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LU Shasha, HUANG Chuan, SHEN Yadong, et al. Research progress of membrane contactor technology on CO<sub>2</sub> Capture [J]. Environmental Chemistry, 2021, 40(4): 1088-1099.

## 膜接触法捕集生物质气 CO<sub>2</sub> 的研究进展\*

鹿莎莎<sup>2</sup> 黄川<sup>1,2\*\*</sup> 申亚栋<sup>1,2</sup> 葛春玲<sup>3</sup> 王里奥<sup>1,2</sup>

(1. 重庆大学煤矿灾害动力学与控制国家重点实验室, 重庆, 400044; 2. 重庆大学环境与生态学院, 重庆, 400045;  
3. 北京城市矿产资源开发有限公司, 北京, 100101)

**摘要** 生物质气中 CO<sub>2</sub> 捕集及 CH<sub>4</sub> 的回收利用具有巨大经济价值和环境效益, 受到各领域的广泛关注. 基于中空纤维膜的气-液膜接触技术以其效率高、能耗少和操作灵活等优势被认为是 CO<sub>2</sub> 捕集领域的重大突破. 本文以中空纤维膜材料为中心, 回顾了近十年来无机膜、传统有机聚合膜、有机微孔聚合膜、混合基质膜和固定载体膜的研究和发展, 论述了各类中空纤维膜的 CO<sub>2</sub> 捕集性能以及当前面临的挑战. 同时从膜润湿、吸收剂以及工艺条件等方面分析了影响 CO<sub>2</sub> 分离性能的主要因素. 并提出开发低成本、高 CO<sub>2</sub> 捕集性能和高稳定性的新型中空纤维膜以及推进膜的中试和示范试点工程作为未来发展的主流方向.

**关键词** 膜接触器, 膜, 生物能源, CO<sub>2</sub> 捕集, CH<sub>4</sub> 提纯.

## Research progress of membrane contactor technology on CO<sub>2</sub> Capture

LU Shasha<sup>2</sup> HUANG Chuan<sup>1,2\*\*</sup> SHEN Yadong<sup>1,2</sup> GE Chunling<sup>3</sup> WANG Li'ao<sup>1,2</sup>

(1. State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing, 400044, China;  
2. College of Environment and Ecology, Chongqing University, Chongqing, 400045, China;  
3. Beijing City Mineral Resources Development Co. LTD, Beijing, 100101, China)

**Abstract:** CO<sub>2</sub> capture and CH<sub>4</sub> recovery from biomass gas have great economic value and environmental benefit, and they have been widely concerned in various fields. Gas-liquid membrane contactor technology based on hollow fiber membrane is considered a major breakthrough in the field of CO<sub>2</sub> capture due to its high separation efficiency, low energy consumption and flexible operation. Focusing on hollow fiber membrane materials, this paper reviewed detailly about the research and development of inorganic membranes, organic polymer membranes, mixed matrix membranes, and fixed-site-carrier membranes in the past decade, and introduced the gas separation performance and current challenges of various hollow fiber membranes, respectively. At the same time, the main factors (membrane wetting, absorbent and operation conditions) affecting CO<sub>2</sub> separation performance of the hollow fiber membrane contactor were analyzed. This paper proposes that future research should focus on creating new hollow fiber membranes with low-cost, high performance of CO<sub>2</sub> separation, high stability and the development of the membranes with excellent performance for pilot test.

**Keywords:** membrane contactor, membranes, bioenergy, CO<sub>2</sub> capture, CH<sub>4</sub> purification.

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\*\* 通讯联系人 Corresponding author, E-mail: hclsjb@163.com

随着化石能源不断消耗与环境污染持续加剧,提高能源燃烧效率、寻找新型可再生能源尤为迫切.生物质气(沼气、垃圾填埋气等)具有比化石燃料更低的碳强度和更高的热能利用率而受到各领域广泛关注<sup>[1]</sup>.生物质气的主要成分为 CH<sub>4</sub>(40%—75%)、CO<sub>2</sub>(20%—55%)和其他微量组分(N<sub>2</sub>、O<sub>2</sub>、H<sub>2</sub>S等).其中,CO<sub>2</sub>的存在会降低生物质气的能源热值,制约其资源化发展.因此,从生物质气中捕集 CO<sub>2</sub>,提纯生物质气,是环境和能源领域最主要的课题之一.

气-液膜接触法是近年来出现的一种新型气体分离技术,充分耦合了化学吸收法和膜分离法,具有能耗低、占地面积小、操作灵活、易于线性放大等优势,并创造出替代传统填料塔的新一代气体分离设备“中空纤维膜接触器”<sup>[2]</sup>.如图 1 所示,在设备运行过程中,膜接触器以浓度梯度作为气体分离驱动力,允许混合气体中 CO<sub>2</sub>等特定气体分子在低压下通过膜孔进入液相主体达到分离目的<sup>[3]</sup>.此外,作为隔离吸收液和气体的关键组成部分——中空纤维膜膜组件,能够在保持气液相不直接混合的前提下,提高气液相有效接触,避免了传统填料塔的运行问题(溢流、液泛、起泡和夹带).

