DEVELOPMENT OF WATER ADSORBENT FROM SPENT BLEACHING EARTH FOR DEHYDRATION OF AZEOTROPE ETHANOL-WATER MIXTURE

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SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy in Chemical Engineering.

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STUDENT’S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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MAY 2017

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Professor Dato' Dr. Rosli bin Mohd Yunus and Professor Dr. Abdurrahman Hamid Nour for his invaluable assistance and guidance, constant dedication as well as endless encouragement throughout my study at Universiti Malaysia Pahang (UMP).

I am also thankful to technical staffs of Faculty of Chemical Engineering and Natural Resources, UMP and for their helping hands and co-operations. My humble regards to others whose names are not mentioned here for their munificence and assistance.

Deep thanks and appreciation are extended to management of TATI University College for moral and financial support through out this study. Deep thanks and appreciation also to all of my friends and colleagues in TATI University College especially in Faculty of Chemical Engineering Technology for their unfailing friendship and unselfish moral and materials support directly or indirectly to complete this study.

To my beloved parents, my wife and children, deep thanks to them for their support, undying love and prayers.

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LIST OF SYMBOLS

Ad%	Single metal ion adsorption percentage
Ad_{tot}%	The total metal ion adsorption percentage
b	Sorption energy related to monolayer adsorption
B	Temkin constant
d_p	Mean pore size diameter
c	Outlet adsorbate concentration
c_e	Adsorbate concentration in equilibrium
c_F	Inlet concentration to adsorbent bed
C	Concentration of water after adsorption process
C_{ads}	Amount of solute adsorbed per mass of adsorbent
C_b	Concentration of adsorbate at the outlet of the bed
C_e	Equilibrium concentration
C_i	Initial concentration or concentration of adsorbate into the bed
C_o	Initial concentration
C_f	Final concentration
$C_{Ca}(0)$	Calcium ion concentration before phase separation
$C_{Ca}(t)$	Calcium ion concentration after phase separation
ΔH_{ads}	Heat of adsorption
ε_b	Bed void fraction
ε	DKR isotherm constant
k_c	Correction factor for Yoon and Nelson model
K_{ad}	DKR isotherm constant
K	Freundlich constant related to operating temperaturel
K	Adsorption equilibrium constant in Klinkenberg model
K_F	Freundlich constant
K_L	Langmuir constant
K_T	Temkin constant
k	Overall mass transfer coefficient
k’	Rate constant for Yoon and Nelson model
Γ_{Ca}	Calcium exchange capacity
M	Molecular weight
M_{CaO}	Molecular mass of calcium oxide
n	Freundlich constant
N	Constant for adsorption system for Freundlich model
P	Pressure
P_o	Initial pressure
Q	Langmuir constant
q_e	adsorption capacity per mass of the adsorbent in equilibrium
q_s	theoretical isotherm saturation capacity
S_{BET}	Total surface area using BET method
t	Sampling time
τ	Dimensionless time in Klinkenberg model
τ	Dehydration time at 50% (i.e $C_b/2$) in Yoon and Nelson model
2Θ	X-ray diffractogram angle
u	Superficial velocity
V	Sample volume
V_a	Aqueous phase volume

V_{micro}	Micropore volume
V_{tot}	Total pore volume
W_{ads}	Weight of adsorbent in the vial
W_{eth}	Weight of ethanol injected into vial
ξ	Dimensionless bed lenght
z	The bed height

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
BET	Brunauer-Emmet-Teller
BFA	Bagasse fly ash
BJH	Barret-Joyner-Halenda
CBC	Calcium Binding Capacity
CEC	Cation Exchange Capacity
DKR	Dubinin-Kaganer-Radushkevich
DOE	Design of Experiment
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
EDXS	Energy Dispersive X-ray Spectroscopy
FAU	Faujasite
FESEM	Field Emission Scanning Electron Microscopy
FIST	Faculty of Industrial Science and Technology
FTIR	Fourier Transformed Infrared
HSFA	High Silicon Fly Ash
ICDD	International Committee of Diffraction Data
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Llasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
IR	Infrared
IZA	International Zeolite Association
JCPDS	Joint Committee on Powder Diffraction Standards
KOH	Kalium Hydroxide
LTA	Linde Type A
MFI	Zeolite ZSM-5
MPOB	Malaysia Palm Oil Board
MOR	Mordenite
OVAT	One-Variable-At-a Time
PAL	Palygorskite
PEG	Polyethylene Glycol
PSA	Pressure Swing Adsorption
PTFE	Polytetrafluoroethylene
RBD	Refined, Bleached and Deodorized
SBE	Spent Bleaching Earth
SEM	Scanning Electron Microscopy
SC	Scanning Calorimetry
TGA	Thermogravimetric Analysis
UMP	Universiti Malaysia Pahang
UV	Ultraviolet
XRD	X-ray Diffractromery
XRF	X-ray Fluororescence
ZSM-5	Zeolite-Socony-Mobile-5

