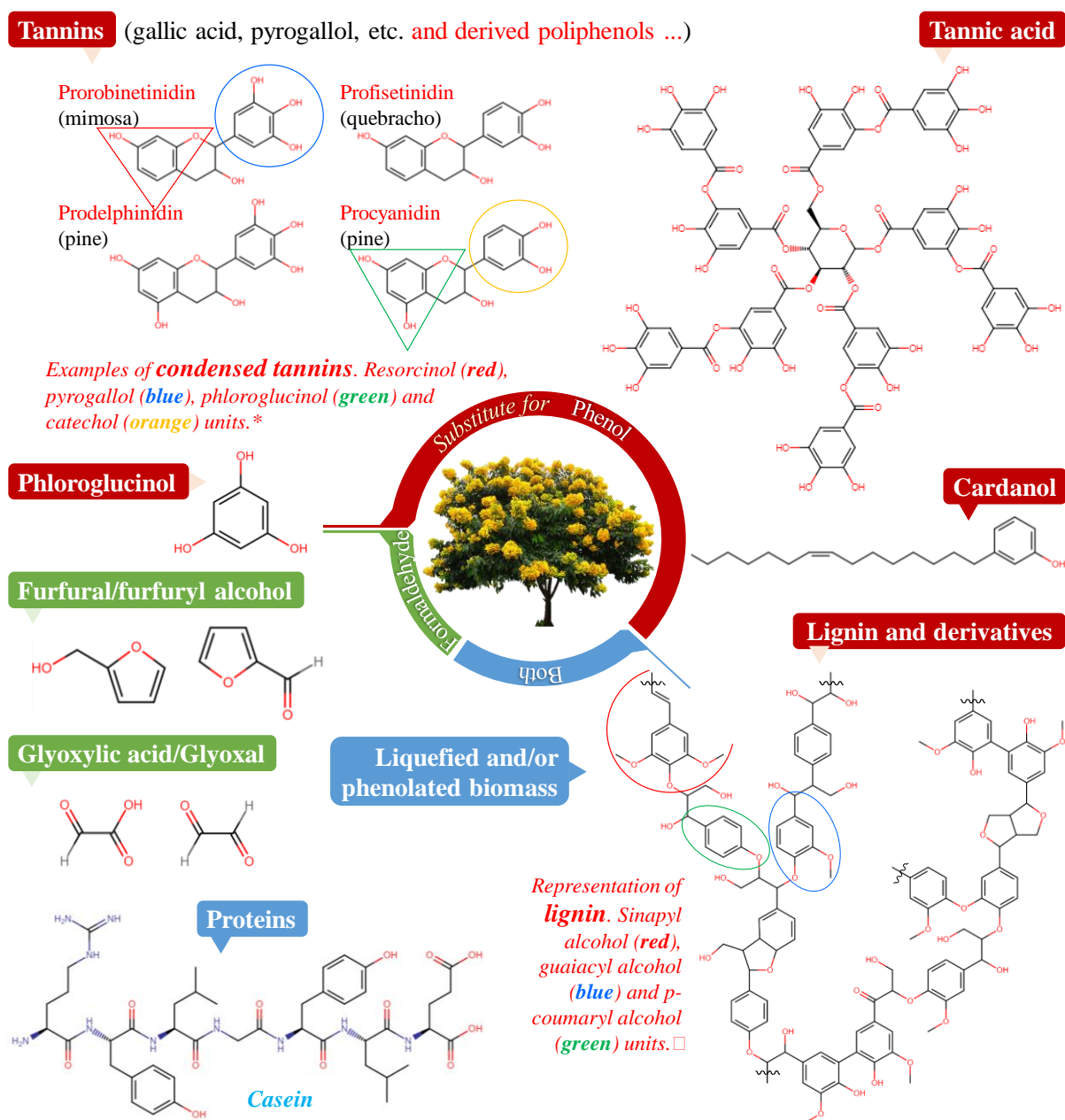


Figure 2. Biosourced substitutes for the preparation of more sustainable phenolic resins. The origin of these substitutes and references on their use in the preparation of phenolic resins are listed in Table S1 of the Supplementary Information. * adapted from [111]. □ adapted from [112].

3.3 Carbonisation of “greener” phenolic resins

The process of carbonisation, or pyrolysis, aims to transform, in the absence of oxygen, the organic network of a polymer into a structured carbon (with the resulting enrichment of the material in this element). Although carbonisation is a necessary step to obtain a molecular sieve for gas separation, other applications such as those related to energy storage or conversion have monopolised the exploration of this process towards templated and self-assembled ordered micro- and mesoporous carbons [113, 114]. Experimental realisations focusing on carbon membranes for the separation of gases obtained by carbonisation of conventional phenolic resins will be discussed in Section 4. In this context, although the pyrolysis conditions of phenolic resins influence the microporous structure of the resulting carbon materials [53], the prefabrication of porous structures by templates has been a successful approach in the synthesis of ordered mesoporous carbons (OMCs) [115]. Table S2 of the Supplementary Information summarises examples of different types of carbon materials obtained after carbonisation of “greener” phenolic resins and the carbonisation/activation conditions used.

Prior to carbonisation, a triblock copolymer template allows the phenolic resin to self-assemble by hydrogen or covalent bonding. Pluronic F127 has thus been widely used in soft-template methods for the preparation of phenolic resins and their corresponding carbonised products [62, 103, 115, 116]. As an example, Figure 3 shows the formation of the assembly structure resulting from the reaction of phloroglucinol and formaldehyde with Pluronic F127 (“PEO-PPO-PEO” in Figure 3) [103]. Pluronic F127 is a triblock copolymers composed of a central hydrophobic poly(propylene oxide) (PPO) chain bearing a hydrophilic poly(ethylene oxide) (PEO) chain at each end. In this way, Pluronic F127 forms micelles in aqueous media by self-assembly of these blocks, resulting in a hydrophobic PPO core and a hydrophilic PEO shell that accommodates phenolic resin (phloroglucinol-formaldehyde in the example) by

hydrogen bonding. In addition to phloroglucinol (included in the picture), this route has also been validated using other single-ring phenolic monomers such as phenol or resorcinol [103, 116]. In this respect, there is only a limited amount of work on this kind of synthesis using biosourced phenolic resins (some of which are included in Table S2, Entries 2, 8 and 10-12). Pluronic F127 has again been used in the soft-template synthesis of OMCs using phloroglucinol and glyoxylic acid as the carbon precursors and subsequent heat treatment in the range of 600-900 °C [117-119]. This organic surfactant produces micelles of defined size and geometry, and its self-assembly via hydrogen and/or covalent bonds in the presence of monomers or oligomers creates a precisely defined mesoporosity after pyrolysis, which destroys the micelles and converts the resin into carbon [62]. Mesoporosity and ordered structure will remain after removal of the template micelles if the crosslinking of the phenolic resin produces a pore wall thickness and an interconnected structure sufficiently developed to resist carbonisation [120].

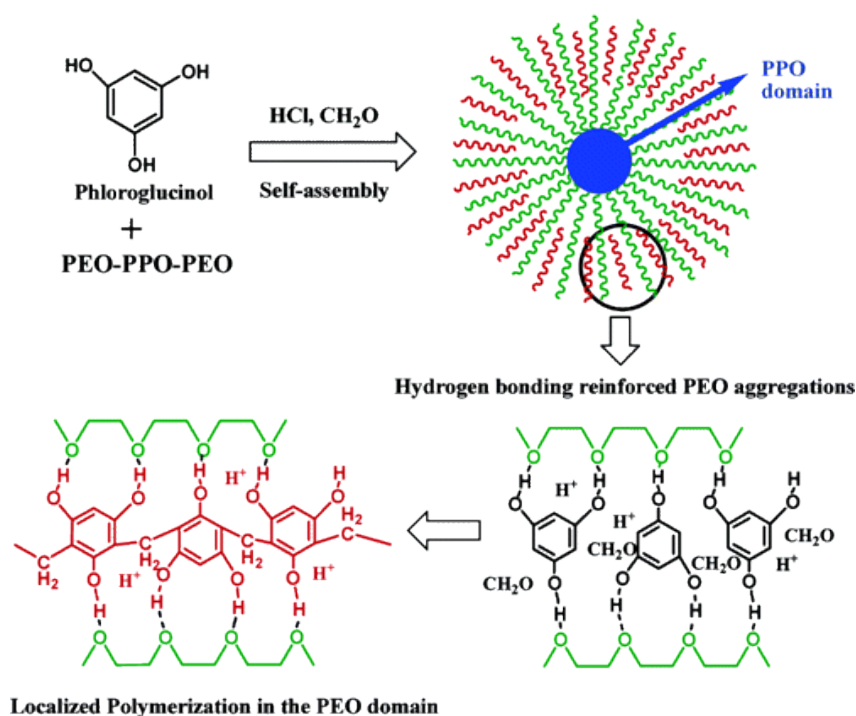


Figure 3. Polymerisation reaction of phloroglucinol and formaldehyde, and formation of the

assembly structure with F127. Phenolic resins form hydrogen-bonded networks with polymers containing poly(ethylene oxide). Reprinted with permission from ref [103].

4 CARBON MEMBRANES BASED ON PHENOLIC RESINS FOR GAS SEPARATION

4.1 Preparation of carbon membranes

4.1.1 General information

The manufacture of a high-performance carbon membrane involves several steps, such as preparation of the phenolic resin, coating of the support (in the case of an asymmetric membrane), pre-treatment, pyrolysis and post-treatment, as will be seen in the following sections, which requires control and optimisation. The precursor used influences the type of carbon membrane after pyrolysis and its gas separation properties [121, 122]. Thermosetting polymers, as is the case of phenolic resins after crosslinking, do not suffer from softening or melting at high temperatures and minimise the occurrence of cracks or holes as well as inorganic impurities in the membrane. Moreover, the high yield of carbon after pyrolysis, low cost and molecular sieving capability in thin films are some of the properties highlighted that make phenolic resins among the most suitable precursors for carbon membranes [36, 45].

Apart from precursor selection, pyrolysis is the most important step to obtain a carbon membrane with a well-defined pore structure, which will determine its performance in gas separation [53]. In this section, the preparation of a carbon membrane for gas separation using phenolic resins (usually non-“green”) as carbon precursors is described. In addition, a summary of the most relevant research on the preparation of carbon membranes from phenolic resins, with emphasis on the characteristics of the synthesis, is given in Table 1.

4.1.2 *Membrane configurations and related preparation methods*

When preparing a carbon membrane, the configuration is essential for its subsequent application and scale-up. In general, carbon membranes can be configured as tubes, plates, capillaries, or hollow fibres [7]. Figure 4a shows the different supported and unsupported CMSM configurations. As shown in Table 1 (see column “Configuration”), since carbon membranes can easily be manufactured in the form of a thin film with a thickness even below 1 micrometre due to the characteristics of phenolic resins as a precursor, they have been preferably supported on flat or tubular supports for laboratory and research applications in gas separation. However, although the supported tube configuration is applicable in the industry, other more developed configurations such as capillary or hollow fibre membranes may be more appropriate in terms of process scalability. Figure 4b-d shows some examples of phenolic resin-based carbon membranes in tube configuration found in the literature. Since the purpose of these membranes is gas separation, achieving high permeation rates would imply that the selective layer, which has molecular sieving properties, should be as thin as possible, a feature that can be addressed by investing effort in the preparation of the appropriate resin solution and coating method of the support.

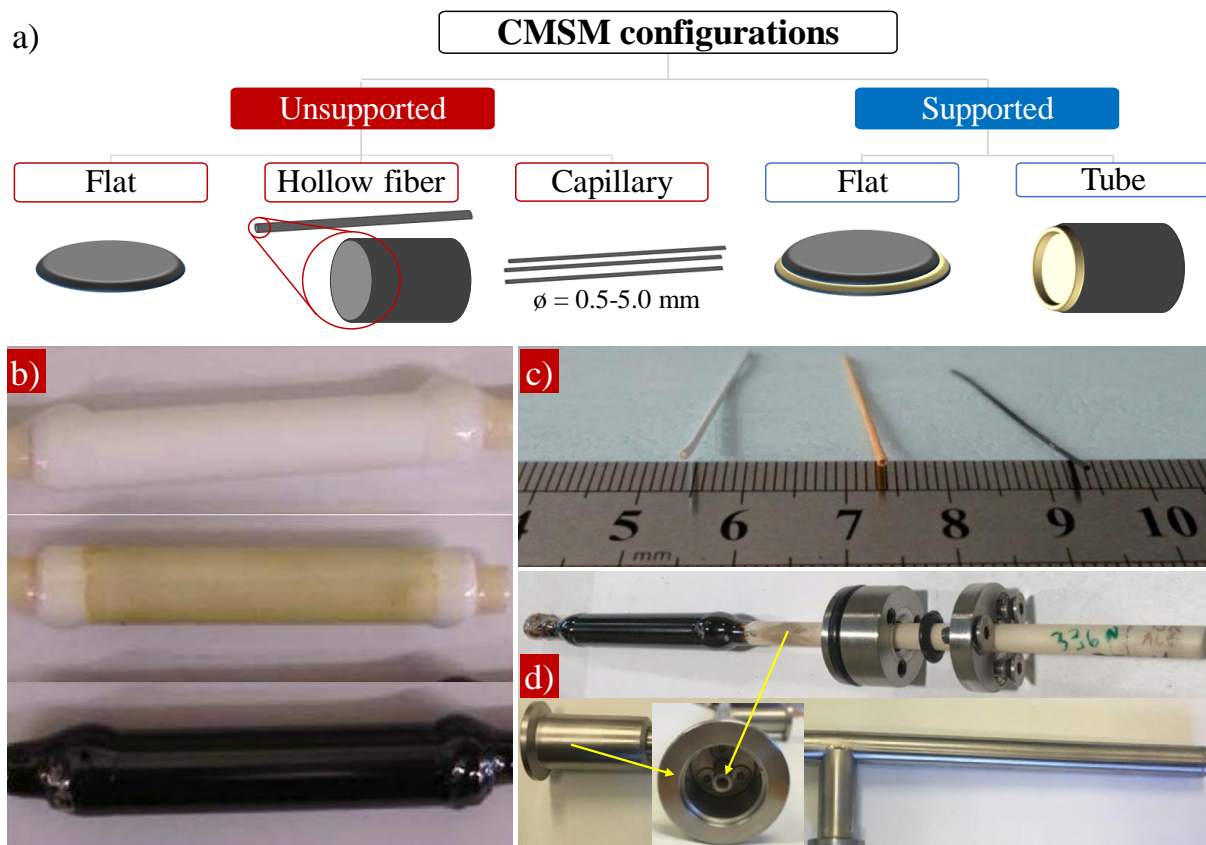


Figure 4. (a) Configurations of CMSMs (adapted from [7]). (b-d) Examples of carbon membranes based on phenolic resin in tube configuration: (b) from top to bottom: porous alumina tube, support after the dip-coating/drying cycle and CMSM tube obtained after carbonisation [79]; (c) from left to right: PVDF hollow-fibre membrane, impregnated PVDF membrane and carbon hollow-fibre membrane obtained after carbonisation [123]; and (d) CMSM tube in a permeation measurement module (inset: steel cylinder for sealing the membrane to the tube of the module) (adapted from [124]). Reproduced with permission from [79] (a), [123] (b) and [124] (c).

The gas permeability of supported membranes is generally higher than that of the freestanding ones, due to the lower diffusional restriction of gases passing through the shorter porous channels of thinner surface membranes. As already mentioned, the option of supporting this kind of film on a macroporous support reduces problems related to the

mechanical properties of carbon membranes [13]. However, a frequent problem such as pinholes must be taken into account when the thickness is below a certain limit [125]. Therefore, thicker films and/or the application of several layers have solved the latter problem as well as the presence of defects, but at the expense of permeation, which has decreased. Table 1 shows some examples of membranes obtained after several coatings, including drying or drying/carbonisation cycles (see column “Coating method”). In this way, after a minimum number of coatings, additional layers increase gas selectivity to a maximum (since the pore network may become blocked), but again at the expense of a decline of permeation [126-130]. On the other hand, Zhou *et al.* studied the application of a multiple coating of dilute (10 wt. %) sulphonated phenolic resin solution, which resulted in a thinner precursor membrane and better separation properties after pyrolysis than those observed for membranes obtained using more concentrated solutions and fewer coatings [128]. The concentration of a solution of a phenol-formaldehyde novolak resin containing HMTA in the range of 30-60 wt.% was studied by Wei *et al.* and it was determined that increasing the concentration has a similar effect to increasing the number of coatings [127]. A sufficiently high concentration ensures a flawless membrane and subjects the gas flow to a molecular sieving mechanism.

