PERVAPORATION FOR BIOFUEL REFINING: MULTICOMPONENT PERMEATION AND COUPLING EFFECTS IN ACETONE-BUTANOL-ETHANOL SOLUTIONS

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by

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Submitted

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Dedicated to my loving family.

To my parents and grandparents,

and to my brother and sister-in-law;

Thank you for believing in me.

Declaration

This is to certify that the thesis titled **"Pervaporation for Biofuel Refining: Multicomponent Permeation and Coupling Effects in Acetone-Butanol-Ethanol Solutions"** has been authored by me. It presents the research conducted by me under the supervision of **Dr. Sharad Kumar Gupta** and **Dr. Rajesh Khanna**. To the best of my knowledge, it is an original work, both in terms of research content and narrative, and has not been submitted elsewhere, in part or in full, for a degree. Further, due credit has been attributed to the relevant state-of-the-art and collaborations (if any) with appropriate citations and acknowledgements, in line with established norms and practices.

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Certificate

This is to certify that the thesis entitled **"Pervaporation for Biofuel Refining: Multicomponent Permeation and Coupling Effects in Acetone-Butanol-Ethanol Solutions"**, submitted by **Abeer Mushtaq Mutto** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a bonafide record of original research work carried out by her under our supervision in conformity with rules and regulations of the institute.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of our knowledge.

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"Fear wist not to evade, as Love wist to pursue"
-The Hound of Heaven, Francis Thompson

In the name of the Almighty, the most beneficent, the most merciful.
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(Abeer Mushtaq Mutto)

that which we are, we are;
One equal temper of heroic hearts,
Made weak by time and fate,
but strong in will
To strive, to seek, to find,
and not to yield.

Ulysses,
Alfred Lord Tennyson

Abstract

The nascent field of biofuels derived from renewable lignocellulosic resources offers a promising solution to the finite supply of fossil fuels and the ensuing climatic, economic and political challenges. However, aspirations of large scale and scalable biorefining of bio-butanol from multicomponent Acetone-Butanol-Ethanol (ABE) fermentation broths through organophilic pervaporation are still challenged, in part, by a limited knowledge on the effect of by-products ethanol and acetone on final recovery. This study, therefore, involves experimental investigations on multicomponent permeation in pervaporation followed by the modeling and quantification of the impact of coupling phenomena on the selective transport of butanol via a diverse portfolio of semi-empirical, statistical, and theoretical frameworks. Equilibrium sorption, pure and mixture permeation experiments were conducted using a commercial polydimethylsiloxane (PDMS) membrane (PERVAP-4060) with individual solvent content $\leq 6wt.\%$ over a temperature range of 303.15–323.15 K, relevant to fermentation processes.

Initially, modified solution-diffusion models are customized to emulate temperature and concentration dependence of permeation in binary and ternary feed mixtures. After initial screening of thermodynamic models and simulation of activity coefficients and volume fractions, a rationally designed experimental and statistically validated empirical investigation of sorption characteristics and the influence of coupling on fluxes in quaternary ABE mixtures using sorption and flux isotherms is followed. Finally, Maxwell-Stefan (MS) diffusion formulations, combined with the UNIQUAC thermodynamic model, are extended to multicomponent ABE feed solutions to resolve coupling into its thermodynamic and kinetic (diffusive) constituents. A generalized and explicit analytical derivation for calculation of

thermodynamic correction factors by UNIQUAC model is proposed, allowing estimation for any number of permeants.

The membrane is observed to be most intrinsically selective towards butanol in all systems and compositions. However, coupling effects were observed to limit permeation, especially at higher solvent concentrations. Analysis of phenomenological parameters reveal that while the additional plasticization by other penetrants benefit butanol permeation, their presence also induced a reduction in the free volume expansion by butanol itself. Furthermore, though sorption isotherms reveal that butanol volume fractions in the membrane remain unaffected by feed composition, flux isotherms also reaffirm that the positive coupling due to additional plasticization decreases at higher solvent concentrations, suggesting other physical associations or cluster formation between penetrants to be the causative factor. Subsequently, a detailed hit-and-trial based strategy is implemented to evaluate the relevance of membrane plasticization, cluster formation and interspecies frictional interactions on effective diffusivities. The optimal model fit is found to be insensitive to variation in MS cross-diffusivities, affirming the trivial contribution of correlation effects between penetrants, provided the expressions for self-diffusivities are adequately tailored for membrane plasticization and clustering. Notably, while only butanol clustering suffices for binary mixtures, additional aggregates involving butanol-water, water-water, and butanol-acetone/ethanol are suggested to play a crucial role in steering diffusivities in ternary solutions.

