

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

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

by

YEE KIAN FEI

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TABLE OF CONTENTS

Acknowledgement	ii
Table of Contents	iv
List of Tables	ix
List of Figures	xi
List of Abbreviations	xvi
List of Symbols	xix
Abstrak	xxi
Abstract	xxiii

CHAPTER 1 – INTRODUCTION

1.1 Carbon nanotubes (CNTs)	1
1.2 Buckypaper (BP)	3
1.3 Pervaporation	4
1.4 Etherification reaction	5
1.4.1 Fuel additive and oxygenate additive	6
1.4.2 Advantages of ETBE as oxygenate additive	7
1.5 Problem statement	8
1.6 Scope	10
1.7 Objectives	12
1.8 Organization of thesis	12

CHAPTER 2 – LITERATURE REVIEW

2.1 Acid treatment on CNTs	15
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2.1.1	Purification	16
2.1.2	Sulfonation	19
2.2	Carbon nanotube-buckypaper (CNT-BP)	21
2.2.1	Fabrication of carbon nanotube-buckypaper (CNT-BP)	21
2.2.2	Application of carbon nanotube-buckypaper (CNT-BP)	26
2.3	Membrane for pervaporation related to the components in the etherification mixture	30
2.4	Modeling of pervaporation	34
2.5	Production of ETBE	37
2.5.1	Gas phase reaction	38
2.5.2	Liquid phase reaction	41
2.5.2 (a)	Reaction between IB and ethanol	41
2.5.2 (b)	Reaction between TBA and ethanol	44
2.6	ETBE production over different types of catalysts	47
2.7	Application of CNTs catalysts in chemical reaction	53
2.8	Statistical design of experiment	56
2.8.1	Response surface methodology (RSM)	56
2.8.2	Central composite design (CCD)	58
2.8.3	Statistical design of experiment in ETBE production	59
2.9	Summary	60
CHAPTER 3 – MATERIALS AND METHODOLOGY		
3.1	Raw materials	61
3.2	Chemicals	62
3.3	Experimental procedure	63

3.3.1	Acid treatment on the MWCNTs	65
3.3.1 (a)	Purification of raw MWCNTs	65
3.3.1 (b)	Sulfonation of purified MWCNTs	66
3.3.2	Preparation of MWCNT-BP	66
3.3.3	Preparation of MWCNT-BP/PVA asymmetric membrane	67
3.3.4	Preparation of feed solution for pervaporation study obtained from etherification reaction	68
3.3.5	Pervaporation experiments	69
3.3.6	Modeling of pervaporation	71
3.4	Characterization	73
3.4.1	Thermal stability	73
3.4.2	Defects	74
3.4.3	Surface chemistry	74
3.4.4	Acid sites.....	75
3.4.5	Structure and surface morphology	75
3.4.6	Internal diameter.....	76
3.4.7	Surface area	76
3.4.8	Contact angle	76
3.4.9	Tensile properties	77
3.4.10	Swelling and sorption studies	77
3.5	Identification of components in reaction mixture and permeate solutions	78
3.6	Calculation methods	78
3.6.1	Conversion of TBA, selectivity of ETBE and yield of ETBE ...	78
3.6.2	Swelling and sorption properties	79

3.6.3	Permeation properties	80
3.7	Etherification process study	81
3.7.1	Conventional approach	81
3.7.1 (a)	Effects of reaction temperature	81
3.7.1 (b)	Effects of molar ratio of ethanol to TBA	82
3.7.1 (c)	Effects of catalyst loading	82
3.7.2	Design of Experiment approach	82
3.8	Catalyst reusability and regeneration studies	84

CHAPTER 4 – RESULTS AND DISCUSSION

4.1	Thermal stability of MWCNTs	87
4.2	Spectroscopic characterization of MWCNTs	89
4.3	Tensile properties of pure PVA and purified MWCNT-BP/PVA asymmetric membrane	92
4.4	Membrane characterization	94
4.5	Swelling and sorption results	96
4.6	Pervaporation results	97
4.6.1	Effects of purified MWCNT-BP of the asymmetric membranes on pervaporation	98
4.6.2	Effects of downstream pressure	103
4.6.3	Effects of feed temperature	105
4.7	Modeling of pervaporation	109
4.8	Characterization of the sulfonated MWCNTs catalysts	115
4.9	Etherification process study through conventional approach	120
4.9.1	Effects of the process variables	120