Polar organic solvents such as N-methyl-2-pyrrolidone, ethanol or methanol were the preferred solvents for controlling the viscosity of phenolic resin solutions and making them suitable for coating, although commercial resins can be received in any state, with prior softening at temperatures below 105 °C being necessary in some cases. Similarly, resin compositions containing additives (such as HMTA in the above-mentioned work of Wei *et al.*) or the preparation of asymmetric membranes were approaches to resolving the occurrence of defects or the need for multiple cycles. This will be discussed in the following sections.

Finally, as shown in Figure 5, several methods were used to coat the support for flat and tubular configurations, namely compression moulding, dip coating, spray coating, spin

coating, casting (where slip casting and tape casting are included), drop casting or traditional dip and solvent evaporation. Vacuum-assisted processes, such as vacuum-assisted dip coating or vacuum slip casting, have improved the coating of the support by promoting the penetration of the precursor solution through the pores to the subsurface of the support, resulting in thinner polymer layers and less prone to defects or cracks in the carbonisation process [79]. Likewise, the optimisation of the coating process is crucial to obtain, after carbonisation, a sufficiently selective layer for gas separation. For example, Carretero *et al.* observed by SEM the need for a minimum time in the dip-coating process for the complete infiltration of the phenolic resin into the desired support layer (see Figure 7c) [131].

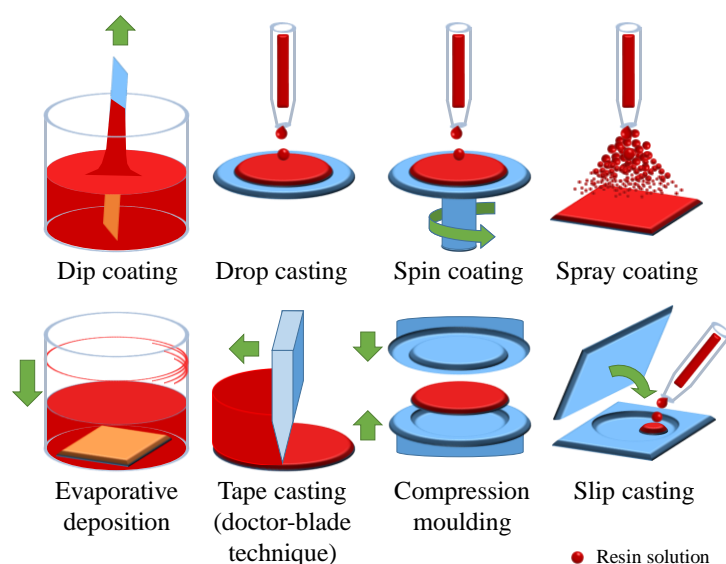


Figure 5. Examples of liquid-phase coating methods.

With regard to the materials selected for membrane supports, α -alumina was the most commonly used, as shown in the literature review. Ceramic supports offer better pore penetration and better adhesion for the polymer solution than metal substrates, making it easier to obtain a thinner carbon layer [132, 133]. Cracking is minimised when the average pore size of the support is at least one order of magnitude smaller than the thickness of the

selective carbon layer [13]. The surface structure of the support influences the pore distribution of the resulting carbon layer and thus the final gas selectivity and permeation [37]. Occasionally, α -alumina supports have been modified to improve their characteristics for subsequent impregnation. In this sense, silica-coated alumina supports (tubes or flat sheets) offered a narrower pore structure for better interaction with the phenolic resin [121, 126, 134, 135]. The silica coating reduced the main pore size of the alumina support (originally 1 μm), improving the permeation of some permanent gases such as N_2 and CH_4 [126].

Table 1. Details of the preparation of membranes for gas separation based on carbonised phenolic resins.

Type of resin/Membrane (Catalyst) *	Configuration	Coating method	Pyrolysis conditions (T: °C; ramp: °C/min; time: min; gas)	Pre-/Post-treatments (T: °C; ramp: °C/min; time: min; gas)	Year Ref.
PFR/Asymmetric CMSM	Supported (flat, porous ceramic sheet)	Compression moulding	800-950; -, 120-180; N_2	-/800-950; -, 30-60; O_2+N_2 (0-5-2.0 % O_2)	1996 [136]
PFR + unidentified additives/Asymmetric CMSM	Unsupported (flat)	Compression moulding	800-950; -, -, inert	-/800-950; -, 20-60; activation gas	1996 [137]
Phenolic resin (Bellpearl S-895; Kanebo Ltd.)/CMSM	Supported (outer face of alumina or silica-coated alumina tubes)	Dip-coating or vacuum impregnation (1-5 layers; 20 min) ^B 20-40 wt. % in methanol	600; 5; 60; N_2	50; -, 1 day; air + 50; -, 1 day; vacuum/-	1997 [126]
Resole-type phenolic resin/Asymmetric microporous carbon membrane	Supported (outer face of a novolak resin tube)	Spray coating (1-3 layers) ^A 20 wt. % in ethanol	800; 0.83; -, N_2	130; -, -, -/800; -, 60; CO_2 (inside or both sides)	1997 [138]
Novolak-type phenolic resin/CMSM	Supported (porous carbon disk)	Spin coating (5000 rpm; 10 min)	500-1000; 5; -, vacuum	150; -, 120; air/-	1999 [36]
Phenolic resin (Bellpearl S-895, Kanebo Ltd.)/CMSM	Supported (alumina tube and silica-coated alumina tube)	Dip coating (2-3 layers; 20 min) ^B 20-40 wt.% in methanol	500-700; 5; 60; N_2	50; -, 1 day; air + 50; -, 1 day; vacuum/-	1999 [121]
Novolak-type phenolic resin/CMSM & ASCM	Supported (inner face of an alumina tube)	Dip coating. 30 wt. % solution	700; -, -, vacuum	150; -, 120; air/- or 150; -, 120; air/300-400; -, 30; air	2000 [49]
Novolak-type phenolic resin/CMSM	Supported (inner face of an alumina tube)	Not disclosed	700; -, -, vacuum	150; -, 120; air/- Regeneration:	2001 [139]

	tube)			120; -; 180; vacuum or 600; -; 60; vacuum	
Novolak-type phenolic resin/CMSM	Supported (inner face of an alumina tube)	Dip coating (1-3 layers) 50 wt. % in NMP	700; 0.5; - ;vacuum	-/- or 150-300; -; 120;air/-	2001 [45]
Resole-type PFR + novolak-type sulphonated phenolic resin (SPFR)/CMSM (KOH)	Supported (alumina tube)	Dip coating (3 layers) ^A 30 wt. % PFR in methanol 10 wt. % PFR/SPFR in methanol	250-800; 5; 90; N ₂	70; -; 300-600; air + 110; -; 600; vacuum/-	2001 [140]
Novolak-type phenolic resin/CMSM & ASCM	Supported (inner face of an alumina tube)	Dip coating	700; -; -; vacuum	150; -; 120; air/- or 150; -; 120; air/100-475; -; 30-360; air	2001 [51]
Novolak-type phenolic resin/CMSM & ASCM	Supported (inner face of an alumina tube)	Dip coating	700; -; -; vacuum	150; -; 120; air/- or 150; -; 120; air + 250-400; -; 60; air/- or 150; -; 120; air/ 300-400; -; 30; air	2001 [50]
Novolak-type PFR + HMTA/CMSM	Supported (outer surface of a green tube: novolak PFR)	Dip coating (1-4 layers; 30 s) ^A 30-60 wt. % in ethanol	900; 0.5; 60; Ar	RT; -; 2 days; air + 120; -; 60; air/-	2002 [127]
Novolak-type phenolic resin/CMSM & ASCM	Supported (inner face of an alumina tube)	Dip coating	700; -; -; vacuum	150; -; 120; air/- or 150; -; 120; air + 75-350; -; 30; air/- or 150; -; 120; air /75-350; -; 30; air or 150; -; 120; air /75-350; -; 30; air + CVD = 500; -; 1-10; N ₂ +TCE Regeneration: 150; -; >2; vacuum	2002 [46]
Novolak-type phenolic resin/ASCM	Supported (inner face of an alumina tube)	Dip coating	700; 1; 60; vacuum	-/-	2003 [141]
Resole-type PFR + novolak-type sulphonated phenolic resin (SPFR)/CMSM (KOH)	Supported (alumina tube)	Dip coating (1-5 layers) ^A 5-40 wt. % solution	500; 5; 90; N ₂	70; -; >300; air + 110; -; 600; vacuum/-	2003 [128]
Novolak-type phenolic resin (Fers Resins, S.A.) /MSCM & ASCM	Supported (inner face of an alumina tube)	Dip coating + 150 °C spinning 50 wt. % in NMP	700-1000; 0.5-10; 0-480; vacuum or N ₂	-/-	2004 [53]
Novolak-type PFR + CMS particles/CMSM-	Supported (green tube: novolak PFR)	Dip coating (1-3 layers) ^A	800; 0.5; -; inert	-/800; -; 20-60; CO ₂	2006 [142]

MMM	+ methyl-cellulose)	40-50 wt. % in ethanol			
Novolak-type phenolic resin/CMSM	Unsupported and Supported (inner face of an alumina tube)	Dip coating (1 layer; 1.5-180 min) 35-50 wt. % solution	700; 1 ; 60; N ₂	170; 2; 120; air/-	2006 [131]
Phenolic resin (Tamanol 758, Arakawa Chemical Inc., USA) + Nickel nanoparticles/CMSM-MMM & ASCM-MMM	Supported (inner face of an alumina tube)	Dip coating (2-4 layers; 3 min) ^B 40 wt.% in ethanol	600; 1; 120; N ₂	RT; -; 1 day; air + RT; -; 360; vacuum/-	2006 [129]
Resorcinol-formaldehyde resin + cationic tertiary amine (TMAB, TPAB or CTAB)/CMSM & ASCM (Na ₂ CO ₃)	Supported (flat, silica-coated alumina)	Spin coating (3-4 layers; 4000 rpm) ^A Ethanol/water solution	800, 5, 480, N ₂	90; -; 1 day; air/-	2006 [134]
Novolak-type PFR or Novolak-type PFR + PEG/CMSM	Supported (green tube: novolak PFR + methyl-cellulose)	Spray coating (multiple layers) 40 wt.% in DMF	800; 0.5; 120; N ₂	150; -; 180; air/-	2007 [143]
Novolak-type phenolic resin (Kangnam Chemical Co., Ltd.)/CMSM	Supported (alumina tube)	Dip coating (5 layers) 35 wt. % in DMF	300; 1; 60; inert + 450; 1; 60; inert	60; -; 2 days; air/-	2007 [122]
Resole-type PFR (MAST Carbon Ltd.)/Asymmetric CMSM & ASCM	Supported (outer face of a novolak phenolic resin + hydroxyethyl cellulose tube)	Spray coating (1 layer) 20 wt. % in ethanol	800; -; -; N ₂	130; -; -; air/- or 130; -; -; air /800; -; 60; CO ₂ (inside or both sides)	2007 [144]
Novolak PFR + HMTA/Asymmetric CMSM	Supported (novolak PFR + methyl-cellulose tube)	Dip coating (1 layer) 60 wt. in alcohol	850; 0.5; 60; Ar	RT; -; 2 days; air + 150; 0.5; 1; air/-	2007 [37]
Phenolic resin + zeolite silicalite-1 particles/ MMM	Supported (alumina tube)	Vacuum slip casting (VSC; 0.05-0.07 MPa, 30-150 s.)	620; 2; 120; N ₂	50; -; 720; air + 100; -; 60; N ₂ + 200; -; 60; N ₂ + 350; -; 60; N ₂ /-	2007 [145]
Phenolic resin (Arakawa Chemical Inc.) + zeolite NaA/MMM	Supported (inner face of an alumina tube)	Dip coating (1-3 layers; 3 min) ^B 40% wt. in ethanol	600; 1; 120; N ₂	RT; -; 1 day; air + RT; -; 6 h; vacuum/-	2008 [146]
Resorcinol-formaldehyde resin/mesoporous carbon membrane (Na ₂ CO ₃)	Unsupported (tube)	Casting on the inner wall of a glass tube	120; 10; 60; N ₂ + 950; 5; 180; N ₂	Dried by freeze-drying at -10 °C/-	2008 [147]
Resorcinol-formaldehyde resin + quaternary ammonium compounds (TMAB or TPAB)/microporous carbon membrane (Na ₂ CO ₃)	Supported (silica-coated alumina; flat)	Spin coating (3-4 layers) ^A Ethanol/water solution	800; 5; 480, N ₂	90; -; 1 day; air/-	2010 [135]
Phenolic resin crosslinker + PVA + Zeolite 5A/MMM	+ Self-standing flat membrane	Casting on a glass plate Ethanol/water solution	550-700; 1; 60; N ₂	70; -; 1 day; air/-	2010 [148]
Resorcinol-Formaldehyde resin + CTAB/mesoporous	Supported (sintered coal fly-ash tube)	Dip coating (2 layers) ^A	800; 2; 60; Ar	RT; -; 2 days; air/-	2010 [149]

carbon membrane (CTAB)					
Resole phenolic resin (Euroresinas - Industrias Químicas S.A.) + boehmite nanoparticles/CMSM-MMM	Supported (alumina tube)	Vacuum-assisted dip coating (1 layer) 12.5 wt.% in NMP	550; 1; 120; N ₂	40; -; 120; air + 90; -; overnight; air/-	2011 [48]
Phenolic resin (Qianjin Chemical Industry Factory) + PVA or phenolic resin + PVA + HMTA/CMSM	Self-standing membranes	Casting on a glass plate Ethanol/water solution	450; 1; 60; N ₂	70; -; 1 day; air/- or 70; -; 1 day; air + 210; -; 30; air/-	2011 [150]
Novolak type PFR + HMTA/Asymmetric CMSM	Supported (novolak PFR + methyl-cellulose tube)	Dip coating (2 layers) 50 wt. % in ethanol	600-900; -; 60; Ar or N ₂	RT; -; 2 days; air + 120-180; 0.25-2; 60-120; air/-	2011 [151]
Phenolic resin (Euroresinas - Industrias Químicas S.A.) + boehmite nanoparticles + ethylenediamine or phenolic resin + boehmite nanoparticles + silver nanoparticles + ethylenediamine /CMSM-MMM	Supported (alumina tube)	Vacuum assisted dip coating 13 wt. % in NMP	550; 1; 120; N ₂	40; -; 120; air + 90; -; overnight; air/-	2012 [152]
Novolak-type phenolic resin (Rezitan Co.)/unknown	Supported (inner face of a graphite tube)	Dip coating (1-4 layers) ^B 35-55 wt. % in methanol/NMP	700; 1; 60; N ₂	RT; -; 1 day; air + 50; -; 720; air + 50; -; 720; vacuum + 150; -; 120; air/-	2013 [130]
Phenolic resin (Euroresinas - Industrias Químicas, SA.) + boehmite nanoparticles/CMSM-MMM	Unsupported and supported (alumina tube)	Vacuum assisted dip coating (1 layer) 12.5-15 wt.% in NMP	550; 1; 120; N ₂	40; -; 120; air + 90; -; overnight; air/-	2014 [153]
Resole-type PFR + F127/OMC membrane (NaOH)	Unsupported and supported (PVDF hollow fibres)	Soaking and solvent evaporation 20 wt. % in ethanol	350; 1; 120; N ₂ + 700; 1; 180; N ₂	100; -; 720; air/-	2014 [123]
Resorcinol-formaldehyde resin (Continental Portugal) + boehmite nanoparticles + ethylenediamine/CMSM-MMM	Supported (alumina tube)	Vacuum assisted dip coating (1 layer) 14-15 wt. % in NMP	110; 1; 30; N ₂ + 500-550; 1; 120; N ₂	70; -; overnight; air + 90; -; 720; air/-	2014 [154]
Resorcinol-formaldehyde resin + F127 + EOA/CMSM & NCM (HCl)	Supported (phenolic resin + HMTA + methyl-cellulose plate)	Dip coating (1 layer; 2-60 s) or drop casting Ethanol/water solution	400; 2; 180; N ₂ + 600; 1; 360; N ₂	30; -; 1 day; air + 100; -; 1 day; air /-	2014 [116]
Resorcinol-formaldehyde resin + F127/CMSM & NCM (NaOH or Na ₂ CO ₃)	Free-standing (flat circular film)	Casting on a glass plate Ethanol solutions	600-800; 1; 180; N ₂	25; -; 1 day; air + 100; -; 1 day; air /-	2014 [155]
Novolak-type PFR + boehmite nanoparticles + ethylenediamine/CMSM-MMM	Unsupported and supported (outer face of an alumina tube)	Vacuum-assisted dip coating (10 s) 16.8 wt. % in NMP solution	500; 1; 120; N ₂ or 100; 1; 30; N ₂ + 450-1000; 1;	100; -; overnight; air/- Regeneration: 100-200; 0.7; 120;	2015 [79, 156]

(Oxalic acid)			120; N ₂	N ₂	
Novolak-type phenolic resin (Kolon industries)/CMSM	Supported (alumina disk and inner face of an alumina/stainless steel composite tube)	Slip casting ^B 20 wt.% in NMP	600-900; 1; 60; vacuum	RT; -; 1 day; air + 150-300; -; 120-240; air/-	2016 [157]
Novolak-type PFR/CMSM	Supported (clay-alumina tubes)	Normal and vacuum-assisted dip coating (5 layers) ^A 40-60 wt. % in ethanol	180; 0.5; 60; N ₂ + 380; 0.5; 90; N ₂ + 780; 0.5; 120; N ₂	RT; -; 1 day; air/-	2016 [158]
Novolak-type PFR (Shandong Resin Corp.) + HMTA or Novolak-type PFR + HMTA + urea /microporous carbon membrane	Supported (porous novolak resin tube)	Dip coating	800; 1; 60; N ₂	RT; -; 3 days; air/-	2017 [159]
Phenolic resin (Air Water Bellpearl Inc.) or phenolic resin + iron acetate/CMSM-MMM	Supported (outer face of alumina tubes)	Dip coating (10 min) 30 wt. % in THF	400-800; □125-260; 10; N ₂	70; -; 480; air + 100; -; 1 day; vacuum/-	2018 [160]
Novolak-type PFR + boehmite nanoparticles + ethylenediamine/CMSM-MMM (Oxalic Acid)	Supported (outer face of an alumina tube)	Vacuum-assisted dip coating (10 s) 16.8 wt. % in NMP solution	500; 1; 120; N ₂	100; -; overnight; air/-	2019 [124]

* = for commercial resins, the catalyst used does not appear in the column.