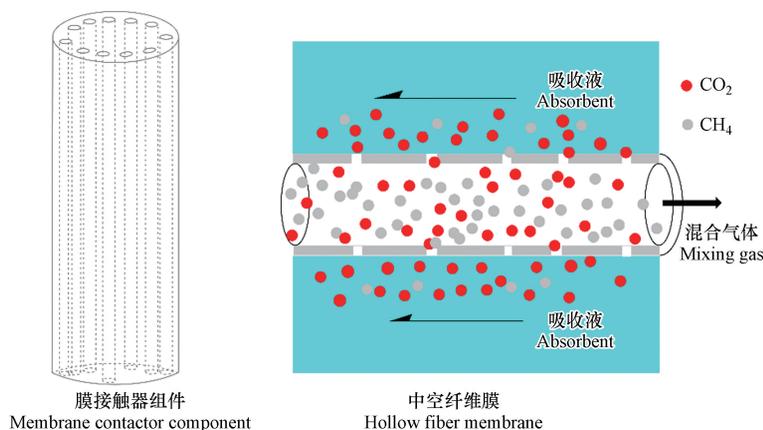


图 1 中空纤维膜接触器组件及气体分离示意图

Fig.1 The diagram of hollow fiber membrane contactor and gas separation

目前,气-液膜接触技术已被国内外学者广泛研究,众多性能优良、适应各类分离环境的新型中空纤维膜相继出现.本文以膜材料为基础,介绍了近十年来中空纤维膜在 CO<sub>2</sub>捕集领域的研究进展,同时分析了膜润湿现象、吸收剂、工艺条件以及膜接触器结构对中空纤维膜接触器 CO<sub>2</sub>捕集性能的影响,并对气-液膜接触技术的未来发展方向做出了展望.

## 1 生物质气 (Biomass gas)

生物质气中最为常见的有垃圾填埋气和沼气.填埋气是生活垃圾在一系列微生物的化学反应作用下产生的混合气体,并且组成随着填埋场的构造、垃圾组分以及气候因素的不同而有所差异.生物质气中含有大量 CH<sub>4</sub>气体,美国国家航空航天局的最新报道中显示,甲烷致全球变暖的能力是 CO<sub>2</sub>的 70 多倍<sup>[4]</sup>,并且存在爆炸等风险.但同时生物质气具有巨大的资源化潜力,据了解,1 m<sup>3</sup>填埋气完全燃烧产生的热值等同于 0.7 kg 无烟煤<sup>[5]</sup>.除了生物质气,燃煤烟气脱碳脱硫也是膜吸收技术主要应用的领域,但燃煤烟气中含有的 SO<sub>2</sub>、NO<sub>x</sub>、水汽等组分会制约烟气的实际脱碳效果,Scholes 等<sup>[6]</sup>在研究中发现,烟气中的水汽在膜内发生竞争吸附,从而降低了 CO<sub>2</sub>的渗透性,导致 CO<sub>2</sub>的分离性能下降.本文主要介绍气液膜接触技术在生物质气的研究进展,在此不做过多阐述.

## 2 气液膜接触技术 (Gas-liquid membrane contactor technology)

### 2.1 膜材料

#### 2.1.1 无机膜

无机膜因其化学性质稳定、抗腐蚀、形变能力强、热稳定性好和寿命长等优势被广泛应用于高温高压下的气体分离与提纯<sup>[7-8]</sup>.然而,质脆易损坏、制造成本较高、抗中毒能力差的缺点也限制了无机膜的

商业推广<sup>[9]</sup>.目前,工业上应用最广泛的无机膜材料为陶瓷膜和碳分子筛膜.

### (1) 陶瓷膜

用于 CO<sub>2</sub> 分离的陶瓷膜所用最常见材料是氧化铝和二氧化硅.然而,位于膜表面高亲水性的羟基极易引发膜润湿,对 CO<sub>2</sub> 分离性能不利.因此,研发克服膜润湿问题的超疏水陶瓷膜成为近年来的研究热点.

氟烷基硅烷(FAS)接枝是提高陶瓷膜疏水性的常用方法之一.以二氧化硅为例(图2),FAS中的氯基可取代陶瓷膜表面羟基上的氢键并结合在膜表面形成改性膜,大量的氟键为改性膜提供了高表面疏水性.Magnone等<sup>[10]</sup>使用氧化铝中空纤维膜进行接枝改性,结果表明,疏水改性后的膜在室温下的CO<sub>2</sub>吸收通量(MEA溶液作为溶剂)达到约 $5.4 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ,远高于其它传统高分子膜.此外,利用含氟烷基硅烷的土壤改性还可降低膜的制造成本.Abdulhameed等<sup>[11]</sup>提出以高岭土作为接枝原料,采用挤压烧结法制备薄膜,获得了接触角为142°的高疏水性中空纤维膜.

