

EFFECT OF ZEOLITE 4A ON WATER CONCENTRATION IN THE SYSTEM OF THE ESTERIFICATION REACTION OF ACETIC ACID WITH 1-BUTANOL

Ratna Dewi Kusumaningtyas

Department of Chemistry, Faculty of Mathematics and Natural Sciences,
State University of Semarang (UNNES), Kampus Sekaran, Semarang, Indonesia

Received 9 March 2006; Accepted 27 April 2006

ABSTRACT

The usual problem encountered on a reversible reaction is that the reaction cannot achieve a complete conversion of reactants since it is limited by the thermodynamic equilibrium. Due to this low conversion, it will face challenges with product purification and recycling of the reactants, which then cause an increase in the operation cost. To obtain higher conversion, it is necessary to shift the equilibrium towards the products by continuously removing the water formed. One popular example of reversible reaction is esterification process. In this research, water removal was conducted through an adsorption process using zeolite 4A. Effect of zeolite 4A on water concentration in the liquid phase esterification of acetic acid and 1-butanol catalyzed by sulfuric acid was investigated. It was performed in an isothermal batch reactor. The molar ratio of 1-butanol - acetic acid was 1.4 times theoretically, the catalyst concentration was 1 % wt and the mixing intensity was 1000 rpm. The influence of the temperature was studied at 40 to 80 °C and the zeolite 4A loading was varied at 1.6 to 5.52 % w/v. The reaction was compared to the conventional esterification reaction carried out under identical conditions but without addition of zeolite 4A. Concentration of each component in the system was analyzed using on-line Gas Chromatography. Effect of removing the water produced during the reaction by using zeolite 4A was demonstrated. It was revealed that the amount of water removed was proportional to the amount of the zeolite 4A to be employed. On the other hand, the increase of the temperature led to the lower amount of water to be adsorbed. Among all the experiments, the best result was achieved on the addition of 5.52 % b/v zeolite 4A at 40 °C, where water concentration was 3.1356 g mole/L and the conversion was 76.11 % at the equilibrium condition. As comparison, water concentration on the conventional reaction performed at 40 °C was 6.9161 g mole/L and the conversion was 62.5 % at the equilibrium condition. The equation illustrating the effect of zeolite 4A loading on the conversion obtained at the equilibrium condition was: $X_{Ae} = 0.6248 + 0.0868 C_{4A}^{0.2848}$, where X_{Ae} was equilibrium conversion of Acetic Acid and C_{4A} was Zeolite 4A loading (g/100 mL liquid).

reversible reaction, esterification, zeolite 4A, water removal, adsorption

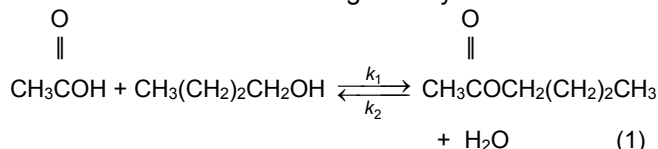
INTRODUCTION

Many industrial processes deal with some obstacles in producing chemicals that are synthesized via reversible reaction. Some examples of reversible reaction are esterification, MTBE synthesis and reaction of manufacturing ethyl benzene, just to name a few. The usual problem encountered on a reversible reaction is that the reaction cannot achieve a complete conversion of reactants since it is limited by the thermodynamic equilibrium. On account of this low conversion, it will face challenges with product purification and recycling of the reactants, which then cause an increase in the operation cost. Separation unit is a costly part on an industrial process due to its investment and energy cost. Investment for separation process and its supporting facility costs as much as 40-70 % of the capital and operating cost in industries [1]. To reduce the costs associated with the separation step, it is important to make some attempts to improve the conversion of the reversible reactions.

It is stated that removal one of the reaction products on the reversible reaction should help to displace the equilibrium of the reaction [2]. Based on that theory, several techniques have been proposed to enhance the yield of the equilibrium-limited reactions by selective removal of a reaction product, among others are reactive distillation method [3], counter-current reactive stripping [4,5], reaction using membrane process [6,7] and reactive adsorption [8-11]. Meanwhile, this research studied about the application of adsorption process using zeolite 4A to continuously remove the water formed in the esterification process with the purpose to improve the conversion beyond equilibrium.

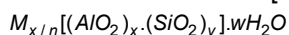
Esterification is a popular example of reversible reactions and it is an industrially relevant reaction. Organic esters are known as important class of chemicals and frequently used as plasticizers, solvents, flavors, perfumes, and pharmaceuticals. One example of esters produced on a large scale is butyl acetate. This compound is widely applied as solvent, extraction agent, hardener and adhesive. Today's world demand

on this ester is about 530,000 tons/ year [12]. The reaction under investigation was the esterification of acetic acid with 1-butanol to give butyl acetate.



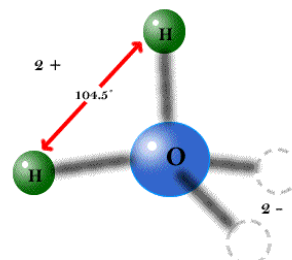
The water formed in this reaction was continuously removed through an adsorption process using zeolite 4A added to the reaction system. Hence, removal of water will drive the reaction towards the product. In this research, effect of zeolite 4A on the water concentration in the system of the esterification reaction of acetic acid and 1-butanol was studied. Its effect on the reaction yield was observed as well.