4.9.1 (a) Effects of reaction temperature	120
4.9.1 (b) Effects of molar ratio of ethanol to TBA	124
4.9.1 (c) Effects of catalyst loading	129
4.10 Etherification process study through RSM approach	133
4.10.1 Development of regression model equations	136
4.10.2 Statistical analysis of results	137
4.10.3 Response surface analysis	142
4.10.4 Optimization of etherification process variables	156
4.11 Comparison of the catalytic performances of various heterogeneous acid catalysts	157
4.12 Catalyst reusability and regeneration studies	161
4.13 Pervaporation performances of purified MWCNT-BP/PVA asymmetric membrane in different feed solutions	163
 CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	165
5.2 Recommendations	166
REFERENCES	168

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

		Page
Table 1.1	Physical properties of different carbon materials (Xie et al., 2005, Schadler, 2004, Coleman et al., 2006)	3
Table 1.2	Properties of ETBE and MTBE (Thiel et al., 1997)	9
Table 2.1	Performance of various types of membrane in pervaporation of water-ethanol, ethanol-ETBE and water-TBA mixtures	35
Table 2.2	Summary of the ETBE production via gas-phase and liquid-phase	46
Table 2.3	Summary of the catalysts used in the production of ETBE	52
Table 2.4	Various reported chemical reactions catalyzed using CNTs catalysts	56
Table 3.1	Source and purity of raw materials and chemicals used in this study	62
Table 3.2	Independent variables and levels used for the central composite design (CCD) for etherification process study	83
Table 3.3	Experimental design matrix for etherification reaction process study	84
Table 4.1	Summary of mechanical properties of pure PVA membrane and purified MWCNT-BP/PVA asymmetric membrane containing different loading of MWCNTs	93
Table 4.2	Compositions of different components in the feed mixture, sorbed solution and sorption selectivity	97
Table 4.3	Pervaporation performance of pure PVA membrane and purified MWCNT-BP/PVA asymmetric membrane	98
Table 4.4	Relative transport coefficients, enthalpy of sorptions and activation energies of water and ethanol of the MWCNT-BP/PVA asymmetric membrane	111
Table 4.5	Experimental design matrix by CCD for the four independent variables used for etherification process study	134
Table 4.6	Exact amount for molar ratio of ethanol to TBA and catalyst loading for data used in Table 4.5	136

Table 4.7	Analysis of Variance (ANOVA) for the regression model equation and coefficients for conversion of TBA	141
Table 4.8	Analysis of Variance (ANOVA) for the regression model equation and coefficients for selectivity of ETBE	141
Table 4.9	Analysis of Variance (ANOVA) for the regression model equation and coefficients for yield of ETBE	142
Table 4.10	Comparisons between conventional approach and RSM approach	157
Table 4.11	Catalytic performances of different heterogeneous acid catalysts in the production of ETBE from TBA and ethanol	158
Table 4.12	Pervaporation performances of purified MWCNT-BP/PVA asymmetric membrane in different feed solutions	164
Table 4.13	Composition of reaction mixtures catalyzed by A-15 and sulfonated MWCNTs	164
Table A.1	Peak area for each of component in standard solution	
Table A.2	Retention time and peak area for each of component in the sample	
Table A.3	Retention time for each component peak in GC chromatogram	
Table D.1	Effect of feed temperature on permeation flux of water	
Table D.2	Effect of feed temperature on permeation flux of ethanol	
Table D.3	Pervaporation data	

LIST OF FIGURES

		Page
Figure 1.1	Schematic diagram of vacuum pervaporation process (Feng and Huang, 1997)	4
Figure 1.2	Schematic diagram of pervaporation based on solution-diffusion model (Feng and Huang, 1997)	5
Figure 2.1	The formation of hydrogen bond in purified MWCNTs (dotted lines) (Hsieh et al., 2010)	19
Figure 2.2	Chemical structure of sulfonated CNTs (Kanbur and KÜçÜkyavuz, 2011)	20
Figure 2.3	Schematic diagram of pressurized filtration process (Zhang et al., 2014)	24
Figure 2.4	Schematic diagram of ETBE production	37
Figure 3.1	Overall research methodology flow diagram	64
Figure 3.2	Apparatus used in fabricating buckypaper by vacuum filtration	67
Figure 3.3	Schematic diagram of reactor	69
Figure 3.4	Schematic diagram of the pervaporation set-up	70
Figure 4.1	(A) TGA and (B) DTG thermograms of the raw MWCNTs, purified and sulfonated MWCNTs	88
Figure 4.2	Raman spectra of (A) raw MWCNTs (B) purified MWCNTs (C) sulfonated MWCNTs	90
Figure 4.3	FT-IR spectra of (A) raw MWCNTs (B) purified MWCNTs (C) sulfonated MWCNTs	91
Figure 4.4	Tensile stress-strain curves obtained from tensile tests for different MWCNT-BP loadings	94
Figure 4.5	(A) Photographs of a round (diameter 4.7 cm) and black, purified MWCNT-BP. (B) Typical SEM image of self-supporting purified MWCNT-BP. (C) Cross-sectional view of purified MWCNT-BP/PVA asymmetric membrane (top layer is the MWCNT-BP; bottom layer is the PVA membrane)	95
Figure 4.6	TEM image of purified MWCNTs	100