A = with intermediate drying/curing steps.

B = with intermediate drying/curing and carbonisation steps.

Abbreviation list: ASCM = adsorption-selective carbon membrane; CMS = carbon molecular sieve; CMSM = carbon molecular sieve membrane; CTAB = cetyltrimethylammonium bromide; DMF = n,n-dimethylformamide; EOA = triethyl orthoacetate; HMTA = hexamethylenetetramine; MMM = mixed matrix membrane; NCM = nanoporous carbon membrane; NMP = n-methyl-2-pyrrolidone; OMC = ordered mesoporous carbon; PEG = polyethylene glycol; PFR = phenol-formaldehyde resin; PVA = poly(vinyl alcohol); SPFR = p-phenolsulphonic acid-formaldehyde resin; TCE = trichloroethane; THF = tetrahydrofuran; TMAB = tetramethylammonium bromide; TPAB = tetrapropylammonium bromide.

4.1.3 Effect of fillers and additives

One of the advantages of polymer membranes is the possibility of involving a filler material in their preparation to improve their structural or gas separation properties [11, 161]. The effect on the gas separation properties of inorganic fillers in MMMs based on CMSs has recently been reviewed elsewhere [162]. Fillers such as zeolites, MOFs, silica, metals nanoparticles or nanostructured carbon materials have been extensively studied in the preparation of MMMs [163], but their use to produce carbon membranes based on phenolic resins as a matrix for gas separation has been less studied in the literature, being exclusively

limited to nickel nanoparticles [129], CMS particles [142], zeolites [145, 146, 148], boehmite [48, 79, 124, 152-154, 156], silver nanoparticles [152] and iron compounds [160] (this type of membranes is indicated as "MMM" in the column "Type of resin/Membrane" in Table 1). Some electron microscopy images of phenolic resin-based MMMs before and after the pyrolysis process can be found in Figure 6.

The addition of boehmite particles to a novolak phenolic resin resulted in defect-free supported membranes with high permeability to permanent gases. Teixeira *et al.* tested the addition of boehmite in the range 0.5-1.2 wt.% and confirmed its effect on the volume and size of the membrane micropores and the resulting gas separation properties [153]. In another work by the same authors [152], CMSMs based on a phenolic resin with boehmite only and boehmite and Ag nanoparticles were prepared, and their respective SEM images can be found in Figure 6d and Figure 6e-f, respectively. The CMSM that included Ag in the resin formulation showed homogeneous integration of Ag nanoparticles with sizes in the range of 10 to 40 nm (see TEM image in Figure 6f) and had a better performance in the separation of N_2/O_2 . Finally, an improvement in the ideal selectivity of CO_2/N_2 and O_2/N_2 has been reported for carbon membranes made from phenolic resin filled with NaA zeolite [146].

Polymer blend solutions containing phenolic resin and polyvinyl alcohol [148, 150], polyethylene glycol (PEG) [143] or triethyl orthoacetate (EOA) [116] have also been reported for the preparation of carbon membranes. The introduction of a second thermolabile polymer may change the final carbon texture and enhance gas permeability. PEG is a thermally unstable polymer that can also act as a neutral surfactant or pore-forming agent during phenolic resin formation, affecting the resulting pore volume of the carbon membrane [143]. Zhang *et al.* used EOA as a co-precursor in the polymerisation of a resorcinol-formaldehyde resin and F127 as a template for the synthesis of a carbon membrane for gas separation [116]. EOA reduced the rate of polymerisation of the precursors during assembly. Furthermore, the

addition of EOA increased the carbon yield of the resin and improved the pore order [164]. Similarly, other surfactants such as Pluronic F127 triblock copolymer [116] or quaternary ammonium compounds (TMAB, TPAB and CTAB) [134, 149, 165] have been used to assist in the formation of soft-templated ordered carbon and carbon membranes with molecular sieving properties.

In addition to formaldehyde or its aldehyde substitute, other crosslinking agents were added to the resin preparation system. In this regard, HMTA or ethylenediamine were used to carry out the polymerisation of the phenolic resin as they act as basic catalysts in the reaction medium, the former by generation of formaldehyde and ammonia upon heating. HMTA has been shown to give the phenolic resin some mobility when heated at low temperature, which reduces the formation of defects or cracks during carbonisation [127].

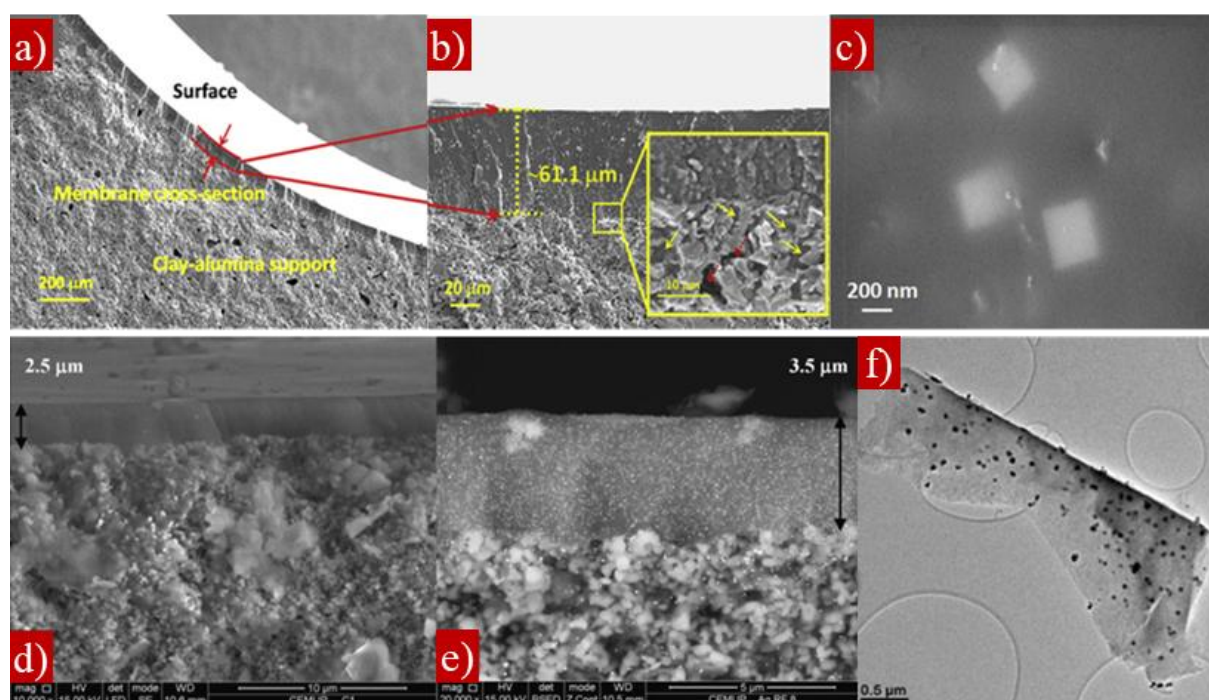


Figure 6. Electron microscopy images of different MMMs based on phenolic resin: (a, b and c) before [166], and (d, e and f) after carbonisation [152]. (a-b) SEM images of the cross-section of the membrane tube and the PFR film with 10 wt. % mesoporous silica; (c) detail of the mesoporous silica particles at high magnification; (d) SEM image of a CMSM based on

phenolic resin with boehmite nanoparticles as filler; (e) SEM image of a CMSM based on phenolic resin with boehmite and Ag nanoparticles; (f) TEM image of the previous membrane where Ag nanoparticles of sizes in the range of 10 to 40 nm are identified. Reproduced with permission from [166] (a, b and c) and [152] (d, e and f).

4.1.4 *Stabilisation of resin precursors and other pre-treatments*

Polymeric membranes are pre-treated before the carbonisation process to ensure the stability of the precursor and its structure during this stage. The result is a carbon membrane of good quality in terms of stability and gas separation performance. In general, this stabilisation (sometimes called curing stage) is carried out while hot in air, and aims at dehydrogenating the polymer with the formation of C=C bonds and oxygen-containing groups, thus improving the intermolecular crosslinking of the phenolic resin. Moreover, the stabilisation minimises carbon volatilisation during the pyrolysis step, which increases the final carbon yield and maintains the morphological structure of the phenolic resin in the carbon produced [8]. The stabilisation process includes the curing step of the resin, which is carried out in air and at temperatures ranging from room temperature to about 170 °C. On the other hand, the pre-oxidation stage, usually performed after curing if performed at all, would involve higher temperatures than the curing step and can reach a maximum of 400 °C [50]. The conditions of these steps (if used) are listed in Table 1 (see “Pre-/Post-treatments” column). Thus, temperature, heating rate and time are important parameters to be considered in the pre-treatment to avoid excessive oxidation that can open the porosity and in an uncontrolled manner, and reduce gas selectivity [151]. Curing or pre-oxidation has been optimised to obtain carbon membranes based on phenolic resin with good gas separation performance [46, 50, 150, 151]. In the case of novolak resin, stabilisation during curing works well when a crosslinking agent (e.g. HMTA) is involved [151].

Among the parameters studied, the heating rate had the greatest influence on the porous structure of the membrane and its gas separation properties [151]. Wei *et al.* observed that a heating rate lower than 0.5 °C/min did not result in a sufficiently smooth outer surface [151], due to the formation of defects (or bubbles) related to the evolution of gases during this thermal step. Moreover, they reported a small effect of the stabilisation temperature in the range 120-180 °C on the resulting carbon membrane. With respect to temperature, high temperatures can partially destroy the original backbone of the polymeric precursors [10]. Zhang *et al.* studied the differences between the use of a crosslinking agent (HMTA) and a pre-oxidation step (in air at 210 °C for 30 min) on the preparation of carbon membranes from a solution mixture of phenolic resin and PVA and their performance in H₂/N₂ separation [150]. The pre-oxidised carbon membranes had a lower degree of crosslinking than that obtained with HMTA prior to pyrolysis, resulting in lower H₂ permeability and selectivity. On the other hand, Centeno and Fuertes reported an increase in gas permeabilities (He, CO₂, O₂, N₂ and CH₄) of CMSMs produced by pre-oxidation in the range 150-300 °C for 2 h [45]. This improvement occurred without altering the permselectivities of the different gas pairs as long as the pre-oxidation temperature did not exceed 250 °C. Once this temperature was exceeded, the permselectivities decreased significantly.

4.1.5 *Pyrolysis process and post-treatments*

After curing, the pyrolysis or carbonisation of the resin results in a porous carbon material with interconnected pores of molecular size for gas sieving. Figure 7 gathers SEM images of phenolic resin-impregnated membranes and carbon membranes obtained after pyrolysis found in literature. The precursor resin, generally supported as a thin film, is slowly heated to temperatures of 450 to 1000 °C in an inert atmosphere or under vacuum. These conditions of temperature, heating rate, time and atmosphere (listed in Table 1, column “Pyrolysis conditions”) will define the textural properties of the final carbon membrane.

Centeno *et al.* have carefully studied the effect of all these variables on the gas separation performance of phenolic resin-based carbon membranes [53]. In addition to significant mass loss, the emission of volatiles (mainly H_2O , CO_2 , CO , NH_3 , CH_4 or H_2) occurs during this stage and are capable of causing cracks, small holes, microscopic bubbles or distortions in the carbon network when high heating rates are used. As mentioned before, the rearrangement of the molecular structure of the resin results in a pore size, pore volume and pore distribution that can be controlled by modifying the pyrolysis parameters exclusively [36, 53, 151, 154, 156].

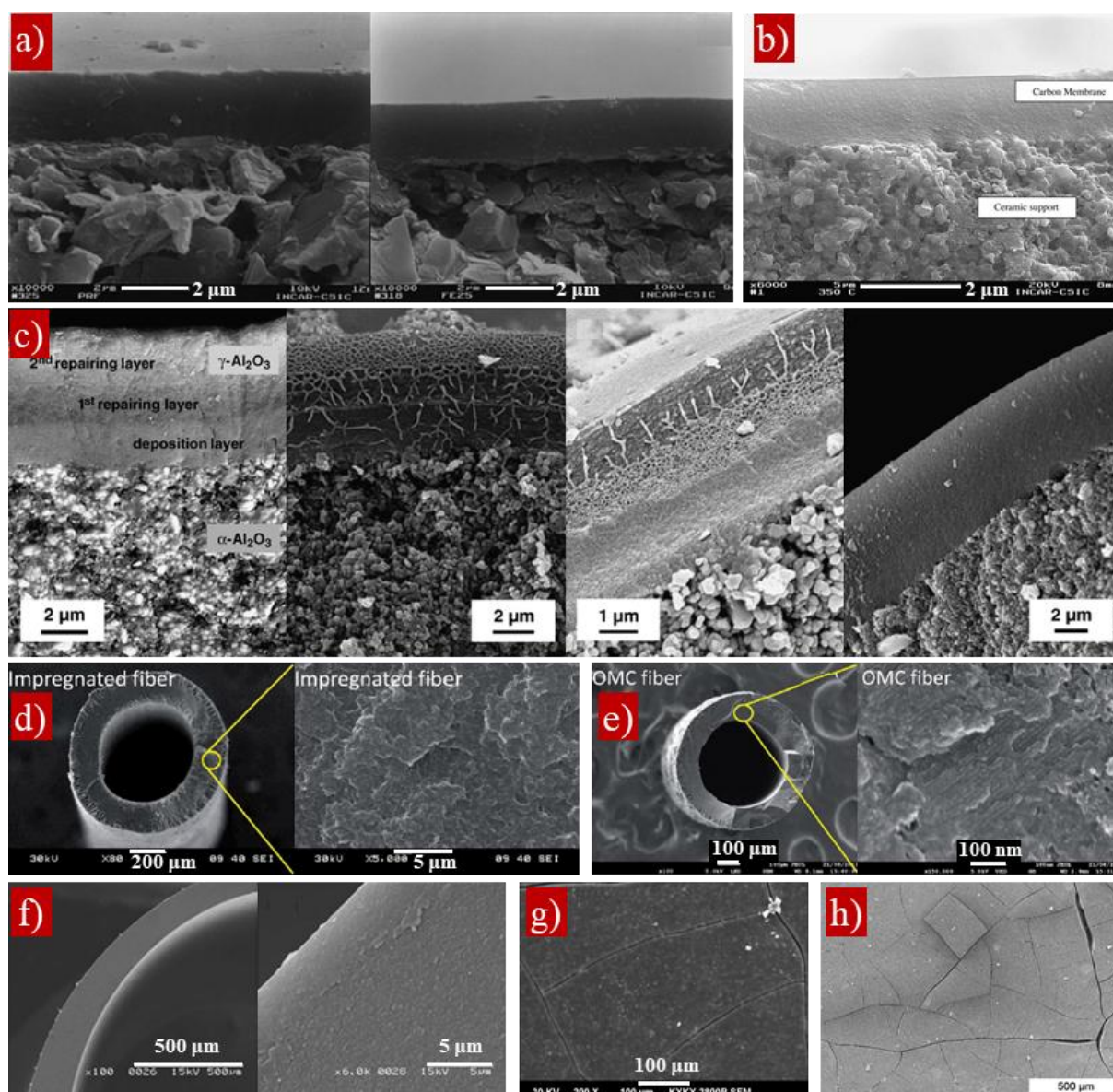


Figure 7. SEM images of examples of phenolic resin-impregnated membranes and carbon membranes obtained after pyrolysis. (a) cross-section of a porous carbon disk coated with a novolak-type phenolic resin film before and after carbonisation [36]; (b) ASCM membrane obtained with a pre-oxidation at 350 °C for 1 h [50]; (c) infiltration sequence of a novolak-type phenolic resin on a γ -Al₂O₃-based support (left image) carried out by dip-coating for 90 s, 2 h and 3 h (the other 3 images in the same row) and carbonisation at 700 °C [131]; PVDF hollow fibre membranes impregnated with a resole resin (d) before and (e) after carbonisation [123]; (f) unsupported tubular carbon membrane obtained by casting and carbonisation of a resorcinol-formaldehyde resin [147]; (g) [145] and (h) [130] show examples of carbon membranes based on phenolic resins without additives presenting surface cracks after pyrolysis. Reproduced with permission from [36] (a), [50] (b), [131] (c), [123] (d and e), [147] (f), [145] (g) and [130] (h).