Overall, by a careful manipulation of solvent ratios – for instance at lower butanol to second component ratios in feed; multicomponent coupling effects were demonstrated to significantly enhance butanol permeances through the polymeric membranes, achieving nearly twice the values observed in binary systems. In contrast, minimal coupling is experienced

at equimolar conditions, allowing multicomponent pervaporation to be satisfactorily modeled as binary separation in such limiting cases. Additionally, the modelling of quaternary ABE fermentation solutions was also simplified to ternary mixtures by showing that mutual interactions between acetone and ethanol have minimal impact on butanol transport utilizing Response Surface Methodology based statistical analysis. Furthermore, a deeper understanding of the physico-chemical origins of coupling effects was achieved, particularly the synergy between membrane plasticization and kinetic coupling mechanisms. These insights can guide the development of superior energy-efficient membrane materials with improved diffusivity and sorption selectivities by optimizing the free-volume-diffusivity paradigms for enhanced targeted recovery from complex industrial feed mixtures.

सारांश

पेट्रोलियम ईंधन की सीमित आपूर्ति और इससे जुड़ी जलवायु, आर्थिक और राजनीतिक चुनौतियों के समाधान के लिए, नवीकरणीय लिग्नोसेल्यूलोसिक संसाधनों से प्राप्त जैव-ईंधन एक आशाजनक विकल्प के रूप में उभर रहा है। हालांकि, बहु-घटक एसीटोन-ब्यूटानॉल-इथेनॉल (ABE) किण्वन मिश्रण से जैव-ब्यूटानॉल के बड़े पैमाने पर और स्केलेबल जैव-रिफाइनिंग को ऑर्गनोफिलिक मेम्ब्रेन पर्वेपोरेशन के माध्यम से प्राप्त करने की महत्वाकांक्षा अभी भी चुनौतियों का सामना कर रही है, जिसमें आंशिक रूप से सह-उत्पाद इथेनॉल और एसीटोन के अंतिम पुनर्प्राप्ति पर प्रभाव के बारे में सीमित जानकारी है। इस अध्ययन में, पर्वेपोरेशन में बहु-घटक पारगमन पर प्रयोगात्मक जांच और अर्ध-अनुभवजन्य, सांख्यिकीय और सैद्धांतिक ढांचों के विविध संग्रह के माध्यम से युग्मन (coupling) घटनाओं के चयनात्मक ब्यूटानॉल परिवहन पर प्रभाव के प्रतिरूपण और परिमाणन को शामिल किया गया है। शुद्ध और मिश्रण सॉर्प्शन और फ्लक्स प्रयोगों को वाणिज्यिक पॉलीडाइमिथाइलसिलोक्सेन (PDMS) मेम्ब्रेन (PERVAP-4060) का उपयोग करके 303.15–323.15 K के तापमान पर और ≤6 वज़न प्रतिशत विलायक सामग्री के साथ किया गया।

शुरुआत में, संशोधित सॉल्यूशन-डिफ्यूजन (solution-diffusion) मॉडल को बाइनरी और टर्नरी फीड मिश्रणों में पारगम्यता के तापमान और सांद्रता पर निर्भरता को प्रदर्शित करने के लिए अनुकूलित किया गया। थर्मोडायनामिक मॉडल्स की प्रारंभिक जांच और एक्टिविटी गुणांक तथा वॉल्यूम फ्रैक्शन का अनुकरण करने के बाद, एक तार्किक रूप से डिज़ाइन किया गया प्रयोगात्मक और सांख्यिकीय रूप से मान्य अनुभवजन्य अध्ययन किया गया, जिसमें सोखने की विशेषताओं और चतुर्धातुक ABE मिश्रणों में फ्लक्स पर युग्मन के प्रभाव को सोखने और फ्लक्स आइसोथर्म (के माध्यम से परखा गया। अंततः, मैक्सवेल-स्टेफन (Maxwell-Stefan) डिफ्यूजन सूत्रों को UNIQUAC थर्मोडायनामिक मॉडल के साथ मिलाकर बहु-घटक ABE फीड समाधानों में विस्तारित किया गया, जिससे युग्मन को थर्मोडायनामिक और गतिज (kinetic) घटकों में विभाजित किया जा सके। UNIQUAC मॉडल द्वारा थर्मोडायनामिक करेक्शन फैक्टर की गणना के लिए एक सामान्य और स्पष्ट विश्लेषणात्मक व्युत्पत्ति प्रस्तावित की गई, जो किसी भी संख्या के विलायक का अनुमान लगाने की अनुमति देती है।