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ABSTRAK

SBE adalah bahan buangan dari loji penapisan minyak sawit dan kebiasannya di buang ke tapak pelupusan sampah. Etanol adalah bahan api alternatif dan mesti kering sebelum boleh digunakan dalam enjin petrol. Dalam kajian ini, penjerap air untuk penulinan campuran azeotrop etanol-air dihasilkan dari SBE mengunakan kaedah pelakuran terubahsuai. Pencirian penjerap air yang terhasil dilakukan menggunakan teknik XRD, FESEM-EDX, ICP-MS dan penganalisa luas permukaan dan keporosan bahan. Enam pembolehubah atau faktor (i.e. penambahan alumina, masa penuaan, suhu penuaan, penambahan KOH, penambahan air dan suhu pelakuran) mempengaruhi penjerapan air dikaji menggunakan teknik OVAT dan teknik faktor penuh berbilang aras DOE yang lebih berstruktur. Akhirnya, kedua-dua penjerap air yang dihasilkan dari SBE dan komersial di gunakan untuk penulinan campuran azeotrop ethanol air menggunakan radas penjerapan skala meja. Analisa XRD menunjukkan penjerap air yang dihasilkan dari SBE bukan dari jenis zeolit A. Walaubagaimanapun imej SEM, menunjukkan bahawa penjerap air tersebut terdiri dari beberapa fasa seperti zeolit A, X, MFI dan fasa amorfos. Tiada hubungkait diperhatikan dari keputusan analisa luas permukaan dan keporosan terhadap penjerapan air bahan penjerap tersebut. Menggunakan teknik OVAT, di dapati bahawa penambahan alumina terbaik adalah pada 80 g/g bahan, masa penuaan 5 hari, suhu penuaan 80^{o}C, penambahan KOH adalah 71% berat bahan, suhu pelakuran 550^{o}C dan penambahan air pada 65% berat bahan terlakur. Analisa varian teknik DOE menunjukkan kesan utama penambahan alumina, penambahan air, suhu pelakuran dan masa penuaan adalah signifikan. Kesan dua hala suhu pelakuran-suhu penuaan dan suhu pelakuran-suhu penuaan juga di dapati signifikan. Kombinasi pembolehubah terbaik adalah pada suhu pelakuran 550^{o}C, suhu penuaan 80^{o}C, masa penuaan 3 hari, penambahan air 65% wt, penambahan KOH 56% berat bahan dan penambahan alumina 80 g/g bahan. Jangkaan air yang diserap adalah 0.0343 g air/g penjerap. Model Yoon dan Nelson di dapati sesuai digunakan untuk data eksperimen lengkung dehidrasi kedua-dua bahan penjerap, untuk penganggaran masa terobos. Dianggarkan bahan penjerap dari SBE mempunyai keupayaan lebih kurang 66% keupayaan penjerap komersil dari segi masa terobos. Kajian ini menunjukkan penjerap berkos murah boleh dihasilkan dari SBE menggunakan kaedah pelakuran terubah suai dan berupaya untuk mengeringkan campuran etanol-air dengan ketulinan lebih 99% berat ethanol untuk digunakan sebagai bahan api bio di dalam enjin petrol.

ABSTRACT

SBE is a waste from palm oil refinery it is normally dumped into landfill. Ethanol is an alternative fuel and it must be anhydrous to be used in petrol driven engine. In this study, water adsorbent to dehydrate the azeotrope mixture of ethanol-water was synthesised from SBE using modified fusion method. The synthesised water adsorbent was characterized using XRD, FESEM-EDX, ICP-MS and surface area and porosity analyser. Six variables or factors (i.e. added alumina, aging time, aging temperature, added KOH, added water and fusion temperature) affecting the water-uptake were studied using OVAT technique followed by structured full multilevel factorial DOE method. Lastly, the synthesised and commercial water adsorbent was used to dehydrate azeotrope mixture of ethanol-water in bench top adsorption apparatus to produce dehydrated ethanol. XRD analysis showed that the water adsorbent was not the type of zeolite A. However from SEM images, it was believed that the water adsorbent consist of several types of phases such as zeolite A, X, MFI plus amorphous phase. No relationship was found between results from surface area and porosity experiments to the water-uptake capacity of the water adsorbent. Using OVAT technique, the best added alumina was found to be 80 g/100 g material, aging time of 5 days, aging temperature of 80^{o}C, added KOH of 71% of material mass, fusion temperature was 550^{o}C and the best added water was 65% of the weight of ground fused material. Analysis of variant of the DOE technique showed that the main effects of added alumina, added water, fusion temperature and aging time were significant. There were two way interaction effects between fusion temperature and aging temperature, and between fusion temperature and aging time. The best variables combinations were at fusion temperature of 550^{o}C, 80^{o}C aging temperature, 3 days of aging time, added water 65% wt, added KOH 56% of material mass and added alumina 80 g alumina/g material, with the expected water-uptake of 0.0343 g H_2O/g adsorbent. Yoon and Nelson model can be used to model the experimental dehydration curve for prediction of breakthrough time. The performance of synthesised water adsorbent was approximately 66% of the commercial water adsorbent in terms of breakthrough time. This study showed that low cost water adsorbent can be produced from spent bleaching earth using modified fusion method and was able to dehydrate ethanol-water mixture more than 99% weight ethanol to be used as bio-fuel in petrol driven engine.