Firstly, temperature strongly influences the structure and transport mechanism in the resin, as well as the separation performance and separation mechanism of the carbon membrane [7-10, 36]. From a simplified point of view point, higher pyrolysis temperatures produce more compact and dense carbon membranes with lower permeability but higher selectivity. To find the adequate microporous structure, a systematic study of the carbonisation of a phenolic resin at different intervals has established a direct correlation between temperature and structure (volume and size of micropores) and the gas permeation properties of the membrane [36, 53, 128]. It has been estimated that pores appear at temperatures up to 500 °C, enlarge up to 800 °C and collapse by shrinkage at higher temperatures. At 1000 °C, the membrane is impermeable to gas and has less porosity than the cured resin.

Centeno and Fuertes conducted experiments at pyrolysis temperatures between 500 and 1000 °C (see conditions in Table 1, Entry 5) using a novolak-type phenolic resin [36]. The membranes exhibited molecular sieving properties with a micropore size of about 0.42 nm and maximum He permeances after carbonisation at 700 °C. In other works, the same authors identified ASCM behaviour for supported novolak-type phenolic resin membranes carbonised at 700 °C and CMSM behaviour for those carbonised at 800 °C [53]. While the former were highly efficient for the separation of hydrocarbons from N₂, the latter demonstrated good selectivity for the separation of O₂/N₂ and CO₂/CH₄ pairs and olefin/paraffin mixtures, as well as significant decreases in gas permeance. Likewise, temperatures between 900 and 1000 °C gave CMSMs with high permselectivities for gas molecules below 0.4 nm.

The heating rate, typically in the range from 1 to 10 °C/min, has a minor but not less important influence on the properties of the carbon membrane, and has also been optimised [53, 151]. Although a high heating rate produces a larger number of defects and lower permeance, as already mentioned, low rates induce more ordered and compact carbon structures with a microporosity more suitable for molecular sieving. Centeno *et al.* tested heating ramps in the range of 0.5-10 °C/min and reported that high carbonisation rates reduce gas permeance but promote molecular sieving [53]. Although no difference was found for low heating rates, membranes obtained above 5 °C/min showed significantly reduced gas permeability, as it favoured the formation of carbon membranes with smaller pores. At 10 °C/min, a more selective membrane was obtained for the separation of pairs of permanent gases, with better molecular sieving properties. Similarly, the authors completed the carbonisation with times of 60 to 480 min at the maximum pyrolysis temperature (also called thermal soaking time) and confirmed that an extension of this parameter had a similar effect to that of increasing the heating rate. The pyrolysis time was stated as a variable to adjust

finally the texture of the membrane and its transport mechanism to separate a specific gas mixture.

The role of the pyrolysis atmosphere has been disclosed by Salleh *et al.* in a review on the preparation of polymer-based carbon membranes [10], and is divided into inert, vacuum and oxidative atmospheres. As can be seen from Table 1 (column “Pyrolysis conditions”), N₂, Ar and vacuum are the most commonly used atmospheres for the carbonisation of phenolic resins in obtaining membranes for gas separation. In this way, the gasification of the polymeric precursor or the carbon membrane is avoided. Oxidising atmospheres (O₂ or CO₂) have been used to produce ASCMs but only after vacuum or inert pyrolysis processes (see previous section). Inert gas is assumed to promote gas release during pyrolysis and avoid pore shrinkage by carbon deposition [53]. This improves the gas permeation of the membrane (up to 5 times more) compared to that obtained by vacuum pyrolysis. The inert gas increases the mass and heat transfers of the gas phase, promoting a more open porous structure, which in some cases can reduce the selectivity of the membrane.

Post-oxidation (considered as an activation stage), has also been estimated in order to modify the carbon structure of the membrane after carbonisation [46, 49-51, 144]. This additional step has led to the development of adsorption-selective carbon membranes (ASCMs), with a pore structure in the range of 0.5 to 0.7 nm, which are more effective in separating hydrocarbons and weakly adsorbable gases [49-51]. According to Fuertes, adsorbed hydrocarbons pass through the pores by surface diffusion, which hinders the diffusion of non-adsorbable gases due to pore shrinkage and improves the selectivity of the membrane [49, 50]. Furthermore, Fuertes compared phenolic resin-based ASCMs treated by pre- or post-oxidation beholding similar gas permeances but substantially higher selectivities for those post-oxidised [50]. Subsequently, ASCMs have also been used for the separation of hydrocarbons pairs (ethylene/ethane; propylene/propane; *n*-butane/*iso*-butane) and pre- and

post-oxidised membranes have shown improved separation performance and a combination of adsorption and molecular sieving mechanisms [46]. This work also studied the treatment of the carbonised membrane by CVD (using N₂ saturated with trichloroethane at 500 °C for a few minutes) before and after post-oxidation. Katsaros *et al.* obtained asymmetric ASCMs by activating with CO₂ at 800 °C for 60 min a carbon membrane derived from phenol-formaldehyde [144]. These membranes showed good CO₂ selectivity for equimolar CO₂/N₂ mixtures and a separation mechanism based on selective adsorption.

As a result of oxidation, the surface of the carbon membrane surface presents oxygenated functional groups that promote the adsorption of water. Due to the clogging effect of water and associated problems such as pore blockage or reduced permeability to other species, the applicability of CMSMs is compromised by their stability over time [8, 51, 52]. To this end, the effect of the ageing of phenolic resin-based carbon membranes on their gas separation properties has been investigated [79, 139, 156]. Menéndez *et al.* reported the separation behaviour of supported carbon membranes stored in different environments (air, nitrogen and propylene) and for different times [139]. Membranes stored in air showed a severe loss of permeance and a slight increase of permselectivity over time. However, the permeance could be partially recovered by regeneration by heat treatment (120 or 600 °C, under vacuum). As a consequence of the above, the authors suggested the use of carbon membranes to separate oxygen-free gas mixtures. In addition to this work, other authors also reported similar separation results after subjecting carbon membranes to regeneration by heat treatments in the range of 100-200 °C under vacuum or N₂ atmosphere [46, 79, 156].

4.2 Performance of carbon membranes in gas separation

4.2.1 *Current status of CMSMs and critical points for industrial applications*

In the previous section, the various techniques for synthesising CMSMs materials have been critically detailed. From a practical point of view, a comparison of the different characteristics, compared to polymeric membranes, is a key starting point and is summarised in Table S3 of the Supplementary Information. It can be seen that, besides increased performance for important industrial applications that will be detailed below, CMSMs also show attractive properties, especially in terms of chemical and thermal resistance. These properties could be of major interest for new applications, especially for the development of hybrid reactor/separator systems. Indeed, in a large number of cases, coupling the separation process with a reactor requires an intermediate cooling step (chemical reactions being most often performed under high-temperature conditions). This constraint can affect the overall energy efficiency of the process and increases the capital cost with the necessity to install heat exchangers. The high chemical resistance is also of great interest, especially to prevent plasticisation effects (typical of glassy polymers exposed to pressurised gas mixtures with CO₂ for instance), or to allow an application with organic vapours (e.g. VOC recovery, hydrocarbon separation, ...). The main limitations of CMSMs today clearly results from the lack of feedback, from the point of views of both industrial processing and large-scale application. Consequently, CMSM cost remains difficult to evaluate. It is expected that significant progress will soon be achieved in these directions. The potential interest in different industrial gas separation applications, as well as the potential market for carbon capture, will be discussed in the following sections. A summary of the different priority performances of CMSMs for each type of application can be found in Table S4 of the Supplementary Information.

4.2.2 Separation of air (O_2/N_2)

Conventionally, the air separation industry, focused on the production of high-purity O_2 , N_2 and noble gases, devotes large amounts of energy to gas separations, most often by cryogenic processes. In this scenario, membrane technologies can limit the energy demand and allow for greater cost effectiveness to products. Thus, the O_2/N_2 pair from the air separation process leads the group of permanent gas pairs most studied in the literature. Nitrogen-Enriched Air (NEA) has been the market leader in membrane gas separation processes for decades [1]. An increased permeance, compared to the performance of existing commercial membranes, has been recently shown to be of great interest for membrane NEA processes [167]. Oxygen-Enriched Air (OEA) is a very promising market, but breakthrough improvements of membrane selectivity are needed to compete with cryogenics or PSA (Pressure Swing Adsorption) / VSA (Vacuum Swing Adsorption) processes [168]. With respect to the O_2 permeability and O_2/N_2 selectivity data offered by membranes based on carbonised phenolic resins (Table 1 and Figure 8), there is evidence that a large proportion of them exceed Robeson's upper bound for this gas pair. It should be noted that the PRCMs were published both before and after 2008 Robeson's compilation [73].

Among the membranes represented, five works stand out from the rest by setting a new upper bound (dashed line in Figure 8) [128, 136, 137, 156, 157]. Wang *et al.* reported in 1996 carbon membranes with the best separation values for the O_2/N_2 pair among the phenolic resin-based carbon membranes to date [136, 137]. Asymmetric flat membranes were prepared by pyrolysis of the resin film at 800-950 °C, followed by uneven post-activation with 0.5-2 % O_2 diluted in N_2 at the same temperature. This resulted in the formation of a molecular sieve with high O_2 permeability through it. Zhou *et al.* presented membranes obtained from the carbonisation of sulphonated phenolic resin as the carbon precursor [128]. An effective contribution of boehmite addition to a novolak resin has been reported by Llosa Tanco *et al.*

in the preparation of CMSMs [156]. Carbonisation temperatures in the range 500-700 °C led to membranes with the highest permeation values. Likewise, a membrane carbonised at 550 °C had the highest separation parameters for the O₂/N₂ pair after 1 day of exposure to air at room temperature. This exposure significantly improved the permselectivity of the CMSM by reducing the pore size through oxygen chemisorption and water physisorption. Finally, Lee *et al.* obtained higher ideal O₂/N₂ separation factors in a flat alumina disc configuration after optimisation of the impregnation step and carbonisation at 800 °C [157]. In this case, the viscosity of the phenolic novolak resin solution and the number of coatings played a key role in the separation performance of the resulting CMSM.

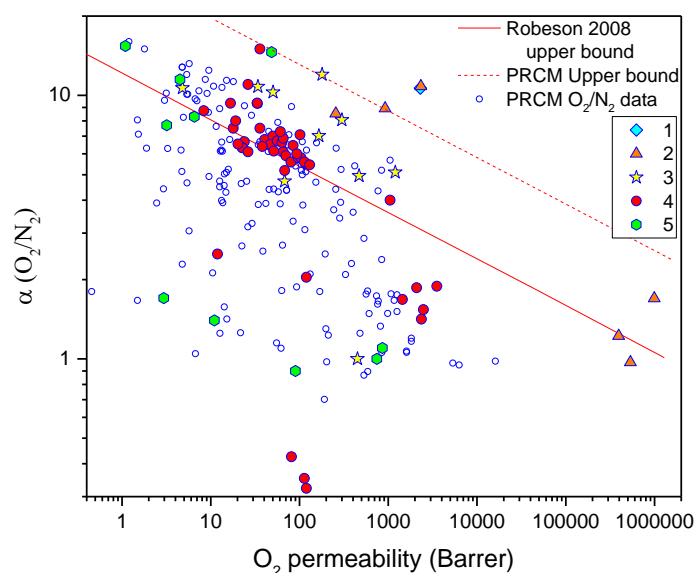


Figure 8. O₂/N₂ ideal selectivity vs. O₂ permeability. PRCM data (from Table 1) and Robeson's 2008 upper bound for polymeric membranes [73]. The dashed line represents the upper bound found for PRCMs in the present review. Featured works: 1 = Wang *et al.* 1996 [136], 2 = Wang *et al.* 1996 [137], 3 = Zhou *et al.* 2003 [128], 4 = Llosa Tanco *et al.* 2015 [156] and 5 = Lee *et al.* 2016 [157].

4.2.3 Natural gas/biogas sweetening (CO₂/CH₄)

The separation of CO₂ from CO₂/CH₄ mixtures is of paramount importance in the natural gas industry. The biogas upgrading application is also developing extremely rapidly, with

membrane gas separation being considered the best available technology [169]. Cellulose acetate and polyimide membranes are commercially available for these applications, with limitations due to plasticisation for natural gas sweetening and a limited selectivity for both natural and biogas treatment. A recent study has shown that membrane materials exhibiting improved selectivity and permeance compared to existing polymers, even at a much higher cost, are extremely attractive [170].

Together with zeolites, CMSMs have shown exceptional separation behaviour for this gas pair in separation processes based on membrane technologies [171]. Based on the data collected in Figure 9 for the CO₂/CH₄ separation, it can be concluded that a large number of carbon membranes based on phenolic resin exceed Robeson's limit for this pair [73]. As with the N₂/O₂ pair, the CMSM obtained by Lee *et al.* [157] and Zhou *et al.* [128] obtained exceptional separation properties for the CO₂/CH₄ pair. Similarly, the membrane obtained after pyrolysis of a novolak resin at 800 °C by Lee *et al.* [157] stands out from the rest due to a surprising selectivity of 667 for this gas pair. On the other hand, the carbonisation of a precursor containing sulphonated phenolic resin produced CMSMs with high O₂ and CO₂ permeations and high O₂/N₂ and CO₂/CH₄ separation factors [128, 140]. The addition of *p*-phenol-sulphonic acid in the preparation of phenolic resin has a positive effect on the CMSM generated after carbonisation since it promotes the binding of sulphonic acid groups to the polymer chains and subsequent decomposition at the beginning of the pyrolysis step. The decomposition of the sulphonic acid groups releases SO₂, H₂O and small fragments of the phenolic resin chains, which improves the microporous structure of the resultant CMSM.

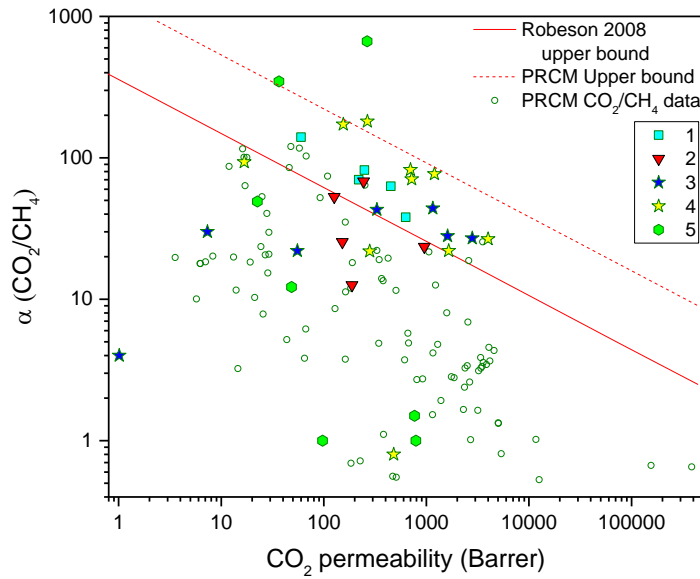


Figure 9. CO_2/CH_4 ideal selectivity vs. CO_2 permeability. PRCM data (from Table 1) and Robeson's 2008 upper bound for polymeric membranes [73]. The dashed line represents the upper bound found for PRCMs in the present review. Featured works: 1 = Okamoto *et al.* 2001 [121], 2 = Menendez and Fuertes 2001 [139], 3 = Zhou *et al.* 2001 [140], 4 = Zhou *et al.* 2003 [128], and 5 = Lee *et al.* 2016 [157].