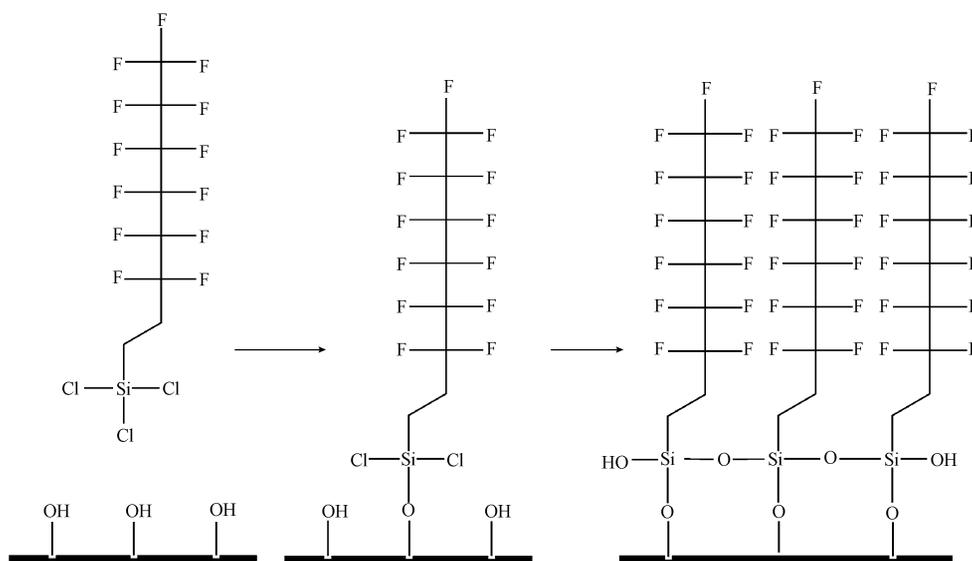


图2 二氧化硅膜表面接枝氟烷基硅烷化学反应过程

Fig.2 The progress of silica membrane surface grafting fluoroalkyl silane reaction

### (2) 碳分子筛膜

与陶瓷膜相比,无序的二维、sp<sup>2</sup>杂化碳结构的碳分子筛膜则具有分子大小的狭缝状传输孔道,不仅为碳分子筛膜提供了与笼状沸石材料相似的分子选择性,还使其具有了更高的机械强度和渗透率,因而受到广泛关注<sup>[12]</sup>.碳分子筛膜的分离机理是基于气体分子的动力学直径差异,与CH<sub>4</sub>相比,CO<sub>2</sub>动力学直径更小,更容易通过传输孔道.Rungta等<sup>[13]</sup>开发出具有优秀CO<sub>2</sub>捕集性能的改性聚酰亚胺基的碳分子筛膜,该膜在675℃下具有高出原膜230%的CO<sub>2</sub>吸收性能,不足在于所用前驱体成本较高.Haider等<sup>[14]</sup>为降低前驱体成本,开发了醋酸纤维素(CA)基的碳分子筛膜,但在高温下如何阻止去乙酰化CA膜纤维形变仍是一个不小的挑战.目前,关于如何降低碳分子筛膜制造成本和发展高性能不对称中空纤维碳膜还有待进一步的研究<sup>[15]</sup>.

#### 2.1.2 有机聚合膜

聚合膜以其易加工、低成本、高气体分离性等优点而广泛用于各类气体分离,在目前的膜基气体分离市场中占主导地位<sup>[16]</sup>.近年来,大量具有优良CO<sub>2</sub>捕集性能的高分子聚合材料被研发出来<sup>[17]</sup>.包括聚砜(PSF)、聚醚醚酮(PEEK)、聚醚酰亚胺(PEI)、聚醚砜(PES)、聚乙烯(PE)、聚丙烯(PP)、聚偏氟乙烯(PVDF)、聚四氟乙烯(PTEF)、聚甲基戊烯(PMP)、聚二甲基硅氧烷(PDMS)等.此外,研究者们还通过化学接枝、表面涂层等表面改性方法增加膜表面疏水性和粗糙度,提高聚合膜抗润湿性能<sup>[18-20]</sup>.然而,普通聚合膜的气体分离性能被限于Robeson上界下方,膜的气体渗透性和选择性相互制约(表1),无法兼具高渗透性和高气体选择性.

表 1 常见有机聚合膜的 CO<sub>2</sub> 分离性能Table 1 The CO<sub>2</sub> separation performance of common organic polymer membranes

聚合膜类型 Polymer film types	名称 Name	操作条件 Conditions	$P_{\text{CO}_2}$ ①/Barrer	CO <sub>2</sub> /CH <sub>4</sub> 选择性 Selectivity	CO <sub>2</sub> /N <sub>2</sub> 选择性 Selectivity	参考文献 Reference
聚砜	PSF	25 °C、3×10 <sup>5</sup> Pa	(45.88±2.65) GPU	21.85	24.93	[21]
		35 °C、10×10 <sup>5</sup> Pa	12.73	20.57	—	[21]
		25 °C、5×10 <sup>5</sup> Pa	11.69	25.28	—	[22]
		25 °C、10×10 <sup>5</sup> Pa	10.69	27.36	—	[22]
磺化聚醚醚酮	SPEEK	25 °C、2×10 <sup>5</sup> Pa	25.4	37	—	[23]
聚酰亚胺	PI	25 °C、4×10 <sup>5</sup> Pa	6.02	8.99	—	[24]
聚二甲基硅氧烷	PDMS	20 °C、1×10 <sup>5</sup> Pa	(3496±160)	3.4±0.3	10.9±0.6	[25]
聚醚砜	PES	A1 25 °C、2×10 <sup>5</sup> Pa	(53.5±2.7) GPU	1.24	3.26	[26]
			(597±18) GPU	0.85	1.89	
			(1569±109) GPU	0.83	1.09	

注:①CO<sub>2</sub>渗透率(CO<sub>2</sub> permeability).