REFERENCES

Abdul Mudalip S.K. 2007. *Effects of Ultrasonic Waves On Vapor Liquid Equilibrium (VLE) of Normal And Azetropic Mixtures*. Master Thesis. Universiti Teknologi Malaysia, Malaysia.

Abd Wafti N.S., Kien Yew C., Shean Yaw T.C and Abdullah L.C. 2011. Regeneration and Characterization of Spent Bleaching Clay. *Journal of Palm Oil Research.* 23: 999-1004.

Anuwattana R. and Khummongkol P. 2009. Conventional Hydrothermal Synthesis of Na-A Zeolite From Cupola Slag and Aluminum Sludge. *Journal of Hazardous Materials.* 166: 227-232.

Al-Asheh S., Banat F. and Al Lagtah, N. 2004. Separation of Ethanol-Water Mixtures Using Molecular Sieves and Biobased Adsorbents. *Chemical Engineering Research and Design.* 82(A7): 855-864.

Ali I., Asim M. and Khan T.A. 2012. Low Cost Adsorbents for the Removal of Organic Pollutants from Wastewater. *Journal of Environmental Management.* 113: 170-183.

Ayele L., Perez-Pariente J., Chebude Y. and Diaz I. 2015. Synthesis of Zeolite A from Ethiopian Kaolin. *Microporous and Mesoporous Materials.* 215: 29-36.

Barcena-Uribarri I., Thein M., Maier E., Bonde M., Bergstrom S. and Benz R. 2013. Use of Nonelectrolytes Reveals The Channel Size and Oligomeric Constitution of The Borrelia Burgdorfer P66 Porin (online). *PloS ONE.* 9(8). http:/www.journal.plos.org./plosone/article/?id=10.1371/journal.pone.00078272

Belviso C., Cavalcante F. and Fiore S. 2010. Synthesis of Zeolite From Italian Coal Fly Ash: Differences in Crystallization Temperature Using Seawater Instead of Distilled Water. *Waste Management.* 30: 839-847.

Bjorgen M., Joensen F., Holm M.S., Olsbye U., Lillerud K.P. and Svelle S. 2008. Methanol to Gasoline Over H-ZSM-5 Catalyst: Improved Catalyst Performance Bt Treatment With NaOH. *Applied Catalyst A: General.* 345: 43-50.

Boey P.L., Saleh M.I., Sapawe N., Ganesan S., Maniam G. P. and Hag Ali D.M. 2011. Pyrolysis of Residual Palm Oil in Spent Bleaching Clay by Modified Tubular Furnace and Analysis of the Products by GC-MS. *Journal of Analytical and Applied Pyrolisis.* 91: 199-204.

Bolto B., Hoang M. and Xie Zongli. 2011. A Review of Membrane Selection For The Dehydration of Aqueous Ethanol By Pervaporation. *Chemical Engineering & Processing: Process Intensification.* 50: 227- 235.

Buasri A., Chaiyut N., Phattarasirichot K., Yongbut P. and Nammueng L. 2008. *Chiang Mai Journal of Science.* 35(3): 447-456.

Burrichter B., Pasel C., Luckas M. and Bathen D. 2014. Parameter Study On The Drying of Isopropanol in a Fixed Bed Adsorber. *Separation and Purification Technology*. 132: 736 – 743.