4.2.4 Carbon dioxide capture and storage (CO_2/N_2)

The separation of CO_2 from power plant flue gases is of emerging interest in capture and storage strategies [172]. Membranes have initially been discarded compared to gas-liquid absorption processes with chemical solvents [173], but are now considered a promising second generation technology [174]. For the separation of the CO_2/N_2 gas pair, tailor-made polymeric membranes have been designed, such as Polaris [175] (MTR company), with a CO_2/N_2 selectivity of 30 and CO_2 permeance of up to 3000 GPU. Pilot demonstrators have recently shown promising performances on real flue gases. Nevertheless, the priority to develop more permeable or more selective membranes is still an open debate.

A completely different target for carbon capture application is also being actively investigated, namely the direct capture of CO_2 from air [176]. Membranes are once more

considered as inappropriate in that case, because of the very high dilution of CO₂ in the feed mixture (400 ppm in place of 15% in flue gases) [177]. However, this may need to be reconsidered if very selective and/or very permeable materials are identified.

Interestingly, carbon membranes operate above the upper bound of polymeric membranes [36, 178]. Figure 10 shows the data collected for the CO₂/N₂ separation. Among other polymeric precursors used to synthesise a MCSM such as polyimide or polypyrrolone, Okamoto *et al.* found that the phenolic resin-derived carbon membrane was the best for CO₂/N₂ separation [121]. The membrane made by Zhang *et al.* gave surprising separation results, far above the upper bound of the polymers: an average CO₂ permeability of 4862 Barrer and a CO₂/N₂ permselectivity of about 86 [155]. This membrane was produced by pyrolysis at 600 °C of a soft-templated resorcinol-formaldehyde resin using Pluronic F-127 as surfactant and NaOH as catalyst. As a result of soft-templating, the authors formed freestanding semi-transparent polymeric membranes, which were carbonised without the participation of a porous support. Again, the membranes obtained by Lee *et al.* [157] and Zhou *et al.* [128] had exceptional separation properties, exceeding Robeson's upper bound. With good gas separation performance, Teixeira *et al.* reported a CMSM that also exceeded the upper limit [153]. The membrane was prepared from a phenolic resin with the addition of boehmite nanoparticles, followed by pyrolysis. Similarly, this research group reported further work on the good performance of boehmite-containing membranes for the separation of the CO₂/N₂ pair [79, 152].

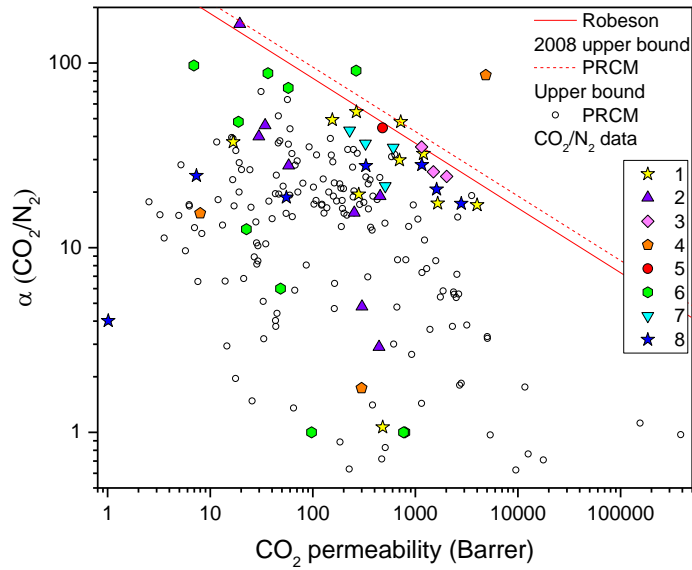


Figure 10. CO₂/N₂ ideal selectivity vs. CO₂ permeability. PRCM data (from Table 1) and Robeson's 2008 upper bound for polymeric membranes [73]. The dashed line represents the upper bound found for PRCMs in the present review. Featured works: 1 = Zhou *et al.* 2003 [128], 2 = Zeng *et al.* 2008 = [146], 3 = Teixeira *et al.* 2014 [153], 4 = Zhang *et al.* 2014 [155], 5 = Llosa Tanco *et al.* 2015 [79], 6 = Lee *et al.* 2016 [157], 7 = Teixeira *et al.* 2012 [152] and 8 = Zhou *et al.* 2001 [140].

4.2.5 Hydrogen purification (H₂/CO₂)

With many industrial applications, hydrogen separation is one of the most established membrane processes. Hydrogen purification has been one of the earliest industrial applications of polymeric membranes and it is now one of the major market of membrane gas separations [179]. It is interesting to note that, for the CO₂/H₂ gas pair, polymeric membranes can be selective towards H₂ (glassy materials with α around 15 and 300 GPU towards H₂) or CO₂ (rubbery materials with α around 10 and 1000 GPU towards CO₂) [180]. The pre-combustion application could be a very large market, with high pressure and high temperature CO₂/H₂ mixtures to be separated. The need for highly selective materials and thermally

resistant membranes is clearly considered as a priority, in order to enable simultaneously a high purity and recovery for H₂ and CO₂.

In this respect, carbon membranes have an outstanding performance in the separation of the H₂/CO₂ pair [181]. As shown in Figure 11, phenolic resin-based carbon membranes offer higher separation performance compared to polymer-type membranes. In fact, they easily exceed Robeson's upper bound [73]. Different membranes synthesised by Wei *et al.* [37, 127] and Qin *et al.* [149, 159], in the same research group, have shown very good separations for this gas pair. They reported membranes obtained from novolak resins made of both phenol-formaldehyde cured by HMTA [37, 127, 159] and resorcinol-formaldehyde with CTAB as surfactant [149]. Among these membranes, the nitrogen-doped membrane stands out by a substantial improvement in H₂ permeability (87761 Barrer for a 7 µm selective carbon layer) [159]. To prepare this membrane, urea was added to a phenol-formaldehyde resin with HMTA. The urea decomposed during the heat treatment, promoting the formation of micropores and nitrogen doping of the resulting carbon membrane. Nitrogen doping would lead to higher adsorption of CO₂ hindering the permeability of this gas compared to that of H₂. In the same sense, Li *et al.* described the preparation of OMC hollow fibre membranes with a very high H₂ permeability [123]. The carbon precursor was obtained by soft-templating a resole phenolic resin using Pluronic F127. This precursor was assembled in the pores of a polyvinylidene fluoride (PVDF) ultrafiltration hollow fibre membrane and then pyrolysed.

Offering higher ideal selectivities, in the range H₂/CO₂ = 11-60, the works of Zhang *et al.* [143] and Rodrigues *et al.* [154] reported a CMSM with remarkable separation performance. As commented for the CO₂/N₂ pair, for which some of their membranes offered separation values above Robeson's upper bound, Rodrigues *et al.* prepared a CMSM by pyrolysis of a supported resorcinol-formaldehyde resin film comprising boehmite and ethylenediamine in its synthesis [154]. Zhang *et al.* [143] reported the positive effect of mixing a phenol-

formaldehyde novolak resin with PEG on the separation performance of the CMSM obtained after carbonisation. PEG acts as a micropore-forming agent enhancing the permeability of permanent gases, especially when the kinetic diameter of the gas is small. Finally, Roy *et al.* reported on the preparation of a conventional CMSM based on a phenol-formaldehyde novolak resin with an average H₂ permeability-H₂/CO₂ selectivity behaviour.

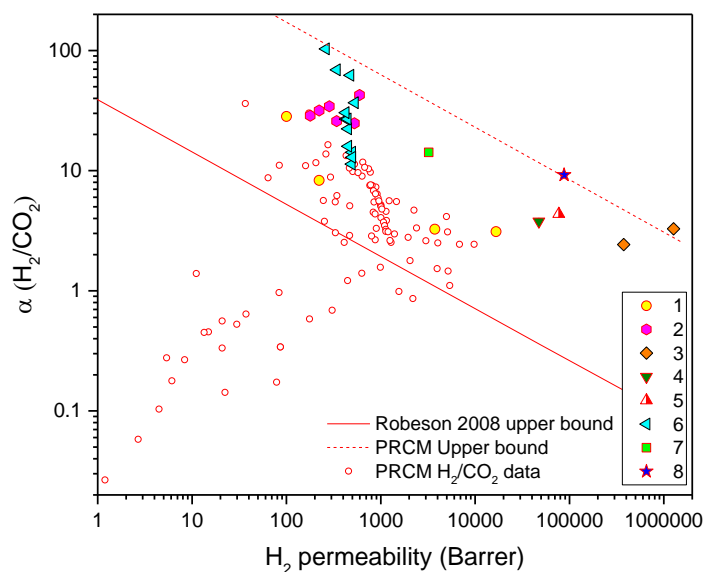


Figure 11. H₂/CO₂ ideal selectivity vs. H₂ permeability. PRCM data (from Table 1) and Robeson’s 2008 upper bound for polymeric membranes [73]. The dashed line represents the upper bound found for PRCMs in the present review. Featured works: 1 = Wei *et al.* 2002 [127], 2 = Zhang *et al.* 2007 [143], 3 = Yoshimune *et al.* 2008 [147], 4 = Qin *et al.* 2010 [149], 5 = Li *et al.* 2014 [123], 6 = Rodrigues *et al.* 2014 [154], 7 = Roy *et al.* 2016 [158] and 8 = Qin *et al.* 2017 [159].

5 “GREENER” PHENOLIC CARBON MEMBRANES IN GAS SEPARATION

Phenol-formaldehyde resins with partial or total substitution of their components by sustainable or biosourced compounds have been studied and implemented in industrial production processes over the last decades. This has been discussed in Section 3.2. Similarly,

although there are meso- and microporous carbons obtained by pyrolysis of this type of green phenolic resins (see Section 3.3), obtaining membranes such as carbon molecular sieves for gas separation did not have a significant impact in research, according to the few articles found in the literature on this topic. Table 2 compiles some examples of carbon membranes obtained from partially or totally “green” phenolic resins studied in the separation of the O_2/N_2 , CO_2/CH_4 , CO_2/N_2 and H_2/CO_2 gas pairs. Additionally, the Robeson-type plots for these membranes and each gas pair are grouped in Figure 12. These plots also include the upper bounds established for polymeric membranes [73] and conventional phenolic resin-based carbon membranes (shown in this review in Figures 8-11), as well as the permeability/selectivity pairs for the selective carbon layer of the phenolic resin-based carbon membranes (represented as crosses).

Natural polyphenols, particularly lignin extracts and thermochemically processed liquid biomass products, have been widely used for the production of phenolic resins (see Figure 2) and have also found a place in the preparation of carbon molecular sieves. The preparation of membranes for gas separation from these materials is rarely reported in the literature, although it may open up a space for new research. In this sense, lignocresols, as polyphenolic extracts of lignocellulose and other liquefied wood products, represented an approach to synthesise CMSMs for gas separation [182-187]. Pyrolysis of these precursors was carried out over a temperature range of 400-800 °C and under vacuum or N_2 atmosphere. In the works of the research group of Kita *et al.* and Koga *et al.* [182-185], a lignocresol fraction was extracted from a lignin matrix by a phase-separation treatment with *p*-cresol and sulphuric acid. This phenolic fraction was mixed with methyl ethyl ketone and used to coat the outer face of an alumina tube. After pyrolysis, the supported CMSM showed separation performances above Robeson’s upper bound for the gas pairs O_2/N_2 , CO_2/CH_4 , and H_2/CO_2 . In fact, the membrane carbonised at 700 °C stands out from the rest for any gas pair; for

example, the permeabilities to O₂ and CO₂ are 17 and 57 Barrer, respectively, and the permselectivities to O₂/N₂ and CO₂/CH₄ are 12 and 260, respectively [184, 185].

CMSMs were produced from liquefied larch sawdust by Zhao *et al.* [186, 187], using formaldehyde (which could be replaced by a more benign or sustainable aldehyde) and Pluronic F127 in the synthesis. The latter was used as a pore-forming agent to obtain an ordered mesoporous carbon. However, the resulting pore structure exhibited a very narrow average pore size (2.1-2.6 nm), resulting in very low gas permeabilities and poor separation performance (as observed in Figure 12c for CO₂ and CO₂/N₂) [186]. After incorporation of Ni nitrate into the resin precursor, which formed 10 nm Ni/NiO nanoparticles in the carbon network, the average pore size of the carbon membrane increased above 3.4 nm. The O₂ and CO₂ permeabilities thus reached very high values exceeding Robeson's upper bound for O₂/N₂ and CO₂/N₂ [187].

There are other natural compounds obtained from plants or algae such as phloroglucinol that have been used to prepare phenolic resin-based CMSMs for gas separation [104, 188, 189]. In the reported cases, Pluronic F127 was used as a surfactant to improve the order and microporosity of the resulting CMSM by a soft-templating process. Tanaka *et al.* reported the preparation and N₂ permeances of CMSMs supported on alumina tube from phloroglucinol-resorcinol-formaldehyde resins [188]. The carbon layer presented a mesoporous structure with an average pore diameter of about 6.4 nm. Wang *et al.* [104] prepared freestanding carbon membranes from phloroglucinol-formaldehyde resins and the participation of HMTA as the curing agent and to prevent cracking during the carbonisation step. Although their separation performance did not exceed Robeson's upper bound for the gas pair tested (O₂/N₂ and CO₂/N₂), the resulting membranes showed high permeation for O₂ and CO₂ and good mechanical performance for a scale-up. Subsequently, Chai *et al.* were able to bring the

separation efficiency of these same membranes closer to the CO₂/N₂ upper bound by adding carbon black as a filler and immobilising an imidazolium-based ionic liquid [189].

Table 2. Carbon membranes for gas separation obtained by carbonisation of green phenolic resins.

Resin formulation	Origin of the green substituent (Supplier)	Carbonisation (Temp.: °C; Ramp: °C/min; Time: min; Gas)	Membrane configuration	Gases tested	Year Ref.
Lignocresol + MEK (Butanone) or THF	Lignocresol (isolated from native wood of Hinoki by phase-separation treatment with <i>p</i> -cresol and sulphuric acid)	400-800; 5 ; 60; N ₂ or vacuum	Supported CMSM (outer face of an alumina tube)	He, H ₂ , CO ₂ , CH ₄ , N ₂ , O ₂	2002 [182] 2004 [183]
Lignocresol + MEK (Butanone) or THF	Lignocresol (synthesised from Hinoki cypress by phase-separation treatment with <i>p</i> -cresol and sulphuric acid)	600, 700; 500; -; N ₂ (high frequency induction heating system)	Supported (outer face of an alumina tube)	H ₂ , CO ₂ , CH ₄ , N ₂ , O ₂	2008 [184] 2009 [185]
Phloroglucinol + formaldehyde + HMTA + F127	Phloroglucinol (-)	400; 1; 120; N ₂ + 850; 5; 120; N ₂	Flat-sheet free standing membrane	He, CO ₂ , N ₂ , O ₂ , C ₃ H ₆	2010 [104]
Resorcinol + phloroglucinol + formaldehyde + F127	Phloroglucinol (Wako Pure Chemical Industries, Ltd.)	600; 1; 60; N ₂	Supported (outer face of an alumina tube)	N ₂	2011 [188]
Liquefied larch wood + formaldehyde + F127	Liquefied larch sawdust	500, 600 and 700; - ; 120; N ₂	Unsupported	CO ₂ , N ₂	2014 [186]
Phloroglucinol + formaldehyde + F127 + carbon black + HMTA + imidazolium-IL	Phloroglucinol (Sigma-Aldrich)	450; -; 120; Ar + 850; 5; 120; Ar	Free-standing (flat circular film)	CO ₂ , N ₂	2014 [189]
Liquefied larch wood + formaldehyde + F127 + Ni(NO ₃) ₂	Liquefied larch sawdust	700; - ; 120; N ₂	Unsupported	CO ₂ , N ₂ , O ₂	2015 [187]

Abbreviation list: CMSM = carbon molecular sieve membrane; HMTA = hexamethylenetetramine; IL = ionic liquid; MEK = methyl ethyl ketone; THF = tetrahydrofuran.

