MULTI-WALLED CARBON NANOTUBES AS PERVAPORATION BUCKYPAPER MEMBRANES AND CATALYSTS FOR ETHERIFICATION REACTION

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by

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LIST OF ABBREVIATIONS

$(CH_3\text{-}CO)_2O$	Acetic anhydride
MWCNT-NH_2	Amine-functionalized MWCNTs
K	Adsorption equilibrium constants
A-15	Amberlyst-15
A-35	Amberlyst-35
NH_4OH	Ammonium hydroxide
ANOVA	Analysis of variance
k_1	Arrhenius coefficient
ARCO	Atlantic Richfield Company
BET	Brunauer-Emmett-Teller
BPA	Bisphenol A
BP	Buckypaper
MWCNT-COOH	Carboxylic acid-functionalized MWCNTs
–COOH	Carboxylic acid groups
CNTs	Carbon nanotubes
CNT-BP	Carbon nanotubes-buckypaper
CVD	Catalytic vapour deposition
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
CCD	Central composite design
DTG	Derivative thermogravimetric analysis
$H_6P_2W_{18}O_{62}.27H_2O$	Diphosphooctadecatungstic acid
DOE	Design of experiment
DSC	Differential scanning calorimetry
DMF	Dimethylformamide
DWCNTs	Double-walled carbon nanotubes
ETBE	Ethyl *tert*-butyl ether
FESEM	Field emission scanning electron microscopy
FCSA	Fluorocarbon sulfonic acid
FT-IR	Fourier transform-infrared spectroscopy

GC	Gas chromatograph
E_a	General activation energy
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
–OH	Hydroxyl groups
I_D	Intensity of the D-band peak
I_G	Intensity of the G-band peak
IB	Isobutene
TPA-K	Keggin-type tungstophosphoric acid
MTBE	Methyl *tert*-butyl ether
MEMS	Microelectromechanical system
MMM	Mixed matrix membranes
MWCNTs	Multi-walled carbon nanotubes
TMA	N-[3-(trimethylamoniopropyl)]methacrylamidemethylsulfate)
NEMS	Nanoelectromechanical system
HNO_3	Nitric acid
NVP	N-vinyl-pyrrolidinone
Pd	Palladium
PFAD	Palm fatty acid distillate
PPA	Phenylphosphonic acid
PTS	Phthalocyaninetetrasulfonic acid
PEEK	Poly(ether ether ketone)
PLA	Poly(lactic acid)
PPS	Poly(phenylene sulphide)
PTFE	Poly(tetra-fluoro-ethylene)
PVA	Polyvinyl alcohol
PVP	Polyvinyl-pyrrolidinone
PVDF	Polyvinylidene fluoride
KBr	Potassium bromide
r	Reaction rate
RSM	Response surface methodology
SEM	Scanning electron microscopy

SMP	Shape-memory polymer
$SiO_2.xH_2O$	Silicic acid
STA	Silicotungstic acid
SWCNTs	Single-walled carbon nanotubes
NaAlg	Sodium alginate
S.D.	Standard deviation
SPESEKK	Sulfonated poly(ether sulfone ether ketone ketone)
SPEEK	Sulfonated poly(ether ether ketones)
H_2SO_4	Sulfuric acid
TBA	*tert*-butyl alcohol
TPD-NH_3	Temperature-programmed desorption of ammonia
TEOS	Tetraethoxysilane
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TiO_2	Titanium oxide
$SOCl_2$	Thionyl chloride
TEM	Transmission electron microscopy
Trix	Triton X-100
H_2O	Water
WHSV	Weight hourly space velocity
XPS	X-ray photoelectron spectroscopy
ZSM-5	Zeolite Socony Mobil-5

LIST OF SYMBOLS

γ	Activity coefficients
$E_{a,i}$	Activation energy of component *i*
$E_{D,i}$	Activation energy for diffusion of component *i*
$E_{P,i}$	Activation energy for permeation of component *i*
T	Absolute feed temperature
Q	Amount of the permeate collected
γ_{i1}	Average activity coefficient of component *i* at the feed side
γ_{i3}	Average activity coefficient of component *i* at the permeate side
°	Degree
S	Degree of swelling
β_{diff}	Diffusion selectivity
α	Distance of axial point from center
p_T	Downstream pressure at permeate side
A	Effective asymmetric membrane area
$\Delta H°$	Enthalpy change
$\Delta H_{S,i}$	Enthalpy of sorption of component *i*
$C_{ETBE,t}$	Final ETBE concentration
$C_{TBA,t}$	Final TBA concentration
R	Gas constant
$\Delta H_{V,i}$	Heat of vaporization of component *i*
x	Independence variable
$C_{TBA,0}$	Initial TBA concentration
x_i	Mole fraction of component *i* in the feed
y_i	Mole fraction of component *i* in the permeate
n	Number of independence variables
p_{i1}	Partial pressure of component *i* on the liquid phase
p_{i3}	Partial pressure of component *i* on the vapour phase
r	Reaction rate
P	Permeability
Q_0	Permeability of the porous layer of membrane
J	Permeation flux

A	Pre-exponential factor
ε	Random error
β	Regression coefficient
β_i	Selectivity of the most preferred component *i*
β_j	Selectivity of the least preferred component *j*
α	Separation factor
β_{sorp}	Sorption selectivity
T	Temperature
δ	Thickness of membrane
Δt	Time interval
$Đ_i$	Transport coefficient of component *i*
$Đ_i^*$	transport coefficient of component *i* at a reference temperature T^* of 293K
P^P	Total pressure of permeate vapour
R	Universal gas constant
P^{sat}	Vapour pressure of pure components
pi_0	Vapour pressure of pure component *i*
X_i	Weight fraction of component *i* in the feed
Y_i	Weight fraction of component *i* in the permeate
W_d	Weight of the dry membrane
W_s	Weight of the swollen membrane