Calinescu I., Sarbu E. and Trifan A. Regeneration of 3A Molecular Sieves, Conventional vs Microwave Heating. *Revista de Chemie*. 64(10): 1146-1150

Chang H., Yuan X., Tian H. and Zeng A. 2006. Experiment and Prediction of Breakthrough Curves for Packed Bed Adsorption of Water Vapor on Cornmeal. *Chemical Engineering and Processing.* 45: 747-754

Chareonpanich M., Jullaphan O. and Tang C. 2011. Bench Scale Synthesis of Zeolite A From Subbituminous Coal Ashes With High Crystalline Silica Content. *Journal of Cleaner Production.* 19: 58-63.

Chen J., Spear S.K., Huddleston J.G. and Rogers R.D. 2004. Polyethylene Glycol and Solutions of Polyethylene Glycol as Green Reaction Media. *Green Chemistry.* 7: 64-82.

Cho K., Ryoo R., Asahina S., Xioa C., Klingstedt M., Umemura A., Anderson M.W. and Terasaki O. 2011. Mesopore Generation By Organosilane Surfactant During LTA Zeolite Crystallization Investigated by High Resolution SEM and Monte Carlo Simulation. *Solid State Science.* 13: 750-756

Diaz I., Kokkoli E., Terasaki O and Tsapatsis M. 2004. Surface Structure Of Zeolite (MFI) Crystals. *Chemical Material*. 16: 5226-5232.

Diaz J.C., Gil-Chavez I.D., Giraldo L. and Moreno-Pirajan J.C. 2010. Separation of Ethanol-Water Mixture Using Type-A Zeolite Molecular Sieve. *E-Journal of Chemistry*. 7 (2): 483-485.

Egeblad K., Kustova M., Klitgaard K.S., Zhu K. and Christensen C.H. 2007. Mesoporous Zeolite and Zeotype Single Crystals Synthesized In Fluoride Media. *Microporous and Mesoporous Materials.* 101: 214-223.

Endres R., Drave H., Mansmann M. and Puppe L. 1981. Process For The Preparation of Zeolite A From Kaolin. *United States Patent 4271130.*

Esmaeli A. and Saremnia B. 2016. Synthesis and Characterization of NaA Zeolite Nanoparticles From *Hordeum vulgare L.* Husk For The Separation of Total Petroleum Hydrocarbon by An Adsorption Process. *Journal of The Taiwan Institute of Chemical Engineers.* 61: 276-268.

Figueroa J.J., Hoss Lunelli B., Maciel Filho R. and Wolf Maciel M.R. 2012. Improvement on Anhydrous Ethanol Production By Extractive Distillation Using Ionic Liquid As Solvent. *Procedia Engineering.* 42: 1016-1026.

Foletto E.L., Castoldi M.M, Oliveira L.H., Hoffman R. and Jahn S.L. 2009. Conversion of Rice Husk Into Zeolitic Materials. *Latin American Applied Research*. 39: 75-78.

Foo K.Y. and Hameed B.H. 2010. Insights Into The Modelling of Adsorption Isotherms Systems. *Chemical Engineering Journal*. 156: 2-10.

Fotovat F., Kazemian H. and Kazemeini M. 2009. Synthesis of Na-A and Faujasitic Zeolites From High Silicon Fly Ash. *Materials Research Bulletin*. 44: 913-917.

Franks F. 1989. Hydration Phenomena in Colloidal Systems. *Water Science Review*. 4: 166-167.

Frilette V.J. and Kerr G.T. 1963. Process For Making Crystalline Zeolites. *United States Patents 3071434*

Frolkova A.K. and Ravae V.M. 2010. Bioethanol Dehydration: State of the Art. *Theoretical Foundation of Chemical Engineering.* 44(4): 545-556.

Frost J. 2014. How to Interprete a Regression Model with Low R-squared and Low p-values. The Minitab Blog. (on-line). http://blog.minitab.com/adventures-in-statitistics/how-to-interprete-a-regression-with-low-r-squared-and-low-p-values (16 Dec 2016)

Gabrus E., Nastaj J., Tabero P. and Aleksandrzak T. 2015. Experimental Studies on 3A and 4A Zeolite Molecular Sieves Regeneration In TSA Process: Aliphatic Alcohols Dewatering-water Desorption. *Chemical Engineering Journal.* 259: 232-242.

Geankoplis C.J. 1995. *Transport Processes & Unit Operations.* Singapore: Prentice Hall International.

Gomis V., Pedraza R., Saquete M.D., Font A. and Garcia-Cano J. 2015. Ethanol Dehydration Via Azeotropic Distillation With Gasoline Fraction Mixtures as Entrainers: A Pilot-scale Study With Industrially Produced Bioethanol and Naphta. *Fuel Processing Technology*. 140: 198-204

Gougazeh M. and Buhl J.C. 2014. Synthesis and Characterization of Zeolite A by Hydrothermal Transformation of Natural Jordanian Kaolin. *Journal of The Association of Arab Universities for Basic & Applied Sciences.* 15: 35-42.