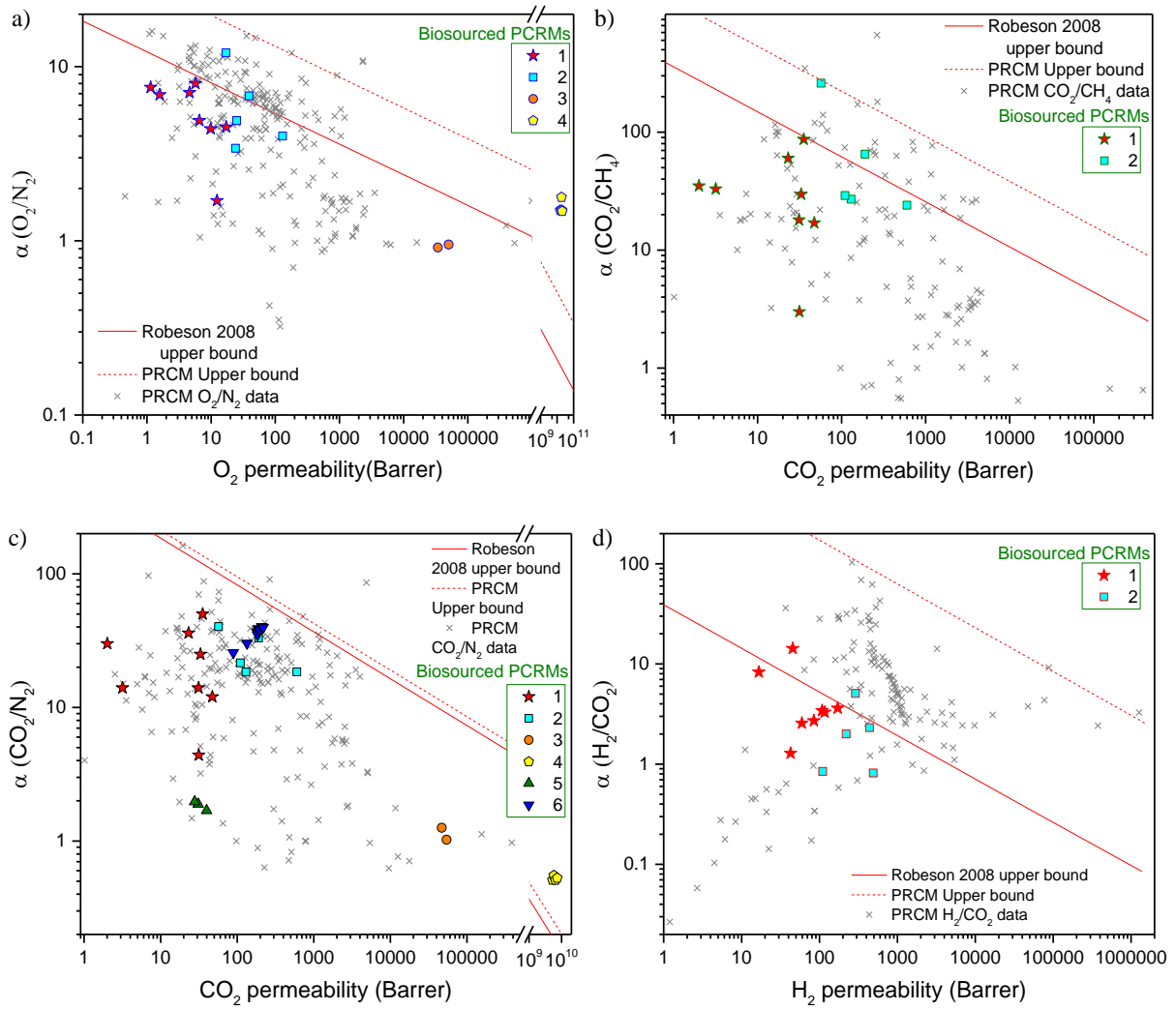


Figure 12. Ideal selectivity vs. permeability for (a) O_2/N_2 ; (b) CO_2/CH_4 ; (c) CO_2/N_2 ; and (d) H_2/CO_2 . Conventional and biosourced-substituted PRCM data (from Table 1 and Table 2, respectively) and Robeson's 2008 upper bound for polymeric membranes [73]. The dashed line represents the upper bound found for conventional PRCMs in the present review. Biosourced-substituted PRCMs: 1 = Kita *et al.* 2002 and Koga *et al.* 2004 [182, 183], 2 = Koga *et al.* 2008 and 2009 [184, 185], 3 = Wang *et al.* 2010 [104], 4 = Zhao *et al.* 2015 [187], 5 = Zhao *et al.* 2014 [186] and 6 = Chai *et al.* 2014 [189].

6 CONCLUSIONS AND PERSPECTIVES

Carbon membranes represent a valuable alternative to polymeric membranes in certain industrial processes where aggressive operating conditions and/or the type of gas to be separated prevent their use. Although the use of carbon membranes is currently limited by their higher cost per unit area, the possibility to fine-tune the textural properties of the resulting membranes by easily modifying the precursor material or synthesis variables makes them an option to consider for the separation of permanent gases. Their success in this application is based on a microporous structure that allows a molecular sieving mechanism. In this review, a comprehensive evaluation of carbon membranes produced using phenolic resins as a precursor is presented, establishing a valid starting point for the development of new membranes including substitutes of sustainable origin. The original phenol-formaldehyde recipe indeed presents an adaptable option for the synthesis of green phenolic resins and a promising pathway for the preparation of membranes for gas separation. In this context, the performance of membranes obtained from conventional and “green” phenolic resins in the separation of O_2/N_2 , CO_2/CH_4 , CO_2/N_2 and H_2/CO_2 gas pairs was discussed. CMSMs based on partially or fully substituted “green” phenolic resins have shown separation performances as good as those offered by conventional resins or polymeric membranes.

Although the results of the separation of these gas pairs are better than those obtained with polymer membranes, some challenges must be overcome in order to establish an industrial synthesis route. Here, we propose some specific guidelines to be considered in future studies:

- i) The advantages of using phenolic resins as carbon precursors, including high carbon yield, porosity control and compositional versatility, among others, open the possibility of suggesting a very large number of compounds of sustainable origin to replace conventional components. This would include all kinds of phenolic extracts of biomass

origin, comprising those from lignin, or extractable compounds from plants, algae or fungi, many of which have already succeeded in preparing phenolic resins.

ii) In general, carbonisation results in a microporous material that allows molecular sieving. However, gas permeation through the carbon membrane can be promoted by a better interconnection of the micropore network. To this end, research towards understanding and development of preparations comprising surfactants or templates would be interesting. To the same end, simulation of the transport mechanism and texture can play an important role in identifying pore interconnections relevant to permanent gas separation.

iii) Although research on membrane ageing or post-activation has been conducted, there is no clear protocol for membrane storage or activation/regeneration to be followed. More studies are needed that reflect the actual deterioration experienced by microporous carbon membranes under these conditions, focusing on valid use and storage protocols where gas separation performance could be compromised.

iv) The vast majority of the membranes presented are supported (generally on porous alumina tubes), which can be interpreted as a preliminary step towards the replacement of polymeric membranes in industrial applications. Thus, dip coating and spin coating have proven to be the most efficient and fastest methods of coating the support. Research should now continue with the implementation of membrane modules based on “greener” phenolic resin solutions that meet the necessary technical and mechanical requirements.

v) Finally, besides the materials challenges detailed above, significant efforts should be made to better evaluate the applicability of CMSMs in a real industrial environment. Robust permeance (not permeability) and selectivity data, obtained with gas mixtures and not from pure gases, are first needed in order to compare them with commercial

polymeric membranes and to allow effective process simulations. Important questions such as the impact of water or trace compounds (small organic molecules, heavy compounds, H_2S , O_2 ...) on CMSM performance and stability (i.e., long term tests with real industrial gas mixtures) also have to be addressed; for zeolite membranes for instance, water can often induce drastic changes and a drying step is then required before the membrane module. The scale-up (large membrane area modules) and processing possibilities (ease and reproducibility of hollow fibre production) are also difficult to evaluate today. These different aspects will have an impact on the overall cost of CMSMs, which is the ultimate information needed for a rigorous evaluation of their interest for industrial use.

Given the advantages offered by CMSMs and phenolic resins as precursors, their development, after the necessary step towards less toxic and more sustainable formulations, suggests a successful future in significant industrial applications. With a high separation performance in terms of permeability/selectivity pair for the separation of gases with very similar kinetic diameters, carbon membranes could be competitive in industrial processes such as the air separation industry for high-purity O_2 , N_2 and noble gases, the natural gas industry and CO_2 capture processes, the separation of CO_2 from power plant flue gases, or H_2 purification processes.

Acknowledgement

This work was initiated within the framework of the project "New membrane materials for separations" carried by the two laboratories involved, and supported by the Institute of Sciences and Systems Engineering (INSIS) of the French National Centre for Scientific Research (CNRS) for inter-team collaboration. It was also partly supported by the

TALiSMAN project, funded by the European Regional Development Fund (ERDF) (2019-000214).

References

- [1] R.W. Baker, Membrane technology and applications, John Wiley & Sons 2004.
- [2] E. Favre, 2.6 Polymeric Membranes for Gas Separation, in: E. Drioli, L. Giorno, E. Fontananova (Eds.), Comprehensive Membrane Science and Engineering (Second Edition), Elsevier, Oxford, 2017, pp. 124-175.
- [3] R. Abedini, A. Nezhadmoghadam, Application of membrane in gas separation processes: Its suitability and mechanisms, *Petroleum and Coal* 52(2) (2010) 69-80.
- [4] C.A. Scholes, G.W. Stevens, S.E. Kentish, Membrane gas separation applications in natural gas processing, *Fuel* 96 (2012) 15-28.
- [5] R.W. Baker, B.T. Low, Gas Separation Membrane Materials: A Perspective, *Macromolecules* 47(20) (2014) 6999-7013.
- [6] J.K. Adewole, A.L. Ahmad, S. Ismail, C.P. Leo, Current challenges in membrane separation of CO₂ from natural gas: A review, *International Journal of Greenhouse Gas Control* 17 (2013) 46-65.
- [7] A.F. Ismail, L.I.B. David, A review on the latest development of carbon membranes for gas separation, *J. Membr. Sci.* 193(1) (2001) 1-18.
- [8] S.M. Saufi, A.F. Ismail, Fabrication of carbon membranes for gas separation—a review, *Carbon* 42(2) (2004) 241-259.
- [9] A.F. Ismail, D. Rana, T. Matsuura, H.C. Foley, Carbon-based membranes for separation processes, Springer Science & Business Media 2011.
- [10] W.N.W. Salleh, A.F. Ismail, T. Matsuura, M.S. Abdullah, Precursor Selection and Process Conditions in the Preparation of Carbon Membrane for Gas Separation: A Review, *Separation & Purification Reviews* 40(4) (2011) 261-311.

- [11] M.G. Buonomenna, W. Yave, G. Golemme, Some approaches for high performance polymer based membranes for gas separation: block copolymers, carbon molecular sieves and mixed matrix membranes, *RSC Advances* 2(29) (2012) 10745-10773.
- [12] W. Salleh, A.F. Ismail, Carbon membranes for gas separation processes: Recent progress and future perspective, *Journal of Membrane Science and Research* 1(1) (2015) 2-15.
- [13] J.B.S. Hamm, A. Ambrosi, J.G. Griebeler, N.R. Marcilio, I.C. Tessaro, L.D. Pollo, Recent advances in the development of supported carbon membranes for gas separation, *Int. J. Hydrogen Energy* 42(39) (2017) 24830-24845.
- [14] O. Sanyal, C. Zhang, G.B. Wenz, S. Fu, N. Bhuwania, L. Xu, et al., Next generation membranes —using tailored carbon, *Carbon* 127 (2018) 688-698.
- [15] W.J. Koros, R. Mahajan, Pushing the limits on possibilities for large scale gas separation: which strategies?, *J. Membr. Sci.* 175(2) (2000) 181-196.
- [16] S. Haider, A. Lindbråthen, M.-B. Hägg, Techno-economical evaluation of membrane based biogas upgrading system: A comparison between polymeric membrane and carbon membrane technology, *Green Energy & Environment* 1(3) (2016) 222-234.
- [17] K. Sears, L. Dumée, J. Schütz, M. She, C. Huynh, S. Hawkins, et al., Recent Developments in Carbon Nanotube Membranes for Water Purification and Gas Separation, *Materials* 3(1) (2010) 127-149.
- [18] R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: A bright future in water desalination, *Desalination* 336 (2014) 97-109.
- [19] P. Li, C. Wang, Y. Zhang, F. Wei, Air Filtration in the Free Molecular Flow Regime: A Review of High-Efficiency Particulate Air Filters Based on Carbon Nanotubes, *Small* 10(22) (2014) 4543-4561.
- [20] K. Goh, H.E. Karahan, L. Wei, T.-H. Bae, A.G. Fane, R. Wang, et al., Carbon nanomaterials for advancing separation membranes: A strategic perspective, *Carbon* 109 (2016) 694-710.
- [21] Z.P. Smith, B.D. Freeman, Graphene Oxide: A New Platform for High-Performance Gas- and Liquid-Separation Membranes, *Angew. Chem. Int. Edit.* 53(39) (2014) 10286-10288.

- [22] R.K. Joshi, S. Alwarappan, M. Yoshimura, V. Sahajwalla, Y. Nishina, Graphene oxide: the new membrane material, *Applied Materials Today* 1(1) (2015) 1-12.
- [23] G. Liu, W. Jin, N. Xu, Graphene-based membranes, *Chem. Soc. Rev.* 44(15) (2015) 5016-5030.
- [24] P. Sun, K. Wang, H. Zhu, Recent Developments in Graphene-Based Membranes: Structure, Mass-Transport Mechanism and Potential Applications, *Adv. Mater. (Weinheim, Ger.)* 28(12) (2016) 2287-2310.
- [25] K. Goh, H.E. Karahan, E. Yang, T.-H. Bae, Graphene-Based Membranes for CO₂/CH₄ Separation: Key Challenges and Perspectives, *Applied Sciences* 9(14) (2019) 2784.
- [26] S.P. Dharupaneedi, R.V. Anjanapura, J.M. Han, T.M. Aminabhavi, Functionalized Graphene Sheets Embedded in Chitosan Nanocomposite Membranes for Ethanol and Isopropanol Dehydration via Pervaporation, *Ind. Eng. Chem. Res.* 53(37) (2014) 14474-14484.
- [27] D.P. Suhas, A.V. Raghu, H.M. Jeong, T.M. Aminabhavi, Graphene-loaded sodium alginate nanocomposite membranes with enhanced isopropanol dehydration performance via a pervaporation technique, *RSC Advances* 3(38) (2013) 17120-17130.
- [28] M. Kiyono, P.J. Williams, W.J. Koros, Generalization of effect of oxygen exposure on formation and performance of carbon molecular sieve membranes, *Carbon* 48(15) (2010) 4442-4449.
- [29] N. Bhuwania, Y. Labreche, C.S.K. Achoundong, J. Baltazar, S.K. Burgess, S. Karwa, et al., Engineering substructure morphology of asymmetric carbon molecular sieve hollow fiber membranes, *Carbon* 76 (2014) 417-434.
- [30] C. Wang, J. Yu, X.-j. Hu, Y. Huang, A review of the development of porous substrate-supported carbon membranes, *Carbon* 85 (2015) 445.
- [31] X.-H. Ma, S.-Y. Yang, Chapter 6 - Polyimide Gas Separation Membranes, in: S.-Y. Yang (Ed.), *Advanced Polyimide Materials*, Elsevier 2018, pp. 257-322.
- [32] C.W. Jones, W.J. Koros, Carbon molecular sieve gas separation membranes-I. Preparation and characterization based on polyimide precursors, *Carbon* 32(8) (1994) 1419-1425.
- [33] K.M. Steel, W.J. Koros, Investigation of porosity of carbon materials and related effects on gas separation properties, *Carbon* 41(2) (2003) 253-266.