### (1) 有机微孔聚合物膜

为进一步提高有机聚合膜的气体分离性能,摆脱渗透率与分离性能的相互制约问题,研究者们发展了有机微孔聚合物膜.有机微孔聚合物(MOPs)膜具有比表面积大、化学物理性质稳定、孔径尺寸可调节、合成方法多样等优点<sup>[27]</sup>,近年来成为 CO<sub>2</sub> 捕集技术研究热点之一.典型的 MOPs 包括热重排(TR)聚合物<sup>[28-29]</sup>和自具微孔聚合物(PIMs)<sup>[30-31]</sup>,见表 2.

TR 聚合物是聚酰亚胺前驱体在 350—450 °C 的热重排反应下形成的苯并恶唑环聚合物<sup>[38]</sup>.2007 年, Park 等<sup>[39]</sup>首次制备了平均孔径为 0.4—0.9 nm 的聚酰亚胺基 TR 聚合物并提出相应气体传输机制.此外,该膜的柔性结构也为相关膜组件开发提供了可行性.不仅如此,TR 聚合物膜在与 CO<sub>2</sub> 相关的混合气体分离过程中表现出优异的分选性能<sup>[28]</sup>.Woo 等<sup>[40]</sup>研制出了 CO<sub>2</sub>/N<sub>2</sub> 分离因子为 16 的超薄 TR-PBO 致密膜,该膜的 CO<sub>2</sub> 透过率可高达 2500 GPU.尽管 TR 聚合物性能优越,但受制于高温和固态膜的热重反应能耗大,生产成本低,工业放大困难等问题.因此,TR 聚合物膜的研究工作目前仍集中在膜的研发上,仅少数文献报道了中空纤维 TR 聚合物膜的应用<sup>[41]</sup>.

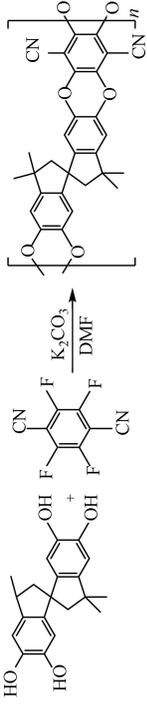
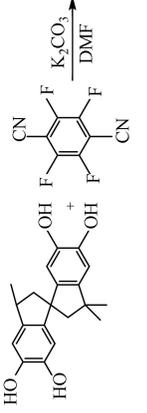
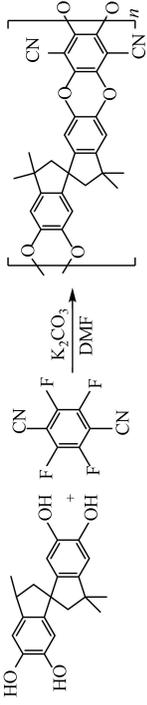
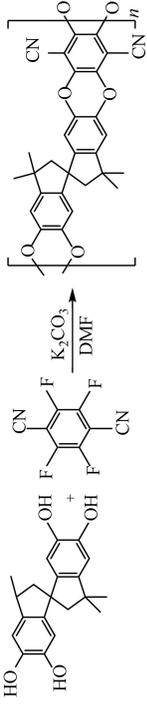
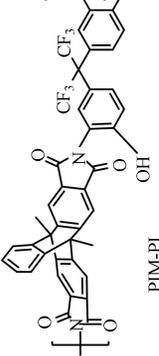
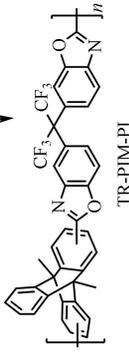
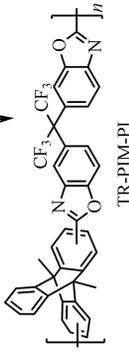
PIMs 是近年来发展的一类具有高气体渗透性及中等气体选择性的聚合物材料,该膜的高气体渗透性来源于刚性扭曲分子链折叠而产生的固有微孔结构.与传统的聚 1-三甲基硅基-1-丙炔(PTMSP)微孔膜相比,PIMs 膜以其相对缓慢的物理老化、更高的气体渗透性和选择性受到关注<sup>[42]</sup>.Budd 等<sup>[35]</sup>与 McKeown 等<sup>[43]</sup>通过比较 PIMs 膜与 PTMSP 膜的物理性能,发现 PIMs 膜具有比 PTMSP 膜更高的比表面积(600—900 m<sup>2</sup>·g<sup>-1</sup>)与自由体积(22%—24%).同时,采用含氮有机杂环基团等亲 CO<sub>2</sub> 功能型材料制备的自具微孔聚合物(TZPIMs)可以进一步提高 CO<sub>2</sub> 渗透性.研究表明<sup>[31]</sup>,TZPIMs 的 CO<sub>2</sub>/N<sub>2</sub> 分离性能超过 Robeson 上界.然而,PIMs 无序的分子结构使其孔径分布更宽,造成孔径调控困难,而膜中的超微孔及闭合孔道也限制了膜的比表面积.

目前,一些研究者开创性地将 PIMs 作为前驱体聚合物,制备 TR 膜,该膜耦合了 PIMs 和 TR 聚合物的结构特征,进一步增加了膜的微孔<sup>[44]</sup>.实验证明<sup>[37]</sup>,所得膜的 CO<sub>2</sub> 的渗透性能和气体分离性能均优于其他普通的 TR-PBO 膜,但国内相关的研究应用较为缺乏.