Green, D.W. and Maloney, J.O. 1997. *Perry's Chemical Engineering Handbook*. 7th ed. New York: McGraw Hill.

Haden W.L., Metuchen J. and Dzierzanowski.1961. Method For Making Synthetic Zeolitic Material. *United States Patent 2992068.*

Hamai K., Takenaka N., Nanzai B., Okitsu K., Bandow H. and Maeda Y. 2008. Influence of Adding Salt On Ultrasonic Atomization In Ethanol Water Solution. *Ultrasonics Sonochemistry*. 16: 150 – 154.

Holmes S.M., Alomair A.A. and Kovo A.S. 2012. The Direct Synthesis of Pure Zeolite Using 'Virgin' Kaolin. *RSC Advances.* 2: 11491-11494

Hsu S.H., Hsu W.C., Chung T.W and Liao C.C. 2013. Dynamic Adsorption Study For Water Removal From Ethanol Solution By Using A Novel Immobilized Starch Sorbent. *Journal of the Taiwan Institute of Chemical Engineers.* 44: 952-956.

Huang Y.P. and Chang J.I. 2009. Biodiesel Production From Residual Oils Recovered From Spent Bleaching Earth. *Renewable Energy*. 35: 269-274.

Inayat A., Knoke I., Spiecker E. and Schwieger W. 2012. Assemblies of Mesoporous FAU-Type Zeolite Nanosheets. *Angewandte Communications*. 51: 1962-1965.

International Zeolite Association. http://www.iza-online.org

Iqbal A. and Ahmad S.A. 2016. Pressure Swing Distillation of Azeotropic Mixture – A Simulation Study. *Perspectives In Science*. Article In Press.

Ismail A.A, Mohamed R.M., Ibrahim I.A., Kini G. and Koopman B. 2010. Synthesis, Optimization and Characterization of Zeolite A and Its Ion Exchange Properties. *Colloids and Surfaces A: Physicochemical And Engineering Aspects.* 399: 80-87.

Izidiro J.C., Fungaro D.A., Abbort J.E. and Wang S. 2012. Synthesis of Zeolites X and A From Fly Ashes For Cadmium and Zinc Removal From Aqueous Solutions in Single and Binary Ion Systems. *Fuel.* 103: 827-834.

Jamil T.S., Gad-Allah T.A., Ibrahim H.S. and Saleh T.S. 2011a. Adsorption And Isothermal Models of Atrazine by Zeolite Prepared From Egyptian Kaolin. *Solid State Sciences.* 13: 198-203.

Jamil T.S., Abdel Ghafar H.H, Ibrahim H.S. and Abd El Maksoud I.H. 2011b. Removal of Methylene Blue By Two Zeolites Prepared From Naturally Occuring Egyptian Kaolin As Cost Effective Technique. *Solid State Sciences.* 13: 1844-1851

Jeong J., Jeon H., Ko K. Chung B. and Choi G. (2012). Production of Anhydrous Ethanol Using Various PSA (Pressure Swing Adsorption) Processes In Pilot Plant. *Renewable Energy*. 42: 41-45.

Jiang J., Feng L., Gu X., Qian Y., Gu Y. and Duanmu C. 2012. Synthesis of Zeolite A From Palygorskite Via Acid Activation. *Applied Clay Science.* 55: 108-113.

Johansen R.T. and DunningH.N. (1957). Water-vapor Adsorption on Clays. *Sixth National Conference on Clays and Clay Minerals.* 249-258.

Katsuki H. and Komarneni S. 2009. Synthesis of Na-A and/or Na-X Zeolite/porous Carbon Composites From Carbonized Rice Husk. *Journal of Solid State Chemistry*. 182: 1749-1753.

Keerthana S., Agilan S. and Muthukumarasamy N. and Velauthapillai D. 2014. Synthesis and Characterization of NaA Zeolite Powder/Film Deposited On Alumina Beads By Dip-coating Method. *Journal of Sol Gel Science Technology*. 72: 637- 643.

Kirpalani D.M. and Suzuki K. 2011. Ethanol Enrichment From Ethanol Water Mixture Using High Frequency Ultrasonic Atomization. *Ultrasonics Sonochemistry*. 18: 1012 – 1017.

Kiss A.A and Ignat R.M. 2012. Innovative Single Step Biodehydration In An Extractive Dividing Wall Column. *Separation and Purification Technology*. 98: 290-297.