Figure 4.7	Schematic diagram of the reaction mixture molecules: (A) initial, (B) intermediate and (C) final stage of pervaporation with purified MWCNT-BP/PVA asymmetric membranes	102
Figure 4.8	Permeation flux of purified MWCNT-BP/PVA asymmetric membrane as a function of downstream pressure at feed temperature of 30 °C with a feed solution of 9 wt% water. The error bars represent the standard deviations (S.D.) of the means	104
Figure 4.9	Separation factor of purified MWCNT-BP/PVA asymmetric membrane as a function of downstream pressure at feed temperature of 30 °C with a feed solution of 9 wt% water. The error bars represent the standard deviations (S.D.) of the means	105
Figure 4.10	Permeation flux of purified MWCNT-BP/PVA asymmetric membrane as a function of feed temperature at downstream pressure of 5 mmHg with a feed solution of 9 wt% water. The error bars represent the standard deviations (S.D.) of the means	106
Figure 4.11	Separation factor of purified MWCNT-BP/PVA asymmetric membrane as a function of feed temperature at downstream pressure of 5 mmHg with a feed solution of 9 wt% water. The error bars represent the standard deviations (S.D.) of the means	107
Figure 4.12	Semi-logarithmic Arrhenius plot of the permeation flux of water and that of other components versus the reciprocal of the absolute temperature	109
Figure 4.13	Semi-logarithmic Arrhenius plot of the transport coefficient of water and ethanol versus the reciprocal of the absolute temperature	110
Figure 4.14	Partial permeation flux of water and ethanol over feed temperature	114
Figure 4.15	TPD-ammonia spectrum of sulfonated MWCNTs	116
Figure 4.16	Pyridine FT-IR spectra of sulfonated MWCNTs (A) before and (B) after pyridine adsorption at room temperature	117
Figure 4.17	Possible Lewis acid sites in sulfonated MWCNT catalysts	118
Figure 4.18	Conversion of TBA against reaction time for different reaction temperatures (a molar ratio of ethanol to TBA of 2:1 and a catalyst loading of 3 wt%). The error bars represent the standard deviations (S.D.) of the means	121

Figure 4.19	ETBE selectivity against reaction time for different reaction temperatures (a molar ratio of ethanol to TBA of 2:1 and a catalyst loading of 3 wt%). The error bars represent the standard deviation (S.D.) of the means	122
Figure 4.20	The ETBE yield against reaction time for the different reaction temperatures (a molar ratio of ethanol to TBA of 2:1 and a catalyst loading of 3 wt%). The error bars represent the standard deviations (S.D.) of the means	123
Figure 4.21	Conversion of TBA against reaction time for different molar ratios of ethanol to TBA (the best reaction temperature was 140 °C and a catalyst loading of 3 wt%). The error bars represent the standard deviations (S.D.) of the means	125
Figure 4.22	ETBE selectivity against reaction time for different molar ratios of ethanol to TBA (the best reaction temperature was 140 °C and a catalyst loading of 3 wt%). The error bars represent the standard deviations (S.D.) of the means	126
Figure 4.23	ETBE yield against reaction time for different molar ratios of ethanol to TBA (the best reaction temperature was 140 °C and a catalyst loading of 3 wt%). The error bars represent the standard deviations (S.D.) of the means	127
Figure 4.24	Conversion of TBA against reaction time for different catalyst loadings (the best reaction temperature was 140 °C and the best molar ratio of ethanol to TBA was 2:1). The error bars represent the standard deviations (S.D.) of the means	130
Figure 4.25	ETBE selectivity against reaction time for different catalyst loadings (the best reaction temperature was 140 °C and the best molar ratio of ethanol to TBA was 2:1). The error bars represent the standard deviations (S.D.) of the means	131
Figure 4.26	ETBE yield against reaction time for different catalyst loadings (the best reaction temperature was 140 °C and the best molar ratio of ethanol to TBA was 2:1). The error bars represent the standard deviations (S.D.) of the means	132
Figure 4.27	A comparative plot between experimental conversion of TBA and predicted conversion of TBA for process study	138
Figure 4.28	A comparative plot between experimental selectivity of ETBE and predicted selectivity of ETBE for process study	139
Figure 4.29	A comparative plot between experimental yield of ETBE and predicted yield of ETBE for process study	139