#### 2.1.3 混合基质膜

混合基质膜(MMMs)是无机膜材料和有机膜材料的结合体.它将纳米颗粒形态的无机材料嵌入到聚合物基质中,巧妙地结合了有机膜的低成本性和无机膜的高渗透性、高选择性与高稳定性,兼具了化学和机械性能强、气体分离效率高、孔径可调节、表面功能可改性和比表面积高等优点,在 CO<sub>2</sub> 捕集领域具有巨大的应用潜力<sup>[45-46]</sup>.用于嵌入 MMMs 的无机材料通常将尺寸控制在 100—1000 nm,且材料呈各向同性或近各向同性.

表 2 有机微孔聚合物膜 CO<sub>2</sub> 分离性能Table 2 The CO<sub>2</sub> separation performance of organic microporous polymer membranes

类型 Types	膜 Films	操作条件 Conditions	$P_{\text{CO}_2}$ /Barrer	CO <sub>2</sub> /CH <sub>4</sub> 选择性 Selectivity	CO <sub>2</sub> /N <sub>2</sub> 选择性 Selectivity	合成路线 Synthesis routes
自具微孔聚合物 PIMs	PIM-1 <sup>[32]</sup>	25 °C, 1×10 <sup>5</sup> Pa	13600	10.0	—	
	AO-PIM-1 <sup>[33]</sup>	35 °C, 2×10 <sup>5</sup> Pa	1153	34	—	
	PIM-1(纯气体条件下) <sup>[34]</sup>	35 °C, 1.5×10 <sup>5</sup> Pa	7010	—	19.5	
	PIM-1(15% CO <sub>2</sub> -85% N <sub>2</sub> ) <sup>[34]</sup>	35 °C, 1.5×10 <sup>5</sup> Pa	7100	—	19	
热重排聚合物 HCPs	TR-PIM-PI <sup>a</sup>	35 °C, 2×10 <sup>5</sup> Pa	1328	27	—	 PIM-PI $\xrightarrow[\text{N}_2]{460\text{ }^\circ\text{C} \text{ 15 min}}$ 
	TR-PIM-PI <sup>b</sup>	35 °C, 2×10 <sup>5</sup> Pa	699	35	—	

注: <sup>a</sup>膜制备完成 1 d 后测试; <sup>b</sup>膜制备完成 15 d 后测试.<sup>a</sup> CO<sub>2</sub> permeability was measured 1 d after membrane preparation; <sup>b</sup> CO<sub>2</sub> permeability was measured 15 d after membrane preparation.

研究表明<sup>[47]</sup>, MMMs 中填料的形态对膜的性能有重要影响,尤其是片状填料,其形态和取向增加了气体渗透路径的曲折性.有机聚合物基质可与多种无机填料结合,一方面增加了气体传质,另一方面填料的化学特性还可以调节膜表面孔隙率、疏水性和粗糙度等,增加膜接触器长周期运行所需的抗润湿性.典型的填料类型及相关性能如表 3 所示,可以看出,添加不同类型填料的混合基质膜通常具有较高的选择性.同时,通过对填料的功能化处理可以进一步提高膜的气体分离性能.Nasir 等<sup>[60]</sup>在碳分子筛混合基质膜中添加烷醇胺溶液,结果表明,加入二乙醇胺(DEA)后,CO<sub>2</sub>/CH<sub>4</sub>选择性和 CO<sub>2</sub>渗透率分别提高了 2 倍.并且该团队在 2—10 bar 的压力下测试了 CO<sub>2</sub>/CH<sub>4</sub>选择性和 CO<sub>2</sub>渗透性,测试出该膜的 CO<sub>2</sub>/CH<sub>4</sub>分离因子可达 20.21.

混合基质膜被认为是膜基气体分离技术未来的重点研究以及发展对象<sup>[61-62]</sup>.但是,填料在有机膜基质中的分布不均匀性和高工业成本性等都会影响混合基质膜分离性能的提高以及实际工程的应用价值.因此,如何在工业应用中保持膜良好分离性能,获得实验预期效果的同时,使用低成本、可持续材料也是混合基质膜今后面临的重要挑战之一.

表 3 不同类型填料与混合基质膜的 CO<sub>2</sub> 分离性能

Table 3 CO<sub>2</sub> separation performance of mixed matrix membranes with different fillers

填料类型 Filler types	名称 Names	膜基质 Membrane substrates	填充率(wt) Fill rates/%	温度、压力 Temperature/ Pressure	$P_{CO_2}/$ Barrer	CO <sub>2</sub> /CH <sub>4</sub> 选择性 Selectivity	CO <sub>2</sub> /N <sub>2</sub> 选择性 Selectivity	参考文献 References
沸石	SAPO34-EDA	PES	20	25 °C、 2×10 <sup>5</sup> Pa	10.091 GPU	12.14	—	[48]
	SAPO34	PSf	10	25 °C、 3.48×10 <sup>5</sup> Pa	317.0 GPU	27.9	—	[49]
二氧化硅	APTMS- MCM-41	PES	20	25 °C、 8×10 <sup>5</sup> Pa	2.72	25.9	22.2	[50]
	羧基官能化二 氧化硅	SPEEK	20	25 °C、 1×10 <sup>5</sup> Pa	1400 GPU	54	57	[51]
金属有机骨架	PEI @ MIL-101 (Cr)	SPEEK	40	25 °C、 1×10 <sup>5</sup> Pa	2490	71.8	80	[52]
	NH2-MIL-53 (Al)	PI	25	35 °C、 1×10 <sup>5</sup> Pa	9	33	—	[53]
沸石咪唑酯骨架	胺改性 ZIF-8	PSf	0.5	27 °C、 4×10 <sup>5</sup> Pa	7.26	34.09	—	[54]
	ZIF-8	XLPEGDA	20	35 °C、 2×10 <sup>5</sup> Pa	840	16.0	48.0	[55]
石墨烯	胺功能化 GO	PES	3	30 °C、 5×10 <sup>5</sup> Pa	13.26	37.88	—	[56]
	GO	PSf	0.25	25 °C、 5×10 <sup>5</sup> Pa	74.47 GPU	29.90	44.4	[57]
碳纳米管	MWCNT	PI-PSf	8	30 °C、 10×10 <sup>5</sup> Pa	5.434	16.98	3.25	[58]
	PDA-TiNTs	PPO <sup>②</sup>	6	—	127.78	14.52	20.81	[59]