Klamrassame T., Pavasant P. and Laosiripojana N. 2010. Synthesis of Zeolite From Coal Fly Ash: Its Application as Water Adsorbent. *Engineering Journal.* 14(1): 37-44.

Koshy N. and Singh D.N. 2016. Fly Ash Zeolites For Water Treatment Applications. *Journal of Environmental Chemical Engineering.* 4: 1460 – 1472.

Kosanovic C., Jelic T.A., Bronic J, Kralj D. and Subotic B. 2011. Chemically Controlled Particulate Properties of Zeolites: Towards The Face-less Particles of Zeolite A. Part 1. Influence of The Batch Molar Ratio [SiO2/Al2O3] On The Size ande Shape of Zeolite A Crystals. *Microporous and Mesoporous Materials.* 137: 72-82.

Kugbe J., Matsue N. and Henmi T. 2009. Synthesis of Linde Type A Zeolite-Goethite Nanocomposite As An Adsorbent For Cationic and Anionic Pollutants. *Journal of Hazardous Material*. 164: 929-935.

Kunnakorn D., Rirksomboon T., Siemanond K., Aungkavattana P., Kuanchertchoo N., Chuntanalerg P., Hemra K., Kulprathipanja S., James R.B. and Wongkasemjit S. 2013. Techno Comparison of Energy Usage Between Azeotropic Distillation and Hybrid System For Water Ethanol Separation. *Renewable Energy*. 51: 310-316.

Kumar S., Singh N and Prasad R. 2010. Anhydrous Ethanol: A Renewable Source of Energy. *Renewable and Sustainable Energy Reviews.* 14: 1830-1834.

Linegar K.L., Adeniran A.E. Kostko A.F. and Anisimov M.A. 2010. Hyrdrodynamic Radius of Polyethylene Glycol in Solution Obtained by Dynamic Light Scattering. *Colloid Journal*. 7(2): 279-281.

Loh S.K., James S., Ngatiman M., Cheong K.Y., Choo Y.M. and Lim W.S. 2013. Enhancement of Palm Oil Refinery Waste – Spent Bleaching Earth (SBE) into bio organic fertilizer and their effects on crop biomass growth. *Industrial Crops and Products.* 49: 775-781.

Loiola A.R., Andrade J.C.R.A, Sasaki J.M. and da Silva L.R.D. 2012. Structural Analysis of Zeolite NaA Synthesized By a Cost Effective Hydrothermal Method Using Kaolin and Its Usage as Water Softener. *Journal of Colloid and Interface Science.* 367: 34-39.

Luyben W.L. 2015. Improved Design of An Extractive Distillation System With An Intermediate-boiling Point Solvent. *Separation and Purification Technology*. 156: 336-347

Maes P.J. and Dijkstra A.J. 1993. Process For Regenerating Spent Bleaching Earth. *United States Patent 5256613.*

Mat R., Ling O.S., Johari A and Mohamed M. 2011. In Situ Biodiesel Production Residual Oil Recovered From Spent Bleaching Earth. *Bulletin of Chemical Reaction Engineering & Catalysis*. 6(1): 53-57.

Mc Cabe W.L., Smith J.C. and Harriot P. 2005. *Unit Operations of Chemical Engineering*. Singapore: Mc Graw Hill.

Meziti C. and Boukerroui A. 2011. Regeneration of Solid Waste From Edible Oil Refinery. *Ceramics International.* 37: 1953-1957.

Micromeritics ASAP 2020 Training Manual. 2010.

Milliken T.H., Oblad A.G. and Mill G.A. 1955. Use of Clays as Petroleum Cracking Catalyst. *1st National Conference On Clays and Clay Technology.* Bulletin 169: 314-169.

Milton R.M. 1959. Molecular Sieve Adsorbents. *United States Patent 2882243.*

Mohamed R.M., Ismail Adel. A., Kini G., Ibrahim I.A and Koopman B. 2009. Synthesis of Highly Ordered Cubic Zeolite A And Its Ion Exchange Behavior. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* 348: 87-92.

Moneim M.A. and Ahmed E.A. 2015. Synthesis of Faujasite From Egpytion Clays: Characterizations and Removal of Heavy Metals. *Geomaterials*. 5: 68 – 76.

Mulia-Soto J.F. and Flores-Tlacuahuac A. 2011. Modeling Simulation and Control of an Internally Heat Integrated Pressure-Swing Distillation Process For Bioethanol Separation. *Computers and Chemical Engineering.* 35: 1532-1546.

Musyoka N.M., Petrik L.F., Hums E., Baser H. and Schwieger W. 2012. In Situ Ultrasonic Monitoring of Zeolite A Crystallization From Coal Fly Ash. *Catalysis Today.* 190 : 38 – 46.