- [34] K. Wang, H. Suda, K. Haraya, The characterization of CO₂ permeation in a CMSM derived from polyimide, *Sep. Purif. Technol.* 31(1) (2003) 61-69.
- [35] Y. Xiao, B.T. Low, S.S. Hosseini, T.S. Chung, D.R. Paul, The strategies of molecular architecture and modification of polyimide-based membranes for CO₂ removal from natural gas—A review, *Prog. Polym. Sci.* 34(6) (2009) 561-580.
- [36] T.A. Centeno, A.B. Fuertes, Supported carbon molecular sieve membranes based on a phenolic resin, *J. Membr. Sci.* 160(2) (1999) 201-211.
- [37] W. Wei, G. Qin, H. Hu, L. You, G. Chen, Preparation of supported carbon molecular sieve membrane from novolac phenol–formaldehyde resin, *J. Membr. Sci.* 303(1) (2007) 80-85.
- [38] G. Bakeri, A.F. Ismail, D. Rana, T. Matsuura, Development of high performance surface modified polyetherimide hollow fiber membrane for gas–liquid contacting processes, *Chem. Eng. J. (Lausanne)* 198-199 (2012) 327-337.
- [39] H.-H. Tseng, K. Shih, P.-T. Shiu, M.-Y. Wey, Influence of support structure on the permeation behavior of polyetherimide-derived carbon molecular sieve composite membrane, *J. Membr. Sci.* 405-406 (2012) 250-260.
- [40] S.M. Saufi, A.F. Ismail, Development and characterization of polyacrylonitrile (PAN) based carbon hollow fiber membrane, *Songklanakarin J. Sci. Technol* 24 (2002) 843-854.
- [41] L.I.B. David, A.F. Ismail, Influence of the thermastabilization process and soak time during pyrolysis process on the polyacrylonitrile carbon membranes for O₂/N₂ separation, *J. Membr. Sci.* 213(1) (2003) 285-291.
- [42] D. Grainger, M.-B. Hägg, Evaluation of cellulose-derived carbon molecular sieve membranes for hydrogen separation from light hydrocarbons, *J. Membr. Sci.* 306(1) (2007) 307-317.
- [43] M.B. Shiflett, H.C. Foley, Reproducible production of nanoporous carbon membranes, *Carbon* 39(9) (2001) 1421-1425.
- [44] A. Gardziella, L.A. Pilato, A. Knop, Phenolic resins: chemistry, applications, standardization, safety and ecology, Springer Science & Business Media 2013.
- [45] T.A. Centeno, A.B. Fuertes, Carbon molecular sieve membranes derived from a phenolic resin supported on porous ceramic tubes, *Sep. Purif. Technol.* 25(1) (2001) 379-384.

- [46] A.B. Fuertes, I. Menendez, Separation of hydrocarbon gas mixtures using phenolic resin-based carbon membranes, *Sep. Purif. Technol.* 28(1) (2002) 29-41.
- [47] V.R. Landi, The glass transition in novolac phenolic molding compounds and the kinetics of its development during cure and postcure. II, *Adv. Polym. Technol.* 7(2) (1987) 209-218.
- [48] M. Teixeira, M.C. Campo, D.A. Pacheco Tanaka, M.A. Llosa Tanco, C. Magen, A. Mendes, Composite phenolic resin-based carbon molecular sieve membranes for gas separation, *Carbon* 49(13) (2011) 4348-4358.
- [49] A.B. Fuertes, Adsorption-selective carbon membrane for gas separation, *J. Membr. Sci.* 177(1) (2000) 9-16.
- [50] A.B. Fuertes, Preparation and characterization of adsorption-selective carbon membranes for gas separation, *Adsorption* 7(2) (2001) 117-129.
- [51] A.B. Fuertes, Effect of air oxidation on gas separation properties of adsorption-selective carbon membranes, *Carbon* 39(5) (2001) 697-706.
- [52] S. Lagorsse, F.D. Magalhães, A. Mendes, Aging study of carbon molecular sieve membranes, *J. Membr. Sci.* 310(1) (2008) 494-502.
- [53] T.A. Centeno, J.L. Vilas, A.B. Fuertes, Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation, *J. Membr. Sci.* 228(1) (2004) 45-54.
- [54] L. Pilato, *Phenolic resins: a century of progress*, Springer 2010.
- [55] A. Pizzi, Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues, *J. Adhes. Sci. Technol.* 20(8) (2006) 829-846.
- [56] K. Hirano, M. Asami, Phenolic resins—100 years of progress and their future, *Reactive and Functional Polymers* 73(2) (2013) 256-269.
- [57] Z. He, *Bio-based wood adhesives: preparation, characterization, and testing*, CRC Press 2017.
- [58] A. Effendi, H. Gerhauser, A.V. Bridgwater, Production of renewable phenolic resins by thermochemical conversion of biomass: A review, *Renew. Sust. Energ. Rev.* 12(8) (2008) 2092-2116.
- [59] K. Van Langenberg, W. Grigsby, G. Ryan, Green adhesives: options for the Australian industry—summary of recent research into green adhesives from renewable materials and identification of those that are closest to commercial uptake, Project No. PNB158-0910. FWPA (2010).

- [60] S. Kalami, M. Arefmanesh, E. Master, M. Nejad, Replacing 100% of phenol in phenolic adhesive formulations with lignin, *J. Appl. Polym. Sci.* 134(30) (2017) 45124.
- [61] D. Wu, R. Fu, Synthesis of organic and carbon aerogels from phenol–furfural by two-step polymerization, *Microporous Mesoporous Mater.* 96(1) (2006) 115-120.
- [62] C. Matei Ghimbeu, L. Vidal, L. Delmotte, J.-M. Le Meins, C. Vix-Guterl, Catalyst-free soft-template synthesis of ordered mesoporous carbon tailored using phloroglucinol/glyoxylic acid environmentally friendly precursors, *Green Chem.* 16(6) (2014) 3079-3088.
- [63] A.H. Faris, A.A. Rahim, M.N.M. Ibrahim, A.M. Alkurdi, I. Shah, Combination of lignin polyol–tannin adhesives and polyethylenimine for the preparation of green water-resistant adhesives, *J. Appl. Polym. Sci.* 133(20) (2016).
- [64] M.A. Hubbe, A. Pizzi, H. Zhang, R. Halis, Critical links governing performance of self-binding and natural binders for hot-pressed reconstituted lignocellulosic board without added formaldehyde: A review, *BioResources* 13(1) (2018) 2049-2115.
- [65] Y. Shirmohammadli, D. Efhamisisi, A. Pizzi, Tannins as a sustainable raw material for green chemistry: A review, *Industrial Crops and Products* 126 (2018) 316-332.
- [66] R.W. Baker, K. Lokhandwala, Natural Gas Processing with Membranes: An Overview, *Ind. Eng. Chem. Res.* 47(7) (2008) 2109-2121.
- [67] P. Bernardo, E. Drioli, G. Golemme, Membrane Gas Separation: A Review/State of the Art, *Ind. Eng. Chem. Res.* 48(10) (2009) 4638-4663.
- [68] S.D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A.G. Russell, et al., Review of recent advances in carbon dioxide separation and capture, *RSC Advances* 3(45) (2013) 22739-22773.
- [69] Á.A. Ramírez-Santos, C. Castel, E. Favre, A review of gas separation technologies within emission reduction programs in the iron and steel sector: Current application and development perspectives, *Sep. Purif. Technol.* 194 (2018) 425-442.
- [70] W.J. Koros, G. Fleming, Membrane-based gas separation, *J. Membr. Sci.* 83(1) (1993) 1-80.
- [71] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.* 62(2) (1991) 165-185.

- [72] L.M. Robeson, W.F. Burgoyne, M. Langsam, A.C. Savoca, C.F. Tien, High performance polymers for membrane separation, *Polymer* 35(23) (1994) 4970-4978.
- [73] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.* 320(1) (2008) 390-400.
- [74] O.R.N. Laboratory, Materials for Separation Technologies: Energy and Emission Reduction Opportunities, Oak Ridge National Laboratory Oak Ridge, 2005.
- [75] D.S. Sholl, R.P. Lively, Seven chemical separations to change the world, *Nature* 532(7600) (2016) 435-437.
- [76] C. Castel, E. Favre, Membrane separations and energy efficiency, *J. Membr. Sci.* 548 (2018) 345-357.
- [77] C. Castel, L. Wang, J.P. Corriou, E. Favre, Steady vs unsteady membrane gas separation processes, *Chem. Eng. Sci.* 183 (2018) 136-147.
- [78] A. Knop, W. Scheib, Chemistry and application of phenolic resins, Springer 1979.
- [79] M.A. Llosa Tanco, D.A. Pacheco Tanaka, S.C. Rodrigues, M. Teixeira, A. Mendes, Composite-alumina-carbon molecular sieve membranes prepared from novolac resin and boehmite. Part I: Preparation, characterization and gas permeation studies, *Int. J. Hydrogen Energy* 40(16) (2015) 5653-5663.
- [80] S.C. Moldoveanu, Analytical pyrolysis of synthetic organic polymers, Elsevier 2005.
- [81] S. So, A. Rudin, Analysis of the formation and curing reactions of resole phenolics, *J. Appl. Polym. Sci.* 41(1- 2) (1990) 205-232.
- [82] M.-F. Grenier-Loustalot, S. Larroque, D. Grande, P. Grenier, D. Bedel, Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics, *Polymer* 37(8) (1996) 1363-1369.
- [83] A. Pizzi, C.C. Ibeh, 2 - Phenol-Formaldehydes, in: H. Dodiuk, S.H. Goodman (Eds.), *Handbook of Thermoset Plastics* (Third Edition), William Andrew Publishing, Boston, 2014, pp. 13-44.
- [84] S. Czernik, A.V. Bridgwater, Overview of Applications of Biomass Fast Pyrolysis Oil, *Energy Fuels* 18(2) (2004) 590-598.
- [85] Y. Zhao, N. Yan, Recent development in forest biomass derived phenol formaldehyde (PF) resole resin for wood adhesives application, *Journal of Biobased Materials and Bioenergy* 8(5) (2014) 465-480.

- [86] C. Amen-Chen, H. Pakdel, C. Roy, Production of monomeric phenols by thermochemical conversion of biomass: a review, *Bioresour. Technol.* 79(3) (2001) 277-299.
- [87] H. Pan, Synthesis of polymers from organic solvent liquefied biomass: A review, *Renew. Sust. Energ. Rev.* 15(7) (2011) 3454-3463.
- [88] A.F. Ang, Z. Ashaari, S.H. Lee, P. Md Tahir, R. Halis, Lignin-based copolymer adhesives for composite wood panels – A review, *Int. J. Adhes. Adhes.* 95 (2019) 102408.
- [89] A.E. Vithanage, E. Chowdhury, L.D. Alejo, P.C. Pomeroy, W.J. DeSisto, B.G. Frederick, et al., Renewably sourced phenolic resins from lignin bio-oil, *J. Appl. Polym. Sci.* 134(19) (2017).
- [90] V. Hemmilä, J. Trischler, D. Sandberg, Bio-based adhesives for the wood industry: an opportunity for the future?, *Pro Ligno*, 2013, pp. 118-125.
- [91] A. Pizzi, H.O. Scharfetter, The chemistry and development of tannin-based adhesives for exterior plywood, *J. Appl. Polym. Sci.* 22(6) (1978) 1745-1761.
- [92] A. Pizzi, Wood products and green chemistry, *Annals of Forest Science* 73(1) (2016) 185-203.
- [93] F. Pichelin, M. Nakatani, A. Pizzi, S. Wieland, A. Despres, S. Rigolet, Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives, *Forest Prod. J.* 56(5) (2006) 31-36.
- [94] J. Valenzuela, E. von Leyser, A. Pizzi, C. Westermeyer, B. Gorrini, Industrial production of pine tannin-bonded particleboard and MDF, *European Journal of Wood and Wood Products* 70(5) (2012) 735-740.
- [95] C. Kamoun, A. Pizzi, Mechanism of hexamine as a non-aldehyde polycondensation resins hardener. Part 1: Hexamine decomposition and reactive intermediates, *Holzforschung und Holzverwertung* 52(1) (2000) 16-19.
- [96] A. Pizzi, N. Meikleham, B. Dombo, W. Roll, Autocondensation-based, zero-emission, tannin adhesives for particleboard, *Holz als Roh- und Werkstoff* 53(3) (1995) 201-204.
- [97] A. Pizzi, A. Stephanou, Fast vs. slow-reacting non-modified tannin extracts for exterior particleboard adhesives, *Holz als Roh- und Werkstoff* 52(4) (1994) 218-222.

- [98] N. Meikleham, A. Pizzi, A. Stephanou, Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. I. ^{13}C -NMR, ^{29}Si -NMR, X-ray, and polarimetry studies and mechanism, *J. Appl. Polym. Sci.* 54(12) (1994) 1827-1845.
- [99] R. Garcia, A. Pizzi, Polycondensation and autocondensation networks in polyflavonoid tannins. II. Polycondensation versus autocondensation, *J. Appl. Polym. Sci.* 70(6) (1998) 1093-1109.
- [100] D. Efhamisisi, M.-F. Thevenon, Y. Hamzeh, A.-N. Karimi, A. Pizzi, K. Pourtahmasi, Induced Tannin Adhesive by Boric Acid Addition and Its Effect on Bonding Quality and Biological Performance of Poplar Plywood, *ACS Sustainable Chemistry & Engineering* 4(5) (2016) 2734-2740.
- [101] I.P. Singh, J. Sidana, S.B. Bharate, W.J. Foley, Phloroglucinol compounds of natural origin: Synthetic aspects, *Nat. Prod. Rep.* 27(3) (2010) 393-416.
- [102] A. Pizzi, R. Horak, D. Ferreira, D. Roux, Condensates of phenol, resorcinol, phloroglucinol, and pyrogallol as model compounds of flavonoid A- and B- rings with formaldehyde, *J. Appl. Polym. Sci.* 24(6) (1979) 1571-1578.
- [103] C. Liang, S. Dai, Synthesis of Mesoporous Carbon Materials via Enhanced Hydrogen-Bonding Interaction, *J. Am. Chem. Soc.* 128(16) (2006) 5316-5317.
- [104] X. Wang, Q. Zhu, S.M. Mahurin, C. Liang, S. Dai, Preparation of free-standing high quality mesoporous carbon membranes, *Carbon* 48(2) (2010) 557-560.
- [105] P.H. Steele, R.E. Kreibicha, P.J. Steynberg, R.W. Hemingway, Finger jointing green southern yellow pine with a soy-based adhesive, *Adhesives Age*. [No volume number]: 49, 50, 52, 54, 56. (1998).
- [106] D.K. Raval, B.N. Narola, A.J. Patel, Synthesis, characterization and composites from resorcinol-urea-formaldehyde-casein resin, *Iranian Polymer Journal (English)* 14(9 (63)) (2005) -.
- [107] J.C. Borges, E. Athanassiadou, S. Tsiantzi, Bio-based resins for wood composites, *Proceedings of the ECOWOOD* (2006).
- [108] I. Yang, M. Kuo, D.J. Myers, A. Pu, Comparison of protein-based adhesive resins for wood composites, *Journal of Wood Science* 52(6) (2006) 503-508.
- [109] Z. Zhong, X.S. Sun, Plywood adhesives by blending soy protein polymer with phenol-formaldehyde resin, *Journal of Biobased Materials and Bioenergy* 1(3) (2007) 380-387.

- [110] D.K. Raval, S.K. Vyas, J.K. Parmar, A study on composites from phenol-formaldehyde-casein resin, *J. Appl. Polym. Sci.* 115(5) (2010) 2838-2846.
- [111] A. Arenillas, J.A. Menéndez, G. Reichenauer, A. Celzard, V. Fierro, F.J. Maldonado Hodar, et al., *Organic and Carbon Gels Derived from Biosourced Polyphenols*, *Organic and Carbon Gels: From Laboratory Synthesis to Applications*, Springer International Publishing, Cham, 2019, pp. 27-85.
- [112] M.S. Karunarathna, R.C. Smith, Valorization of Lignin as a Sustainable Component of Structural Materials and Composites: Advances from 2011 to 2019, *Sustainability* 12(2) (2020) 734.
- [113] R. Ryoo, S.H. Joo, M. Kruk, M. Jaroniec, Ordered Mesoporous Carbons, *Adv. Mater.* (Weinheim, Ger.) 13(9) (2001) 677-681.
- [114] M. Inagaki, M. Toyoda, Y. Soneda, S. Tsujimura, T. Morishita, Templated mesoporous carbons: Synthesis and applications, *Carbon* 107 (2016) 448-473.
- [115] T.-Y. Ma, L. Liu, Z.-Y. Yuan, Direct synthesis of ordered mesoporous carbons, *Chem. Soc. Rev.* 42(9) (2013) 3977-4003.
- [116] B. Zhang, Y. Shi, Y. Wu, T. Wang, J. Qiu, Preparation and characterization of supported ordered nanoporous carbon membranes for gas separation, *J. Appl. Polym. Sci.* 131(4) (2014).
- [117] C.M. Ghimbeu, M. Soprony, F. Sima, C. Vaultot, L. Vidal, J.-M. Le Meins, et al., "Light-assisted evaporation induced self-assembly": an efficient approach toward ordered carbon materials, *RSC Advances* 5(4) (2015) 2861-2868.
- [118] C. Nita, M. Bensafia, C. Vaultot, L. Delmotte, C. Matei Ghimbeu, Insights on the synthesis mechanism of green phenolic resin derived porous carbons via a salt-soft templating approach, *Carbon* 109 (2016) 227-238.
- [119] M. Sopronyi, F. Sima, C. Vaultot, L. Delmotte, A. Bahouka, C. Matei Ghimbeu, Direct synthesis of graphitic mesoporous carbon from green phenolic resins exposed to subsequent UV and IR laser irradiations, *Sci. Rep.* 6(1) (2016) 39617.
- [120] W. Xin, Y. Song, Mesoporous carbons: recent advances in synthesis and typical applications, *RSC Advances* 5(101) (2015) 83239-83285.