注:②聚苯醚(Polyphenylene Oxide).

#### 2.1.4 固定载体膜

固定载体(FSC)膜中的活性载体可以与 CO<sub>2</sub> 发生可逆化学反应,促进 CO<sub>2</sub> 在膜中的传质,具有良好的 CO<sub>2</sub> 捕集性能和应用潜力.载体是 FSC 膜的核心,通常以共价键的形式被固定在高分子骨架上,载体在其平衡位置附近的振动使待分离组分由一个载体转移到另一个未发生络合的载体<sup>[63]</sup>.载体的位置分布、密度和种类都会对膜结构产生影响,进而影响膜的气体分离性能.此外,载体与膜基质间以化学键结合使 FSC 膜与支撑液膜相比乳化液膜具有更高的稳定性.Tong 等<sup>[64]</sup>对 FSC 膜的载体转移机理进行了综述,如图 3 所示,CO<sub>2</sub> 分子可在水中与氨基官能团反应,并根据溶液扩散(SD)机理和促进传输(FT)机理过 FSC 膜.而非反应性气体分子(如 N<sub>2</sub>、O<sub>2</sub>)只能通过 SD 传输.待分离反应组分 A(CO<sub>2</sub>)的气体渗透通量是溶液扩散和促进扩散的总和.

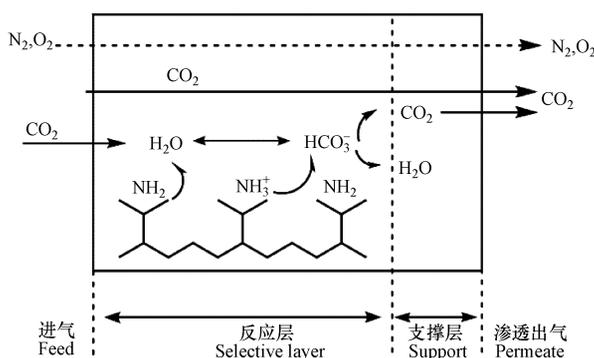


图3 基于聚乙烯基胺的FSC膜气体传输机制<sup>[64]</sup>

Fig.3 Gas transfer mechanism of FSC membrane based on polyvinyl amine

提高SD机理和FT机理的运输作用对增加FSC膜的CO<sub>2</sub>传质通量至关重要,但是,载体饱和后再进一步提高原料气中CO<sub>2</sub>分压并不能提高FT机理的贡献.因此,在应用中需权衡能耗和气体进料通量,确定最佳操作条件<sup>[65]</sup>.He等<sup>[66]</sup>对FSC膜进行了CO<sub>2</sub>捕集测试,结果表明,单级膜系统在2 bar的进料压力和0.2 bar的渗透压力下,CO<sub>2</sub>渗透率可达到60%以上,且系统可快速对进料中CO<sub>2</sub>的组分变化做出响应.此外,引入碱性载体,开发具有更高CO<sub>2</sub>反应动力学和负载量的新型载体材料可以进一步提高FSC膜的性能.Han等<sup>[67]</sup>研发出一种2-(1-哌嗪基)-乙胺肌氨酸盐/聚乙烯基胺复合FSC膜,该膜在65°C下具有1451 GPU的CO<sub>2</sub>渗透率和高达165的CO<sub>2</sub>/N<sub>2</sub>分离因子.然而,尽管FSC膜具有远高于商品膜的CO<sub>2</sub>捕集性能,但缺乏搭载FSC膜的膜组件系统以及相关工艺流程、操作条件,同时,如何在高温高压环境保持载体活性仍需进一步研究.

## 2.2 膜润湿现象

膜润湿是制约气液膜接触技术发展的主要挑战之一.通常,膜有3种运行状态:完全润湿、部分润湿以及未润湿.研究发现,仅10%的膜润湿便能造成70%膜相传质阻力的增加<sup>[68]</sup>.Wang等<sup>[69]</sup>利用DEA为吸收剂,在PP膜中模拟了CO<sub>2</sub>的吸收实验,数据表明,非润湿模式下的CO<sub>2</sub>传质通量是润湿模式下的6倍.此外,膜润湿机理的研究是现阶段攻克膜润湿现象的重点,Wang等<sup>[70]</sup>研究发现暴露于DEA溶液中的两种膜材料的表面形貌都发生了改变,由此推断DEA水溶液与膜材料之间的化学反应导致膜材料疏水性的降低而引起的.Lv等<sup>[71]</sup>经过90 d的长周期实验,发现吸收剂分子扩散到PP膜导致膜孔膨胀,并改变了PP膜的表面形貌以及疏水性,于是提出了吸收-膨胀-润湿机理.另外,在本课题组前期的研究中发现,MEA溶液与PVDF膜之前会发生消去反应引入羟基,引起膜的老化以及膜润湿现象,从而降低膜的疏水性能.