Nii S., Maatsura K., Fukazu T., Toki M. and Kawaizumi F. 2006. A Novel Method To Separate Organic Compounds Through Ultrasonic Atomization. *Chemical Engineering Research and Design.* 84 (A5): 412 -415.

Novembre D., Di Sabatino B., Gimeno D. and Pace C. 2011. Synthesis and Characterization of Na-X, Na-A and Na-P Zeolites and Hydroxysodalite From Metakaolin. *Clay Minerals.* 46: 339 – 354.

Nurbas M., Kacar Y. and Kutsal T. 2002. Determining The Overall Mass Transfer Coefficient For Adsorption of Cu2+ Ions Onto Ca-Alginate In Fixed Bed Column. *The European Journal of Mineral Processing and Environmental Protection.* 2(2): 55-60

Ojha K., Pradhan N.C. and Samanta A.N. 2004. Zeolite From Fly Ash: Synthesis and Characterization. *Bulletin Material Science.* V27 (No. 6): 555-564.

Ojumu T.V., Du Plesis P.W. and Petrik L.F. 2016. Synthesis of Zeolite A From Coal Fly Ash Using Ultrasonic Treatment – A Replacement For Fusion Step. *Ultrasonics Sonochemistry*. 31: 342-349.

Okewale A.O., Etuk B.R. and Igbokwe P.K. 2011. Comparative Studies on Some Starchy Adsorbents for The Uptake of Water From Ethanol Water Mixtures. *International Journal of Engineering Technology.* 11(5): 18-27.

Osmundsen C.M., Holm M.S., Dahl S. and Taarning E. 2012. Tin Containing Silicates: Structure-activity Relations. *Proceeding of The Royal Society A.* 468: 2000-2016.

Padala S., Le M.K., Kook S. and Hawkes E.R. 2012. Imaging Diagnostics of Ethanol Port Fuel Injection Sprays For Automobile Engine Application. *Applied Thermal Engineering.* 52: 24 -37. .

Parag S., Bhadraiah K. and Raghavan V. 2010. Emissions From Ethanol- Blended Fossil Fuel Flames. *Experimental Thermal and Fluid Science.* 35: 96 -104.

Perea D.E., Arslan I., Liu J., Ristanovic Z., Kovarik L., Arey B.W., Lercher J.A., Bare S.R. and Weckhuysen B.E. 2015. Determining The Location and Nearest Neighbours of Aluminum In Zeolites With Atom Probe Tomography. *Nature Communications.* DOI: 10.1038.

Pereira P.F., Marra M.C., Munoz R.A.A. and Richter E.M. 2012. Fast Batch Injection Analysis System For On Site Determination of Ethanol In Gasohol and Fuel Ethanol. *Talanta.* 90: 99 – 102.

Prokof'ev V.Y., Gordina N.E. and Efremov A.M. 2013. Synthesis of Type A Zeolite From Mechanoactivated Metakaolin Mixtures. *Journal of Material Sciences*. 48: 6276-6285.

Purnomo W.P., Salim C. and Hinode H. 2012. Synthesis of Pure Na-X and Na-A Zeolite From Bagasse Fly Ash. *Microporous and Mesoporous Material*. 162: 6-13.

Rezaee A., Rangkoy H.A., Khavanin A., Jonidi A., Soltani R.D.V and Nili-Ahmadabadi A. (2011). Adsorption Properties & Breakthrough Model of Formaldehyde On Bone Char. *International Journal of Environmental Science and Development.* 2(6): 423-427.

Rida K, Boraoui S. and Hadnine S. 2013. Adsorption of Methylene Blue From Aqueous Solution By Kaolin & Zeolite. *Applied Clay Science.* 83-84: 99 – 105.

Rios C.A., Williams C.D. and Fullen M.A. 2009. Nucleation And Growth History of Zeolite LTA Synthesized From Kaolinite By Two Different Methods. *Applied Clay Science.* 42:446-454.

Rios C.A., Williams C.D. and Castellanos A. 2010. Synthesis of Zeolite From Thermally Treated Kaolinite. *Rev. Fac. Ing. Antioquia*. 53: 30-41.

Rios C.A., William C.D. and Castellanos O.M. 2012. Crystallization of Low Silica Na-A and Na-X Zeolites From Transformation of Kaolin and Obsidian by Alkaline Fusion. *Ingeniera y Competitividad.* 14(2): 125-137.

Rondon W., Freire D., Benzo Z.D., Sifontes A.B., Gonzalez Y., Valero M. and Brito J.L. 2013. Application of 3A Zeolites Prepared From Venezuelan Kaolin for Removal of Pb(II) From Wastewater and Its Determination by Flame Atomic Absorption Spectrometry. *American Journal of Analytical Chemistry.* 4: 584-593.