- [121] K.-i. Okamoto, M. Yoshino, K. Noborio, H. Maeda, K. Tanaka, H. Kita, Preparation of Carbon Molecular Sieve Membranes and Their Gas Separation Properties, Membrane Formation and Modification, American Chemical Society 1999, pp. 314-329.
- [122] C.H. Jung, G.W. Kim, S.H. Han, Y.M. Lee, Gas separation of pyrolyzed polymeric membranes: Effect of polymer precursor and pyrolysis conditions, *Macromol. Res.* 15(6) (2007) 565-574.
- [123] J. Li, J. Qi, C. Liu, L. Zhou, H. Song, C. Yu, et al., Fabrication of ordered mesoporous carbon hollow fiber membranes via a confined soft templating approach, *J. Mater. Chem. A* 2(12) (2014) 4144-4149.
- [124] D. De Meis, E. Serra, M. Richetta, M.A. Llosa Tanco, D.A. Pacheco Tanaka, Fusion Exhaust Gas Separation with a Carbon Molecular Sieve (CMS) Membrane, *Interceram - International Ceramic Review* 68(4) (2019) 14-17.
- [125] J.M.S. Henis, M.K. Tripodi, Composite hollow fiber membranes for gas separation: the resistance model approach, *J. Membr. Sci.* 8(3) (1981) 233-246.
- [126] H. Kita, H. Maeda, K. Tanaka, K.-i. Okamoto, Carbon Molecular Sieve Membrane Prepared from Phenolic Resin, *Chem. Lett.* 26(2) (1997) 179-180.
- [127] W. Wei, H. Hu, L. You, G. Chen, Preparation of carbon molecular sieve membrane from phenol-formaldehyde Novolac resin, *Carbon* 40(3) (2002) 465-467.
- [128] W. Zhou, M. Yoshino, H. Kita, K.-i. Okamoto, Preparation and gas permeation properties of carbon molecular sieve membranes based on sulfonated phenolic resin, *J. Membr. Sci.* 217(1) (2003) 55-67.
- [129] L. Zhang, X. Chen, C. Zeng, N. Xu, Preparation and gas separation of nano-sized nickel particle-filled carbon membranes, *J. Membr. Sci.* 281(1) (2006) 429-434.
- [130] M. Mahdyarfar, T. Mohammadi, A. Mohajeri, Defect formation and prevention during the preparation of supported carbon membranes, *New Carbon Materials* 28(5) (2013) 369-377.
- [131] J. Carretero, J.M. Benito, A. Guerrero-Ruiz, I. Rodríguez-Ramos, M.A. Rodríguez, Infiltrated glassy carbon membranes in γ -Al₂O₃ supports, *J. Membr. Sci.* 281(1) (2006) 500-507.

- [132] K. Briceño, D. Montané, R. Garcia-Valls, A. Iulianelli, A. Basile, Fabrication variables affecting the structure and properties of supported carbon molecular sieve membranes for hydrogen separation, *J. Membr. Sci.* 415-416 (2012) 288-297.
- [133] W. Wei, S. Xia, G. Liu, X. Gu, W. Jin, N. Xu, Interfacial adhesion between polymer separation layer and ceramic support for composite membrane, *AIChE J.* 56(6) (2010) 1584-1592.
- [134] N. Nishiyama, Y.-R. Dong, T. Zheng, Y. Egashira, K. Ueyama, Tertiary amine-mediated synthesis of microporous carbon membranes, *J. Membr. Sci.* 280(1) (2006) 603-609.
- [135] Y.-R. Dong, M. Nakao, N. Nishiyama, Y. Egashira, K. Ueyama, Gas permeation and pervaporation of water/alcohols through the microporous carbon membranes prepared from resorcinol/formaldehyde/quaternary ammonium compounds, *Sep. Purif. Technol.* 73(1) (2010) 2-7.
- [136] S. Wang, M. Zeng, Z. Wang, Asymmetric molecular sieve carbon membranes, *J. Membr. Sci.* 109(2) (1996) 267-270.
- [137] S. Wang, M. Zeng, Z. Wang, Carbon Membranes for Gas Separation, *Sep. Sci. Technol.* 31(16) (1996) 2299-2306.
- [138] F.K. Katsaros, T.A. Steriotis, A.K. Stubos, A. Mitropoulos, N.K. Kanellopoulos, S. Tennison, High pressure gas permeability of microporous carbon membranes, *Microporous Materials* 8(3) (1997) 171-176.
- [139] I. Menendez, A.B. Fuertes, Aging of carbon membranes under different environments, *Carbon* 39(5) (2001) 733-740.
- [140] W. Zhou, M. Yoshino, H. Kita, K.-i. Okamoto, Carbon Molecular Sieve Membranes Derived from Phenolic Resin with a Pendant Sulfonic Acid Group, *Ind. Eng. Chem. Res.* 40(22) (2001) 4801-4807.
- [141] T.A. Centeno, A.B. Fuertes, Influence of separation temperature on the performance of adsorption-selective carbon membranes, *Carbon* 41(10) (2003) 2016-2019.
- [142] X. Zhang, H. Hu, Y. Zhu, S. Zhu, Effect of carbon molecular sieve on phenol formaldehyde novolac resin based carbon membranes, *Sep. Purif. Technol.* 52(2) (2006) 261-265.
- [143] X. Zhang, H. Hu, Y. Zhu, S. Zhu, Carbon molecular sieve membranes derived from phenol formaldehyde novolac resin blended with poly(ethylene glycol), *J. Membr. Sci.* 289(1) (2007) 86-91.

- [144] F.K. Katsaros, T.A. Steriotis, G.E. Romanos, M. Konstantakou, A.K. Stubos, N.K. Kanellopoulos, Preparation and characterisation of gas selective microporous carbon membranes, *Microporous Mesoporous Mater.* 99(1) (2007) 181-189.
- [145] C. Kong, J. Wang, J. Yang, J. Lu, A. Wang, Q. Zhao, Thin carbon-zeolite composite membrane prepared on ceramic tube filter by vacuum slip casting for oxygen/nitrogen separation, *Carbon* 45(14) (2007) 2848-2850.
- [146] C. Zeng, L. Zhang, X. Cheng, H. Wang, N. Xu, Preparation and gas permeation of nano-sized zeolite NaA-filled carbon membranes, *Sep. Purif. Technol.* 63(3) (2008) 628-633.
- [147] M. Yoshimune, T. Yamamoto, M. Nakaiwa, K. Haraya, Preparation of highly mesoporous carbon membranes via a sol-gel process using resorcinol and formaldehyde, *Carbon* 46(7) (2008) 1031-1036.
- [148] B. Zhang, F.Y. Meng, Y.H. Wu, C.B. Fu, T.H. Wang, Preparation and Gas Permeation of Zeolite 5A Hybrid PR/PVA Based Carbon Membranes, *Advanced Materials Research* 129-131 (2010) 241-245.
- [149] G. Qin, C. Wang, W. Wei, Preparation of a mesoporous carbon membrane from resorcinol and formaldehyde, *Carbon* 48(14) (2010) 4206-4208.
- [150] B. Zhang, Y.H. Wu, T.H. Wang, J.S. Qiu, T.J. Xu, X.H. Sun, Effects of Curing Method on the Gas Separation Performance of Phenolic Resin/Poly(vinyl Alcohol)-Based Carbon Membrane Materials, *Mater. Sci. Forum* 675-677 (2011) 1185-1188.
- [151] W. Wei, G.T. Qin, P.J. Tang, L.P. Wu, Effects of Pyrolysis Conditions on the Permeance of Phenol-Formaldehyde Resin Based Carbon Membrane for CO₂ Separation, *Advanced Materials Research* 239-242 (2011) 1804-1808.
- [152] M. Teixeira, M. Campo, D.A. Tanaka, M.A. Tanco, C. Magen, A. Mendes, Carbon-Al₂O₃-Ag composite molecular sieve membranes for gas separation, *Chem. Eng. Res. Des.* 90(12) (2012) 2338-2345.
- [153] M. Teixeira, S.C. Rodrigues, M. Campo, D.A. Pacheco Tanaka, M.A. Llosa Tanco, L.M. Madeira, et al., Boehmite-phenolic resin carbon molecular sieve membranes—Permeation and adsorption studies, *Chem. Eng. Res. Des.* 92(11) (2014) 2668-2680.

- [154] S.C. Rodrigues, R. Whitley, A. Mendes, Preparation and characterization of carbon molecular sieve membranes based on resorcinol–formaldehyde resin, *J. Membr. Sci.* 459 (2014) 207-216.
- [155] B. Zhang, X. Dang, Y. Wu, H. Liu, T. Wang, J. Qiu, Structure and gas permeation of nanoporous carbon membranes based on RF resin/F-127 with variable catalysts, *J. Mater. Res.* 29(23) (2014) 2881-2890.
- [156] M.A. Llosa Tanco, D.A. Pacheco Tanaka, A. Mendes, Composite-alumina-carbon molecular sieve membranes prepared from novolac resin and boehmite. Part II: Effect of the carbonization temperature on the gas permeation properties, *Int. J. Hydrogen Energy* 40(8) (2015) 3485-3496.
- [157] P.-S. Lee, D. Kim, S.-E. Nam, R.R. Bhawe, Carbon molecular sieve membranes on porous composite tubular supports for high performance gas separations, *Microporous Mesoporous Mater.* 224 (2016) 332-338.
- [158] S. Roy, R. Das, M.K. Gagrai, S. Sarkar, Preparation of carbon molecular sieve membrane derived from phenolic resin over macroporous clay-alumina based support for hydrogen separation, *J. Porous Mater.* 23(6) (2016) 1653-1662.
- [159] G. Qin, Y. Zhang, W. Wei, Facile synthesis of a nitrogen-doped carbon membrane for CO₂ capture, *Mater. Lett.* 209 (2017) 75-77.
- [160] I. Kumakiri, K. Tamura, Y. Sasaki, K. Tanaka, H. Kita, Influence of Iron Additive on the Hydrogen Separation Properties of Carbon Molecular Sieve Membranes, *Ind. Eng. Chem. Res.* 57(15) (2018) 5370-5377.
- [161] G. Dong, H. Li, V. Chen, Challenges and opportunities for mixed-matrix membranes for gas separation, *J. Mater. Chem. A* 1(15) (2013) 4610-4630.
- [162] L. Li, R. Xu, C. Song, B. Zhang, Q. Liu, T. Wang, A review on the progress in nanoparticle/C hybrid CMS membranes for gas separation, *Membranes* 8(4) (2018) 134.
- [163] P.S. Goh, A.F. Ismail, S.M. Sanip, B.C. Ng, M. Aziz, Recent advances of inorganic fillers in mixed matrix membrane for gas separation, *Sep. Purif. Technol.* 81(3) (2011) 243-264.
- [164] S. Tanaka, N. Nishiyama, Y. Egashira, K. Ueyama, Synthesis of ordered mesoporous carbons with channel structure from an organic–organic nanocomposite, *Chem. Commun. (Cambridge, U. K.)* (16) (2005) 2125-2127.

- [165] N. Nishiyama, T. Zheng, Y. Yamane, Y. Egashira, K. Ueyama, Microporous carbons prepared from cationic surfactant–resorcinol/formaldehyde composites, *Carbon* 43(2) (2005) 269-274.
- [166] B. Bera, J.K. Das, N. Das, Mesoporous silica based composite membrane formation by in-situ cross-linking of phenol and formaldehyde at room temperature for enhanced CO₂ separation, *Microporous Mesoporous Mater.* 256 (2018) 177-189.
- [167] M. Bozorg, B. Addis, V. Piccialli, Á.A. Ramírez-Santos, C. Castel, I. Pinnau, et al., Polymeric membrane materials for nitrogen production from air: A process synthesis study, *Chem. Eng. Sci.* 207 (2019) 1196-1213.
- [168] B. Belaissaoui, Y. Le Moullec, H. Hagi, E. Favre, Energy Efficiency of Oxygen Enriched Air Production Technologies: Cryogeny vs Membranes, *Energy Procedia* 63 (2014) 497-503.
- [169] M. Scholz, M. Alders, T. Lohaus, M. Wessling, Structural optimization of membrane-based biogas upgrading processes, *J. Membr. Sci.* 474 (2015) 1-10.
- [170] M. Bozorg, Á.A. Ramírez-Santos, B. Addis, V. Piccialli, C. Castel, E. Favre, Optimal process design of biogas upgrading membrane systems: Polymeric vs high performance inorganic membrane materials, *Chem. Eng. Sci.* 225 (2020) 115769.
- [171] D.D. Iarikov, S. Ted Oyama, Chapter 5 - Review of CO₂/CH₄ Separation Membranes, in: S.T. Oyama, S.M. Staggs-Williams (Eds.), *Membrane Science and Technology*, Elsevier 2011, pp. 91-115.
- [172] C.E. Powell, G.G. Qiao, Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases, *J. Membr. Sci.* 279(1) (2006) 1-49.
- [173] E. Favre, Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption?, *J. Membr. Sci.* 294(1) (2007) 50-59.
- [174] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO₂ capture technology—The U.S. Department of Energy's Carbon Sequestration Program, *International Journal of Greenhouse Gas Control* 2(1) (2008) 9-20.
- [175] T.C. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes, *J. Membr. Sci.* 359(1) (2010) 126-139.
- [176] D.W. Keith, Why Capture CO₂ from the Atmosphere?, *Science* 325(5948) (2009) 1654.

- [177] E.S. Sanz-Pérez, C.R. Murdock, S.A. Didas, C.W. Jones, Direct Capture of CO₂ from Ambient Air, *Chem. Rev.* (Washington, DC, U. S.) 116(19) (2016) 11840-11876.
- [178] M. Anderson, H. Wang, Y. Lin, Inorganic membranes for carbon dioxide and nitrogen separation, (2012).
- [179] R. Prasad, R. Shaner, K. Doshi, Comparison of membranes with other gas separation technologies, CRC Press, Inc.: Boca Raton, FL1994.
- [180] T.C. Merkel, M. Zhou, R.W. Baker, Carbon dioxide capture with membranes at an IGCC power plant, *J. Membr. Sci.* 389 (2012) 441-450.
- [181] N. Sazali, A comprehensive review of carbon molecular sieve membranes for hydrogen production and purification, *The International Journal of Advanced Manufacturing Technology* 107(5) (2020) 2465-2483.
- [182] H. Kita, K. Nanbu, T. Hamano, M. Yoshino, K.-i. Okamoto, M. Funaoka, Carbon molecular sieving membranes derived from lignin-based materials, *J. Polym. Environ.* 10(3) (2002) 69-75.
- [183] T. Koga, H. Kita, K. Tanaka, K.-i. Okamoto, M. Funaoka, Molecular Sieve Carbon Membrane from Lignin-based Materials, Asian Pacific Confederation of Chemical Engineering congress program and abstracts Asian Pacific Confederation of Chemical Engineers congress program and abstracts, The Society of Chemical Engineers, Japan, 2004, pp. 913-913.
- [184] T. Koga, H. Kita, T. Suzuki, K. Uemura, K. Tanaka, I. Kawafune, et al., Carbon Membranes from Wood Materials and their Separation Properties, *Transactions of the Materials Research Society of Japan* 33(4) (2008) 825-828.
- [185] T. Koga, H. Kita, K. Uemura, K. Tanaka, I. Kawafune, M. Funaoka, Structure and Separation Performance of Carbon Membranes from Lignin-based Materials, *Transactions of the Materials Research Society of Japan* 34(3) (2009) 371-374.
- [186] X. Zhao, W. Li, S. Liu, Ordered mesoporous carbon membrane prepared from liquefied larch by a soft method, *Mater. Lett.* 126 (2014) 174-177.
- [187] X. Zhao, W. Li, Z. Huang, S. Liu, Synthesis of nickel-incorporated larch-based carbon membranes with controllable porous structure for gas separation, *Journal of Nanoparticle Research* 17(11) (2015) 433.

- [188] S. Tanaka, N. Nakatani, A. Doi, Y. Miyake, Preparation of ordered mesoporous carbon membranes by a soft-templating method, *Carbon* 49(10) (2011) 3184-3189.
- [189] S.-H. Chai, P.F. Fulvio, P.C. Hillesheim, Z.-A. Qiao, S.M. Mahurin, S. Dai, “Brick-and-mortar” synthesis of free-standing mesoporous carbon nanocomposite membranes as supports of room temperature ionic liquids for CO₂–N₂ separation, *J. Membr. Sci.* 468 (2014) 73-80.