मेम्ब्रेन को सभी प्रणालियों और संघटनों में ब्यूटानॉल के प्रति सबसे अधिक आंतरिक रूप से चयनात्मक पाया गया। हालांकि, युग्मन प्रभाव ने विशेष रूप से उच्च सॉल्वेंट सांद्रता पर पारगम्यता को सीमित कर दिया। प्रकट परिघटनात्मक मानकों के विश्लेषण से पता चला कि अन्य प्रवेशकों द्वारा अतिरिक्त प्लास्टिसाइज़ेशन ने ब्यूटानॉल पारगम्यता को लाभ पहुंचाया, लेकिन उनकी उपस्थिति ने ब्यूटानॉल द्वारा मुक्त आयतन (free volume) के विस्तार को भी कम कर दिया। इसके अलावा, यद्यपि सोखने की आइसोथर्म यह दर्शाती हैं कि मेम्ब्रेन में ब्यूटानॉल का आयतन अंश फीड संघटन से अप्रभावित रहता है, फ्लक्स आइसोथर्म भी यह पुनः पुष्टि करती हैं कि अतिरिक्त प्लास्टिसाइज़ेशन के कारण सकारात्मक युग्मन उच्च सॉल्वेंट सांद्रता पर घट जाता है, जो प्रवेशकों के बीच अन्य भौतिक संघों या क्लस्टर निर्माण को इसका संभावित कारण बताता है। इसके बाद, प्रभावी विसरणशीलता पर मेम्ब्रेन प्लास्टिसाइज़ेशन, क्लस्टर निर्माण और प्रजातियों के बीच घर्षणीय अंतःक्रियाओं की प्रासंगिकता का मूल्यांकन करने के लिए एक विस्तृत हिट-एंड-ट्रायल रणनीति लागू की गई। आदर्श मॉडल फिट को MS क्रॉस-डिफ्यूजिविटी में बदलाव के प्रति असंवेदनशील पाया गया, यह पुष्टि करते हुए कि प्रवेशकों के बीच सहसंबंधीय प्रभाव का योगदान नगण्य है, बशर्ते कि आत्म-विसरणशीलता के लिए अभिव्यक्तियों को मेम्ब्रेन प्लास्टिसाइज़ेशन और क्लस्टरिंग के लिए ठीक से तैयार किया गया हो। विशेष रूप से, जबकि केवल ब्यूटानॉल क्लस्टरिंग बाइनरी मिश्रणों के लिए पर्याप्त है, ब्यूटानॉल-पानी, पानी-पानी, और ब्यूटानॉल-एसीटोन/एथेनॉल को शामिल करने वाले अतिरिक्त समुच्चय टर्नरी समाधान में विसरणशीलता को नियंत्रित करने में महत्वपूर्ण भूमिका निभाते हैं।

कुल मिलाकर, सॉल्वेंट अनुपात में सावधानीपूर्वक हेरफेर द्वारा — जैसे कि फीड में ब्यूटानॉल और दूसरे घटक के कम अनुपात पर — बहु-घटक युग्मन प्रभावों ने पॉलीमेरिक मेम्ब्रेन के माध्यम से ब्यूटानॉल की पारगम्यता को उल्लेखनीय रूप से बढ़ाया, जिससे बाइनरी सिस्टम की तुलना में लगभग दो गुना अधिक मूल्य प्राप्त हुआ। इसके विपरीत, सममोलर स्थितियों में न्यूनतम युग्मन देखा गया, जिससे ऐसे सीमित मामलों में बहु-घटक परवपरेशन को बाइनरी पृथक्करण के रूप में संतोषजनक ढंग से मॉडल किया जा सका। इसके अतिरिक्त, क्वाटरनरी ABE किण्वन समाधान का मॉडलिंग टर्नरी मिश्रणों तक सरलीकृत किया गया, यह दर्शाते हुए कि एसीटोन और एथेनॉल के बीच पारस्परिक अंतःक्रियाओं का ब्यूटानॉल परिवहन पर न्यूनतम प्रभाव पड़ता है। इस सरलीकरण के लिए प्रतिक्रिया सतह पद्धति (Response Surface Methodology) आधारित सांख्यिकीय विश्लेषण का उपयोग किया गया। इसके अलावा, युग्मन प्रभावों की भौतिक-रासायनिक उत्पत्ति की एक गहन समझ प्राप्त की गई, विशेष रूप से मेम्ब्रेन प्लास्टिसाइज़ेशन और

गतिज युग्मन तंत्र के बीच तालमेल पर। इन जानकारियों से अधिक ऊर्जा-कुशल मेम्ब्रेन के विकास में मार्गदर्शन मिल सकता है, जिनमें प्रसारशीलता और सोखने की चयनात्मकता में सुधार किया जा सकता है, ताकि जटिल औद्योगिक फीड मिश्रणों से लक्षित पुनर्प्राप्ति को बढ़ावा दिया जा सके।