Seader J.D. and Henley E.J. 1998. *Separation Process Principles.* USA: John Wiley.

Shigemoto N. and Hayashi H. 1993. Selective Formation of Na-X Zeolite From Coal Fly Ash By Fusion With Sodium Hydroxide Prior To Hydrothermal Reaction. *Journal of Material Science*. 28: 4781- 4786.

Simo M., Brown C.J. and Hlavacek V. 2007. Simulation of Pressure Swing Adsorption In Fuel Ethanol Production Process. *Computers and Chemical Engineering*. 32: 1635-1649.

Su S., Ma H. and Chuan X. 2016. Hydrothermal Synthesis of Zeolite A From K-Feldspar and its Crystallization Mechanism. *Advanced Powder Technology.* 27: 139-144.

Suhartani S., Hidayat N and Wijaya S. 2011. Physical Properties Characterization of Fuel Briquette Made From Spent Bleaching Earth. *Biomass & Bioenergy.* 35: 4209-4214.

Sun N., Okoye C, Niu C. H. and Wang H. 2007. Adsoprtion of Water and Ethanol by Biomaterials. *International Journal of Green Energy.* 4: 623-634.

Tanaka H. and Fujii A. 2009. Effect of Stirring On The Dissolution of Coal Fly Ash And Synthesis of Pure-Form Na-A and –X Zeolites By Two Step Process. *Advanced Powder Technology*. 20: 473-479.

Takaya H., Nii S., Kawaizumi F. and Takahashi K. 2004. Enrichment of Surfactant From Its Aqueous Solution Using Ultrasonic Atomization. *Ultrasonics Sonochemistry.* 12: 483 – 487.

Tavasoli M., Kazemian H., Sajdadi S. and Tamizifar M. 2014. Synthesis and Characterization of Zeolite NaY Using Kaolin With Different Synthesis Methods. *Clay and Clay Minerals.* 62(6) : 508-518

Tsai W.T., Chang C.Y., Ho C.Y. and Chen L.Y. (1999). Simplified Description of Adsorption Breakthrough Curves of 1,1-Dicholo-1-fluoroethane (HCFC-141b) on Activated Carbon With Temperature Effect. *Journal of Colloid and Interface Science.* 214: 455-458.

Uragami T., Banno M. and Miyata T. 2015. Dehydration of An Ethanol-Water Azeotrope Through Alginate-DNA Membranes Cross-linked With Metal Ions Pervaporation. *Carbohydrate Polymers.* 134: 38-45

Volli V. and Purkait M.K. 2015. Selective Preparation of Zeolite X and A Form Fly Ash and Its Use as Catalyst For Biodiesel Production. *Journal of Hazardous Material*. 297: 101-111.

Vaiciukyniene D., Kantautas A., Vaitkevicius V., Jakevicius L. Rudzionis Z. and Paskevicius M. 2015. Effects of Ultrasonic Treatment on Zeolite NaA Synthesized From By-Product Silica. *Ultrasonics Sonochemistry*.27: 515-521.

Vaughan D.E. 1985. Process For Direct Synthesis of Sodium and Potassium Containing Zeolite A. *United States Patent 4534947.*

Walls W.D., Rusco F. and Kendix M. 2011. Biofuels Policy and The US Market For Motor Fuels: Empirical Analysis of Ethanol Splashing. *Energy Policy*. 39: 3999 – 4006.

Wang Y., Gong C., Sun J., Gao H., Zheng S and Xu S. 2010. Separation of Ethanol/Water Azeotrope Using Compound Starch-Based Adsorbents. Bioresource Technology. 101: 6170-6176.

Watanabe Y., Yamada H., Tanaka J., Komatsu Y. and Moriyoshi Y. 2004. Ammonium Ion Exchange of Synthethic Zeolites: The Effect of Their Open Window Sizes, Pore Structures and Cation Exchange Capacities. *Separation Science and Technology*. 39 (9): 2091-2104.

Yamamoto T., Kim H.K., Kim B.C., Endo A., Thongprachan N. and Ohmori T. 2012. Adsorptive Characteristics of Zeolites For Dehydration of Ethanol: Evaluation of Diffusivity of Water In Porous Structure. *Chemical Engineering Journal*. 181-182: 443 – 448.

Yusof A.M, Nizam N.A. and Abdul Rashid N.A. 2010. Hydrothermal Conversion of Rice Husk Ash To Faujasite Type and NaA Type of Zeolite. *Journal of Porous Matter*. 17: 39-47.