目前所知的应对膜润湿现象的相关技术有:(1)选用疏水性膜(参考2.1节);(2)选用合适的吸收剂(参考2.3节);(3)改善工艺条件.选用合适的气液相流速以及操作压力,当操作压力超过突破压力(Yong-Laplace公式),会出现膜润湿现象;(4)对膜进行改性研究.膜改性手段分别有混合制膜法<sup>[72]</sup>、化学接枝法以及表面喷涂法<sup>[73]</sup>.

## 2.3 吸收剂

生物质气提纯净化的研究大多采用醇胺类溶液作为吸收剂,氨基酸盐类、离子液体、碳酸钾以及复合溶剂等新型吸收剂也有部分涉及.理想的吸收剂应具备高吸收容量、高速率、高表面张力、低再生能耗以及对设备腐蚀性小等优势<sup>[74]</sup>.

醇胺溶液包括MEA、DEA、TEA、TETA<sup>[75]</sup>以及MDEA,其中,MEA是使用最广泛的一种吸收剂.晏水平等<sup>[76]</sup>采用MEA作为沼气中CO<sub>2</sub>分离的吸收剂,CO<sub>2</sub>传质速率最高可达18.03 mol·m<sup>-2</sup>·h<sup>-1</sup>.此外,贺清尧等<sup>[77]</sup>研究了有机胺基氨基酸盐混合体系对生物质气的提纯性能,以MDEA为主体吸收剂,分别添加不同质量的MEA、乙醇胺基甘氨酸(MEAGLY)以及乙醇胺基肌氨酸(MEASAR).实验发现,随着MEA、MEAGLY、MEASAR的配比逐渐提高,CO<sub>2</sub>的吸收效率呈现递增的趋势,但再生效率与之相反;数据表明,MDEA与活化剂质量配比为3:2时可以实现CO<sub>2</sub>吸收-再生的最优性能.

相较于传统醇胺溶液,碳酸钾溶液具备更高的表面张力、再生能力以及高经济适用性<sup>[74]</sup>.Mehdipour 等<sup>[78]</sup>采用实验与数值模型结合的方式,研究了非润湿状态和部分润湿状态下 K<sub>2</sub>CO<sub>3</sub>溶液对 CO<sub>2</sub>的分离性能,并与 DEA 进行比较.结果表明,在最佳条件下 K<sub>2</sub>CO<sub>3</sub>溶液的 CO<sub>2</sub>吸收效率要优于 DEA.

离子液体是目前的一个研究热门.Dai 等<sup>[79]</sup>选用[Bmim][TCM]为吸收剂,并在 80℃和 20 bar 的操作条件下获得了  $2.5 \times 10^{-4} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  的 CO<sub>2</sub>传质通量.Shen 等<sup>[80]</sup>对比了不同配比下的[Bmin][BF<sub>4</sub>]+K<sub>2</sub>CO<sub>3</sub>复配溶液的 CO<sub>2</sub>吸收通量,发现[Bmin][BF<sub>4</sub>]:K<sub>2</sub>CO<sub>3</sub>为 1:9 时,性能最佳,更优于甘氨酸、肌氨酸、L-亮氨酸以及 L-脯氨酸四种氨基酸溶剂.但离子液体的高成本,使其不适宜大规模的工业应用

## 2.4 工艺条件对 CO<sub>2</sub>分离性能的影响

### (1) 压力

近年来,高压条件下的 CO<sub>2</sub>捕集得到研究者的广泛关注.从理论上讲,系统压力升高会增加气相中 CO<sub>2</sub>浓度,增加传质驱动力,使更多 CO<sub>2</sub>气体分子通过膜孔进入气液界面与吸收液反应,从而提高 CO<sub>2</sub>捕集效率<sup>[81]</sup>.Gao 等<sup>[82]</sup>考察了 10—20 kPa 的 CO<sub>2</sub>分压下 PVDF 中空纤维膜接触器的传质性能,结果发现 CO<sub>2</sub>传质通量随 CO<sub>2</sub>分压成正相关.Li<sup>[83]</sup>、Zhang 等<sup>[84]</sup>的实验亦得到相同结果.值得注意的是,在运行过程中需要考虑膜材料抗压性能和气体压缩能耗带来的成本增加.若液相压力大于膜的临界压力将导致吸收液渗入膜孔,造成膜部分润湿而增加传质阻力<sup>[85]</sup>.气相压力大于膜的临界压力则易导致膜穿透损坏膜组件,使气液相直接接触.

### (2) 温度

温度是影响液相吸收剂吸收 CO<sub>2</sub>的重要因素,提高吸收剂温度有助于提高 CO<sub>2</sub>捕集效率.Shirazian 等<sup>[86]</sup>对比了 288 K 和 298 K 下的吸收剂脱碳速率,发现脱碳速率随温度的升高增加了约 10%.此外,Wu 等<sup>[87]</sup>研究了吸收剂温度变化对 CO<sub>2</sub>分离效率和传质速率的影响,发现当吸收温度从 298 K 提高到 325 K 时,CO<sub>2</sub>分离率和传质率分别提高了 30%和 40%.然而,在实际操作中需权衡增加吸收液温度所带来的能耗增加.也需要考虑膜材料耐热性,保证接触器运行过程中膜材料不因温度过高发生结构变化.