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Abbreviations

A or AcO	**A**cetone
B or BuOH	**B**utanol
E or EtOH	**E**thanol
W	**W**ater
VLE	**V**apor-**L**iquid **E**quilibrium
PDMS	**P**oly(**dim**ethyl**s**iloxane)
OVAT	**O**ne **V**ariable at a **T**ime
DOE	**D**esign of **E**xperiment
RSM	**R**esponse **S**urface **M**ethodology
HSP	**H**ansen **S**olubility **P**arameter
MS	**M**axwell-**S**tefan
FID	**F**lame **I**onization **D**etector
C-CCD	**C**ircumscribed **C**entral **C**omposite **D**esign
GA	**G**enetic **A**lgorithm
RMSE	**R**oot **M**ean **S**quared **E**rror
rRMSE	**r**elative **R**oot **M**ean **S**quared **E**rror
MAPE	**M**ean **A**bsolute **P**ercentage **E**rror
ANOVA	**A**nalysis of **N**ariance
adj	**A**djoint of matrix
det	**D**eterminant of matrix

Symbols

A_{ij}	**Adjustable parameter** between the $\boldsymbol{i}^{th}$ and $\boldsymbol{j}^{th}$ component
a_{ij}	**Adjustable parameter** between the i^{th} and j^{th} component
$\mathbf{a_{CP}}$	**Boundary layer parameter** (m^{-1})
$\dot{\mathbf{a}}$	**Activity**
Ar	**Area of membrane** (m^2)
α	**Intrinsic selectivity**
η	**Viscosity** (Pa s)
β	**Separation factor**
b_{ij}	**Adjustable parameter** between the $\boldsymbol{i}^{th}$ and $\boldsymbol{j}^{th}$ component
$\mathbf{b_{CP}}$	**Boundary layer parameter**
$C_i(x_i)$	**Coupling factor** for component i at concentration x_i
χ	**Empirical coefficient** in regression equation
δ	**Thickness of membrane active layer** (m)
Δ_d	**Dispersion solubility parameter** ($MPa^{1/2}$)
Δ_h	**Hydrogen-bonding solubility parameter** ($MPa^{1/2}$)
Δ_p	**Polar solubility parameter** ($MPa^{1/2}$)
D	**Diffusivity** (m^2/s)
d	**Semi cell thickness** at the edge of test cell (m)
D.f	**Driving force**
E_D	**Activation energy of diffusivity** (kJ mol^{-1})
E_γ	**Coefficient in Clausius Clapeyron equation** (kJ mol^{-1})
E_{evap}	**Energy of evaporation** (kJ mol^{-1})
E_p	**Activation energy of permeation of component i** (kJ mol^{-1})

E_{pv} **Activation energy of pervaporation** (kJ mol^{-1})

E_S **Activation energy of solubility** (kJ mol^{-1})

ϵ **Semiempirical plasticization coefficient**

ε **Tolerance for error**

f^{sat} **Fugacity at saturation pressure**

f^v **Fugacity of vapor phase**

$\mathbf{f}_i$ **Fugacity coefficient**

G_{ij} **Interaction parameter** between the ith and the jth component

Γ **Thermodynamic correction factor matrix**

I **Polarization Index**

J **Molar diffusive flux** (mol $m^{-2}s^{-1}$)

j **Mass flux** (kg $m^{-2}s^{-1}$)

k_l **Mass transfer coefficient** in the liquid side boundary layer (m/s)

K **Overall permeance coefficient** (mol m^{-2} Pa^{-1} s^{-1})

K_l **Liquid boundary layer permeance coefficient** (mol m^{-2} Pa^{-1} s^{-1})

K_m **Membrane permeance coefficient** (mol m^{-2} Pa^{-1} s^{-1})

κ_{ij} **Non-randomness parameter** between the **i**th and **j**th component

μ **Chemical potential**

M **Molecular weight** (mol kg^{-1})

$\bar{V}$ **Partial molar volume** (m^3/mol)

N_c **Number of components** in the liquid feed mixture

N_e **Total number of experimental data points**

N^V **Volumetric flux** (m^3/ m^2s)

P **Pressure in permeate channel** (Pa)

P^{sat} **Vapor pressure of component** (Pa)

q **Area/Surface parameter** of pure component

r **Volume parameter** of pure component

R **Gas constant** (J mol^{-1} K^{-1})

