CO_2 REMOVAL USING POLYVINYLIDENE FLUORIDE MIXED MATRIX MEMBRANE IN MEMBRANE GAS ABSORPTION

NOR AINI AHMAD

UNIVERSITI SAINS MALAYSIA

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by

NOR AINI AHMAD

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%	Percentage
θ	Angle (^{o})
^{o}C	Temperature in degree celsius
A_i	effective membrane contact area
cm	Unit of length in centimetre
d_i,	The inner diameter of the hollow fiber
d_o	The outer diameter of the hollow fiber
d_{ln}	The logarithm mean diameter of the hollow fiber
g	Weight in gram
H	Henry's constant
J_{CO2}	CO_2 absorption flux
K_L	The liquid mass transfer coefficient in liquid
K_m	The Membrane mass transfer coefficient in liquid
K_o	Overall mass transfer coefficient
ml	Millilitre
nm	Unit of length in nanometer (10^{-9} m)
Q_g	Gas flow rate
Q_L	Liquid flow rate
R_a	Average roughness
R_q	The root-mean-square roughness
R_m	Membrane resistance
Re	Reynold number
Sh_L	Sherwood number
V_L	Ratio of absorbent flow rate (m^3/s) per cross-sectional area (m^2)
v%	Volume percentage
wt%	Weight percentage

LIST OF ABBREVIATIONS

AFM	Atomic force microscope
$CaCO_3$	Calcium carbonate
CH_4	Methane
CO_2	Carbon dioxide
DEA	Diethanolamine
DMAC	Dimethylacetamide
DMF	N-, N-Dimethylformamide
DSC	Differential Scanning Calorimetry
D0	Neat PVDF hollow fiber membrane
D1	PVDF hollow fiber membrane with 1 wt% of SAPO-34
D3	PVDF hollow fiber membrane with 3 wt% of SAPO-34
D5	PVDF hollow fiber membrane with 5 wt% of SAPO-34
EDX	Energy-dispersive X-ray spectroscopy
FS	Flat Sheet membrane
FTIR	Fourier transform infrared
HF	Hollow fiber membrane
H_2	Hydrogen
H_2S	Hydrogen sulphide
H_3PO_4	Ortho-Phosphoric acid
LEP	Liquid entry pressure
LiCl	Lithium chloride
LDPE	Low density poly ethylene
M-AP	Aminopropylisobutyl
MEA	Monodiethanolamine
MGA	Membrane gas absorption
MOF	Metal-organic framework

M-SP	Flat sheet PVDF membrane contains 10 wt% of trisilanolisobutyl POSS and nonsolvent
M-S34	PVDF membrane contains 10 wt% SAPO-34 POSS and nonsolvent
MMT	Montmorillonite clays
M-0	PVDF membrane contains nonsolvent
NaOH	Sodium Hydroxide
NMP	n-methyl-2- Pyrrolidone
NH_3	Ammonia
N_2	Nitrogen
OH	Hydroxyl group
O_2	Oxygen
PBI	Poly[2,2’-(m-phenylene)-5,5’-dibenzimidazole
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEI	Polyethylenimine
PEEK	Poly(ether ether ketone)
PES	Polyethersulfone
POME	Palm oil mill effluent
POSS	Polyhedral oligomeric silsesquioxane
PP	Polypropylene
PSA	Pressure swing adsorption
PSf	Polysulfone
PTFE	Polytetrafluorethylene
PVDF	Polyvinylidene fluoride
P0	Neat flat sheet PVDF membrane
P-0F	Neat flat sheet PVDF membrane with post silane modification
P-10 PBI	Flat sheet PVDF membrane contains 10 wt% of PBI

P-10S34	Flat sheet PVDF membrane contains 10 wt% of SAPO-34
P-10S34F	Flat sheet PVDF membrane contains 10 wt% of SAPO-34 with post silane modification
P-10MS34	Flat sheet PVDF membrane contains 10 wt% of hydrophobic SAPO-34
P-15PBI	Flat sheet PVDF membrane contains 15 wt% of PBI
P-20PBI	Flat sheet PVDF membrane contains 20 wt% of PBI
P-25PBI	Flat sheet PVDF membrane contains 25 wt% of PBI
P-5S34	Flat sheet PVDF membrane contains 5 wt% of SAPO-34
P-5S34F	Flat sheet PVDF membrane contains 5 wt% of SAPO-34 with post silane modification
P-5S34-5PBI	Flat sheet PVDF membrane contains 5 wt% of SAPO-34 and 5 wt% of PBI
SEM	Scanning electron microscopy
SMM	Surface modifying macromolecule
SiO	Silica oxide
SAPO-34	Silicoaluminophosphate-34
TGA	Thermogravimetric analysis
ZSM5	ZSM5 zeolite