Figure 4.30	Response surfaces for conversion of TBA predicted by the model at 4 h reaction time and catalyst loading of (A) 2 wt% (B) 3 wt% (C) 4 wt%	144
Figure 4.31	Response surfaces for selectivity of ETBE predicted by the model for different levels of reaction temperature and reaction time at 3 wt% catalyst loading and molar ratio of ethanol to TBA of 2.5:1	146
Figure 4.32	Response surfaces for selectivity of ETBE predicted by the model for different levels of reaction temperature and molar ratio of ethanol to TBA at 3 wt% catalyst loading and 4 h reaction	148
Figure 4.33	Response surfaces for selectivity of ETBE predicted by the model for different levels of reaction temperature and catalyst loading at 4 h reaction time and molar ratio of ethanol to TBA of 2.5:1	149
Figure 4.34	Response surfaces for selectivity of ETBE predicted by the model for different levels of reaction time and molar ratio of ethanol to TBA at reaction temperature of 130 °C and 4 wt% catalyst loading	151
Figure 4.35	Response surfaces for selectivity of ETBE predicted by the model for different levels of molar ratio of ethanol to TBA and catalyst loading at reaction temperature of 140 °C and 4 h reaction time	152
Figure 4.36	Response surfaces for yield of ETBE predicted by the model for different levels of reaction temperature and reaction time at molar ratio of ethanol to TBA of 2 and 4 wt% catalyst loading	154
Figure 4.37	Response surfaces for yield of ETBE predicted by the model for different levels of reaction temperature and catalyst loading at 4 h reaction time and molar ratio of ethanol to TBA of 2:1	155
Figure 4.38	Effects of recycling the sulfonated MWCNTs on the conversion of TBA and the ETBE selectivity and yield after 4 h of reaction (at a reaction temperature of 140 °C, molar ratio of ethanol to TBA of 2:1 and a catalyst loading of 3 wt%)	162
Figure 4.39	Effects of sulfonated MWCNTs regeneration on the conversion of TBA and the ETBE selectivity and yield after 4 h of reaction (at a reaction temperature of 140 °C, molar ratio of ethanol to TBA of 2:1 and a catalyst loading of 3 wt%)	163
Figure A.1	A typical GC chromatogram for ETBE sample	

- Figure E.1 Proposed mechanism of sulfonation for generation of Lewis acid sites (Structures A and B)
- Figure F.1 Proposed mechanism of sulfonation for generation of Lewis acid site (Structure C)
- Figure G.1 Proposed mechanism of dehydration of TBA to IB over sulfonated MWCNT catalysts
- Figure H.1 Proposed mechanism for etherification reaction between TBA and ethanol over sulfonated MWCNT catalysts

LIST OF ABBREVIATIONS

$(\text{CH}_3\text{-CO})_2\text{O}$	Acetic anhydride
MWCNT-NH ₂	Amine-functionalized MWCNTs
K	Adsorption equilibrium constants
A-15	Amberlyst-15
A-35	Amberlyst-35
NH ₄ OH	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 ₆ P ₂ W ₁₈ O ₆₂ .27H ₂ O	Diphosphooctadecatungstic acid
DOE	Design of experiment
DSC	Differential scanning calorimetry
DMF	Dimethylformamide
DWCNTs	Double-walled carbon nanotubes
ETBE	Ethyl <i>tert</i> -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 ₂ O 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 <i>tert</i> -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 ₂ O	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 ₂ SO ₄	Sulfuric acid
TBA	<i>tert</i> -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 ₂ O	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
ΔH°	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
D_i	Transport coefficient of component i
D_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
p_{i0}	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 dituliskan 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 pembolehkan 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 °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/m²·j dan faktor pemisahan lebih kurang 400 telah diperolehi.

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BUCKYPAPER MEMBRANES AND CATALYSTS FOR ETHERIFICATION
REACTION**

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