R^2 **Coefficient of Determination**

R^2_{adj} **Adjusted coefficient of Determination**

Re_R **Reynolds number** at the cell edge

ρ	**Mass density** (kg/m^3)
ρ^{mol}	**Molar density** (mol/m^3)
S	**Degree of swelling**
$\mathcal{S}$	**Solubility coefficient** (mol m^{-3} Pa^{-1})
Sc	**Schmidt Number**
t	**Time** (s)
τ_{ij}	**Interaction parameter** between the $\mathbf{i}^{th}$ and the $\mathbf{j}^{th}$ component
θ	**Area fraction**
u	**Velocity of/in feed stream** (m s^{-1})
U	**Uncoded Variable**
V^L	**Liquid phase molar volume** (m^3/mol)
w	**Weight fraction**
W	**Weight** (kg)
X	**Coded Variable** in **RSM**
x	**Mole fraction in liquid feed**
y	**Mole fraction in permeate**
Y	**Response Variable** in **RSM**
Z	**Coordination number**
z	**Axial coordinate along thickness of the membrane** (m)
ω	**Distance of star points** from the central point in **RSM**
ξ	**Clustering constant**
[B]	**Diffusional matrix** in **MS** formulations (s/m^2)
$[\mathrm{B}]^{-1}$	**Inverse diffusional matrix** (m^2/s)
$Đ_{ij}$	**MS cross-diffusivity** (m^2/s)
$Đ_{ij}^V$	**Modified MS cross-diffusivity** (m^2/s)
$Đ_{im}^V$	**MS self-diffusivity** (m^2/s)

Subscripts

i, j, k	Component i, j, k in the mixture
m	Membrane
dry	In dry membrane
wet	In wetted swollen membrane
tot	Total components
b	Butanol
e	Ethanol
a	Acetone
w	Water
exp	Experimental reading
theo	Model prediction
bulk	Bulk liquid in feed stream
l	Liquid component
s	Organic solvent
p	Permeate
0	At the upstream (feed side) interface of the membrane
δ	At the downstream (vacuum side) interface of the membrane

Superscripts

o	For pre-exponential factors
f	In liquid feed phase
m	In membrane phase
cen	Denotes central point of the design matrix
C	Depicts combinatorial term
R	Depicts Residual term
$'$	Depicts Modified parameters for UNIQUAC-HB
exp	Experimental reading
cal	Model calculation
$^{-}$	Averaged quantity
$\sim$	For pre-exponential factors
$`$	Considering water as a plasticizing component
tern	In ternary mixtures
bin	In binary mixtures
-1	Inverse of the matrix
con	Conjoint of the matrix
T	Transpose of the matrix

Outline of Thesis

A concise overview of the organization of the dissertation is outlined as follows:

Chapter 1: Introduces the research problem of this thesis, focusing on the advantages and challenges associated with adapting pervaporation for biorefining of multicomponent fermentation systems. It emphasizes the potential of organophilic pervaporation for biobutanol recovery while providing a general theoretical background to familiarize the reader with the basic concepts related to pervaporation and multicomponent coupling phenomena.

Chapter 2: An exhaustive literature review is presented regarding the nature of coupling phenomena and multicomponent permeation in pervaporation of ABE solutions. The choice for membrane selection is justified. A detailed review of the established modeling techniques for multicomponent pervaporation is also included underlining the scope and drawbacks of each. The rationale and motivation for defining objectives of research is developed based on the gaps highlighted in literature.

Chapter 3: Provides an elaborate description of the experimental methodology and model solution techniques used in the present study. The experimental design, analytical techniques, and membrane performance evaluation metrics are presented, along with the methods for parameter estimation, model solution, and validation.

Chapters 4 to 6 sequentially present the results and discussion part of this study.

Chapter 4 : Membrane permeation in binary and ternary ABE solutions is studied to describe and isolate the effect of added acetone and ethanol on transport of butanol

through the membrane . Modified solution diffusion models are developed to gain insights into the nature and magnitude of coupling effect at different operating conditions.

Chapter 5 : Sorption characteristics and influence of thermodynamic coupling effects on butanol permeation in quaternary ABE solutions are studied. Various local composition thermodynamic models and statistically validated regression models are developed to uncover significance of interaction effects and sorption on final butanol fluxes in quaternary mixtures.

Chapter 6 : The nature and origin of coupling phenomena is investigated . The resolution of thermodynamic and kinetic coupling effects is aided by the exhaustive analysis of Maxwell-Stefan formulations and MS diffusivities derived for multicomponent systems. The role of diffusive or kinetic coupling on permeation of butanol is addressed.

Chapter 7: Overall conclusions from this work are summarized , highlighting its limitations. Recommendations are provided for future research.