PENYINGKIRAN CO_2 MENGGUNAKAN MATRIK CAMPURAN MEMBRAN POLIVINILIDENA FLUORIDA DALAM MEMBRAN PENYERAPAN GAS

ABSTRAK

Teknologi penyingkiran karbon dioksida (CO_2) sangat penting untuk penulenan sumber tenaga seperti biogas. Antara teknologi penyingkiran CO_2, membran penyerapan gas (MGA) boleh digunakan untuk menyingkirkan CO_2 pada tekanan rendah. MGA mengintegrasi kelebihan membran dan proses penyerapan kimia dalam satu unit. Namun, pembasahan membran semasa pengendalian jangka panjang menggalakkan peningkatan ringtangan jisim walaupun menggunakan membran hidrofobik. Membran polivinilidena fluorida (PVDF) kerap kali digunakan untuk MGA, tetapi andaian ternyah fluoride PVDF ke dalam larutan amina menyebabkan berlakunya pembasahan membran. Dalam kajian ini, polimer poli[2,2'-(m-fenilena)-5,5'-dibenzimidazol (PBI) yang mempunyai rintangan kimia dan kestabilan haba yang tinggi telah diadun bersama polimer PVDF untuk meningkatkan sifat kimia dan fizik membran. Selain itu, zeolit SAPO-34 yang mempunyai sifat afiniti penyerapan terhadap CO_2 dicampur ke dalam membran PVDF untuk meningkatkan penyerapan CO_2. Gabungan membran PVDF dengan zeolit SAPO-34 juga diubahsuai menjadi hidrofobik menggunakan silana. Ikatan hydrogen dalam adunan polimer melalui penderma (-NH-) dan proton penerima (-N=) dari PBI menggalakkan penghasilan boleh-larut campuran. Membran PVDF/PBI dengan bebanan 20 wt% PBI menghasilkan penyerapan CO_2 tertinggi sebanyak 3.07 x 10^{-4} mol/m^2s. Manakala, fluks CO_2 membran PVDF meningkat sehingga 60 % ke 4.53 x 10^{-4} mol/m^2s apabila membran PVDF diadun bersama 10 wt% SAPO-34. Praubahsuai zarah zeolit SAPO-

34 menggunakan fluorokarbon salina mengagalkan pembentukan struktur membran berliang, kesannya rintangan membran semasa penyerapan CO_2 bertambah tinggi. Pascaubahsuai membran PVDF/SAPO-34 menggunakan silana meningkatkan penyerapan CO_2. Tambahan itu, peningatan ketara berlaku di mana sudut sentuhan dan tekanan kemasukan cecair meningkat kesannya keseluruhan pemindahan jisim *(K_o)* menjadi 12.46 x 10^{-6} m/s. Ujikaji CO_2 lembap ke sistem MGA dengan gabungan PVDF/SAPO-34 pascaubahsuai, mengurangkan sedikit telapan CO_2 menjadi 10.65 x 10^{-6} m/s. Namun, K_o untuk membran PVDF/SAPO-34 pascaubahsuai hampir sama dengan K_o membran PVDF/SAPO-34 tanpa pengubahsuaian silana. Ujikaji kebasahan membran dengan larutan 2 M dietahnolamina (DEA) menunjukkan adunan polimer dan zeolit dalam membran PVDF/SAPO-34 mengurangkan pembengkakan membran. Akan tetapi, interaksi tidak diinginkan berlaku antara kumpulan fluoroalkil dan amina mengaruhkan kebasahan membran PVDF/SAPO-34 pascaubahsuai oleh amina. Seterusnya, gentian geronggang PVDF/SAPO-34 dengan bebanan zeolit SAPO-34 berbeza (1, 3 dan 5 wt%) telah dihasilkan. Fluks CO_2 tertinggi dicapai sehingga 8.73 x 10^{-4} mol/m^2s apabila 3 wt% zeolite SAPO-34 telah dimasukkan ke dalam adunan gentian geronggang PVDF/SAPO-34. Gentian geronggang PVDF/SAPO-34 menunjukkan rintangan jisim yang rendah berbanding membran kepingan rata PVDF/SAPO-34. Fluks CO_2 gentian geronggang PVDF/SAPO-34 meningkat 140 % kali ganda lebih tinggi berbanding fluks CO_2 gentian geronggang PVDF asli apabila 2 M DEA digunakan sebagai cecair penyerap. Gentian geronggang PVDF asli terampul hampir 71.0 % dalam DEA tetapi adunan gentian geronggang PVDF/SAPO-34 mengurangkan pembengkakan dengan amina sehingga 47.7 %.

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ABSTRACT

Carbon dioxide (CO_2) removal technology is important in the purification of energy source such as biogas. Among the CO_2 removal techniques, membrane gas absorption (MGA) can be used to separate CO_2 at low pressure. MGA integrates the advantages of membrane and chemical absorption process in a single unit. However, membrane wetting in the long operation can induce the increment of mass transfer resistance even using hydrophobic membranes. Polyvinylidene fluoride (PVDF) is the commonly used membrane in MGA, but PVDF defluorination in amine solutions was postulated to cause membrane wetting. In this research, poly[2,2'-(m-phenylene)-5,5'-dibenzimidazole (PBI) with the great chemical resistance and thermal stability was blended into PVDF membrane to enhance the physical and chemical properties membrane. Besides that, SAPO-34 zeolite with CO_2 absorption affinity was incorporated into PVDF membrane to improve CO_2 absorption. PVDF membrane incorporated with SAPO-34 zeolite was hydrophobically modified using silane. Hydrogen bonding in the polymer blend due to donor (-NH-) and proton acceptor (-N=) of PBI encouraged the formation of miscibility blend. PVDF/PBI membrane with 20 wt% of PBI showed the highest CO_2 flux of 3.07 x 10^{-4} mol/m^{2}s. The CO_2 flux of PVDF membrane increased 60 % to 4.53 x 10^{-4} mol/m^{2}s when it was blended with 10 wt% of SAPO-34 zeolite. The pre-modified SAPO-34 zeolite using fluorocarbon silane retarded the formation of porous structure, resulting in a great membrane resistance for CO_2 transfer. The post-modification of PVDF/SAPO-34 membrane using silane caused improvement in CO_2 absorption. The significant