TIUB-NANO KARBON DINDING BERLAPIS SEBAGAI MEMBRAN KERTAS-BUCKY PENYEJATTELAPAN DAN PEMANGKIN UNTUK TINDAK BALAS ETERIFIKASI

ABSTRAK

Membran asimetrik disediakan terlebih dahulu daripada pembentukan berstruktur tiub-nano karbon dinding berlapis kertas-bucky (TNKDB-KB) sebagai lapisan pra-memilih dan kemudiannya struktur tersebut disalut dengan selapis polivinil alkohol (PVA) yang nipis. Membran asimetrik tersebut digunakan dalam proses penyejattelapan untuk penyahidratan campuran berbilang komponen yang diperolehi daripada tindak balas eterifikasi. Keputusan penyejattelapan menunjukkan bahawa membran asimetrik mempamerkan masing-masing dua dan empat kali ganda peningkatan bagi fluks telapan air dan faktor pemisahan. Kesan ini adalah disebabkan kumpulan hidrofilik pada MWCNTs yang telah ditulenkan dan saluran-nano pada lapisan pra-memilih, yang memihak kepada penyerapan molekul air. Model larutan-resapan bagi Rautenbach adalah memadai bagi menerangkan proses penyejattelapan. Dalam kajian proses tindak balas eterifikasi, pemangkin MWCNTs yang telah disulfonasikan mempunyai tapak asid Lewis telah disediakan melalui proses pensulfuran dengan asid sulfurik. Prestasi bermangkin oleh pemangkin pensulfuran MWCNTs telah dikaji dalam proses tindak balas eterifikasi bagi *tert*-butil alkohol (TBA) dan etanol. Kesan pembolehubah proses (suhu tindak balas, masa tindak balas, nisbah molar etanol kepada TBA, bebanan pemangkin) terhadap penukaran TBA, kememilihan etil *tert*-butil eter (ETBE) and hasil ETBE telah dikaji melalui dua pendekatan berbeza: pendekatan konvensional dan pendekatan

metodologi permukaan sambutan (RSM). Bagi pendekatan konvensional, keadaan tindak balas optimum terdiri daripada masa tindak balas selama 4 j pada suhu 140 ^{o}C, nisbah molar etanol kepada TBA 2:1 dan 3 % berat bebanan pemangkin. Optimum penukaran TBA, kememilihan ETBE dan hasil ETBE masing-masing ialah 64 %, 68 % dan 44 %. Sebaliknya, keputusan yang diperolehi daripada pendekatan RSM menunjukkan bahawa pembolehubah-pembolehubah individu dan interaksi-interaksi mereka memberikan kesan ketara kepada tindak balas eterifikasi. Tindak balas selama 4 j pada 146 °C, nisbah molar bagi etanol kepada TBA 2.17:1 dan 3.26 % berat bebanan pemangkin memberikan penukaran TBA yang optimum sebanyak 72 %. Tambahan pula, optimum kememilihan dan hasil ETBE masing-masing ialah 60 % and 43 %. Kedua-dua pendekatan mempunyai pembolehubah-pembolehubah proses optimum yang seakan-akan sama. Walau bagaimanapun, pendekatan RSM dapat memberi pembolehubah-pembolehubah proses optimum yang lebih tepat dan khusus kerana nilai-nilainya dianggarkan daripada persamaan-persamaan model. Satu mekanisma eterifikasi telah dicadangkan bagi menerangkan tindak balas eterifikasi. Pemangkin pensulfuran MWCNTs menunjukkan penurunan prestasi bermangkin yang tidak ketara selepas empat eksperimen yang dilakukan secara berturut-turut dan mudah dipulihkan selepas penjanaan semula. Selepas itu, campuran tindak balas optimum digunakan sebagai larutan suapan bagi penyahhidratan air menggunakan membran asimetrik baru. Jumlah fluks penyerapan lebih kurang 7 g/m^{2}·j dan faktor pemisahan lebih kurang 400 telah diperolehi.

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ABSTRACT

Asymmetric membranes were prepared by first forming multi-walled carbon nanotube-buckypaper (MWCNT-BP) structures as the pre-selective layer followed by coating the structures with a thin layer of polyvinyl alcohol (PVA) to form novel MWCNT-BP/PVA asymmetric membranes. The resultant asymmetric membranes were applied in the pervaporation process for dehydration of multi-component mixture obtained from an etherification reaction process. The pervaporation results revealed that the asymmetric membranes exhibited two- and four-fold enhancements of the water permeation flux and separation factor, respectively, compared to the pure PVA membrane. This effect was observed due to the hydrophilic group on the purified MWCNTs and the nanochannels of the pre-selective layer, which favour the permeation of water molecules. A solution-diffusion model of Rautenbach was adequately in describing the pervaporation process. In the etherification reaction process study, sulfonated MWCNTs catalyst containing Lewis acid sites was prepared *via* sulfonation process with sulfuric acid. The catalytic performances of sulfonated MWCNTs catalyst were investigated in the etherification reaction process of *tert*-butyl alcohol (TBA) with ethanol. The effect of process variables (reaction temperature, reaction time, molar ratio of ethanol to TBA, catalyst loading) on the conversion of TBA, selectivity of ethyl *tert*-butyl ether (ETBE) and yield of ETBE were investigated using two different approaches: conventional approach and