### (3) 气液相流速

气液相流速是影响膜接触器捕集性能的重要控制条件.通常,CO<sub>2</sub>的捕集效率与气相流速成负相关,与液相流速成正相关.这是因为增加气相流速会缩短 CO<sub>2</sub>在膜内的停留时间,部分 CO<sub>2</sub>来不及与吸收剂反应,导致捕集效率降低.与气相相反,增加液相流速可以减少边界层厚度,降低传质阻力,使更多新鲜吸收剂与 CO<sub>2</sub>反应,提高捕集效率<sup>[88]</sup>.Zhang 等<sup>[89]</sup>通过模拟流速对 CO<sub>2</sub>捕集效率的影响发现当气体流量从  $0.28 \text{ m} \cdot \text{s}^{-1}$  增加到  $1.40 \text{ m} \cdot \text{s}^{-1}$  时,CO<sub>2</sub>的捕集效率下降约 50%,当液相流量从  $0.015 \text{ m} \cdot \text{s}^{-1}$  提升到  $0.085 \text{ m} \cdot \text{s}^{-1}$  时,CO<sub>2</sub>的吸收效率上升约 38%.值得注意的是,由于提高气液相流速均可降低传质阻力,CO<sub>2</sub>传质通量与气液相流速均成正相关.因此,在实际操作中需要选择适合的气液相流速,保证 CO<sub>2</sub>高通量传质的同时最大限度地提高 CO<sub>2</sub>捕集效率.

### (4) 膜接触器结构

膜接触器结构对 CO<sub>2</sub>捕集的影响主要体现在膜壁厚度、膜填充率、有效长度、孔隙率、曲折因子等方面.增加壁厚将延长气体在膜中的停留时间,使沿程阻力增加,降低 CO<sub>2</sub>捕集效率.闫云飞等<sup>[90]</sup>研究了膜壁厚度对 CO<sub>2</sub>分离效率的影响,结果发现膜壁厚度从 80 μm 增加至 200 μm,吸收剂(DEA)的 CO<sub>2</sub>捕集效率降低约 40%.膜填充率和有效长度可以增加气液面接触面积,提高单位时间 CO<sub>2</sub>吸收量.Eslami 等<sup>[91]</sup>研究了膜填充率对 CO<sub>2</sub>捕集效率的影响,结果发现当膜数量从 3000 根增加至 10000 根时,CO<sub>2</sub>捕集效率从 36%增加至 100%.Rezazakemi 等<sup>[92]</sup>通过增加膜的有效长度也得到类似结论.膜孔隙率增加可以减小膜相阻力,提高气体扩散系数和膜的传质系数,进而提高 CO<sub>2</sub>分离效率.当膜孔隙率一定时,曲折因子与膜相阻力呈正相关,曲折因子增加会导致膜相阻力增加,CO<sub>2</sub>分离效率降低.因此,为了保证膜组件的整体性能,在应用中应尽量减小膜壁厚度与曲折因子,增加膜填充率、孔隙率及有效长度.

## 3 结语 (Conclusion)

气-液膜接触技术作为 CO<sub>2</sub>捕集领域的关键技术,具有巨大的发展潜力.气-液膜接触法具有气液接触面积大、传质速率快、操作灵活、设备体积小、可线性放大、能耗少等优点,已被广泛应用于生物质气中

CO<sub>2</sub>的捕集.本文综述了近十年来气-液膜接触技术的发展,得出结论如下:(1)目前膜材料的研究主要包括无机膜、有机膜、混合基质膜和固定载体膜等,都具有各自的优缺点和适用条件.新型膜材料虽然研究广泛,但缺少中试和示范应用,作为工业推广还需进一步研究.此外,如何保证膜材料气体分离性能的同时降低制造成本仍旧是重要挑战.(2)提高膜的压力、温度、液相流速、降低气相流速,减小膜壁厚度、曲折因子,增加膜填充率、孔隙率及有效长度可以增加 CO<sub>2</sub>捕集效率.(3)开发低成本、低再生成本、高 CO<sub>2</sub>去除率的新型吸收剂以及控制膜润湿问题依旧是今后的研究重点.

目前,气-液膜接触技术在 CO<sub>2</sub>捕集领域表现出巨大的应用前景,但与工业上普遍使用的其他优势技术相比,尚处于发展阶段.气-液膜接触技术的研究工作大部分仍然停留在实验室研发阶段,迫切需要更多中试和示范成果来推动气-液膜接触技术的工业化.同时,膜的老化、塑化、溶胀、润湿以及污染等问题依旧是制约中空纤维膜接触器长期稳定运行的重大阻碍,进一步研发低成本、高 CO<sub>2</sub>捕集性能和高稳定性的新型中空纤维膜,优化膜组件工艺设计与工艺布置将成为未来研究方向.相信随着气-液膜接触技术的进一步研究与发展,中空纤维膜性能不断提升,有望在 CO<sub>2</sub>捕集的工业领域大规模应用,推动我国生物质气提纯产业的发展.

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