Zeolite 4A was selected as the material to adsorb the water formed in the esterification reaction because of its properties. Zeolite 4A is an aluminosilicate crystal containing sodium and having an inorganic polymer crystal with tetrahedral framework of AlO_4 dan SiO_4 . Structural formula of Zeolite is [13]:



On that formula, n is valence of cation M; w is number of water molecule per cell unit; x and y is total number of tetrahedral per cell unit. This material is a micro-porous solid possessing high surface area and a uniform size pore diameter of 4Å. This uniform size of pore diameter will lead this material to selectively adsorb or reject species based on its diameter [13]. Zeolite 4A should selectively adsorb the water since the molecular diameter of water is 2.82 -3.2 Å [14]. On the other side, the effective diameter of the other molecules in the system (acetic acid, 1-butanol, and n-butyl acetate) are larger than 4Å, meaning that those species will not be adsorbed by the adsorbent (zeolite 4A). Moreover, zeolite 4A is rich in alumina which has polar properties. Hence, this material has hydrophilic surface, which should be selective for polar molecule as water [15].

Water is a polar molecule. It means that the electron density is not evenly distributed. Water has positive charge surrounding the hydrogen atoms and negative charge surrounding the oxygen atoms [16]. It will then result in the hydrogen bond as illustrated on Fig 1 [17]. Based on the above mentioned theory, this work aimed at investigating the effectiveness of zeolite 4A in adsorbing the water produced in the esterification reaction system as well as its effect in improving the reaction yield. The result of this research was expected to give contribution in providing alternative method of reactive separation technique, enhancing conversion of reversible reaction.



Ball and stick model of water.

Fig 1. Model of Water Molecule [17]

EXPERIMENTAL SECTION

Determination of Surface Area of Zeolite 4A (BET Method)

Brunauer-Emmet-Teller (BET) method is the most popular procedure to determine surface area of solid materials. In this work, surface area of Zeolite 4A was analyzed using NOVA (NO Void Analysis) - Quantachrome instrument. Determination of surface area consisted of two steps, namely treatment and analysis step.

Sample was treated prior to the analysis process. Initially sample was heated in the oven at 150 °C for 5 hours in order to release the vapor and undesired gases (impurities) in it. Sample was then cooled, put into the sample cell, and weighed. The next step was vacuum degassing, which was intended to intensively clean the sample from its vapor and impurities content. Degassing process of zeolite 4A took place at 150 °C for 6 hours. Sample was then cooled and weighed for measuring its dry weight.

The next step was sample analysis to determine the surface area and the pore volume. It was performed by means of adsorption of N_2 at temperature of 77 K, known as the standard boiling point of liquid nitrogen. Surface area of the Zeolite 4A was then determined using BET Isotherm. The equilibrium isotherm evaluated was those in the range of $\frac{P}{P_0} = 0.05-0.35$. Computation was done with the aid of NOVWIN software.

Esterification Reaction

Apparatus

Materials for this experiment are acetic acid (Merck), 1-butanol (Merck), sulfuric acid (Merck) and Zeolite 4A obtained from PT Pusri Palembang. Esterification of acetic acid with 1-butanol was carried out in an isothermal batch reactor. The 1000 mL three-neck flask reactor was equipped with mechanical stirrer, thermometer, sampling device, and a reflux condenser to prevent the escape of volatile compounds. The experiments were conducted with the

Table 1. Temperature program for GC analysis

Rate, °C / min	temperature, °C	Held for, min
initial	200	5
40	230	35

molar ratio of 1-butanol - acetic acid maintained constant at 1.4 times theoretically, the catalyst concentration fixed at 1 % wt of acetic acid and 1-butanol based, and the mixing intensity held constant at 1000 rpm. The influence of the temperature was investigated at 40 to 80 °C and the adsorbent (Zeolite 4A) concentration was varied at 1.6 to 5.52 % w/ v.

Experimental procedure

Acetic acid was preheated to the desired reaction temperature, and 1-butanol was heated in a separate vessel. When the liquid in the reactor reached the desired reaction temperature, then the second reactant was quickly poured into to the reactor. The initial time of the reaction was started when all the 1-butanol had been added to the reactor, and at that moment the sample for the initial condition ($t=0$) was withdrawn (3 mL). Then sulfuric acid catalyst and the adsorbent (zeolite 4A), which had been degassed by using *Quantachrome NOVA* Instrument, were added to the reaction system. The reaction was conducted for 120 minutes. During the reaction, samples were taken according to the sampling program. Concentration of each component (acetic acid, alcohol, ester, and water) was analyzed periodically using Gas Chromatography. For comparison purposes the conventional esterification reaction was also performed under identical condition but in the absence of Zeolite 4A as water adsorbent.

Gas Chromatography

Concentration of each component in the samples withdrawn from the esterification process (acetic acid, 1-butanol, water, and *n*-butyl acetate) was analyzed using Gas Chromatography. Sample (0.5 μ L) was injected into the port injection using syringe, then area of each component was measured. The instrument of Gas Chromatography was Shimadzu GC-14B with TCD; Helium as carrier gas at 41,095 mL/min; Porapak Q packing column in 5 m length. Temperature of the injector and detector were 250 °C. Temperature program was shown in Table 1. Typical retention times were: water, 3.03 min, acetic acid, 8.447 min, 1-butanol, 14.899 min, *n*-butyl acetate 32.221 min.

RESULT AND DISCUSSION

Surface Area of Zeolite 4A (BET method)

BET isotherm applied for determining the surface area of solid material is [18]:

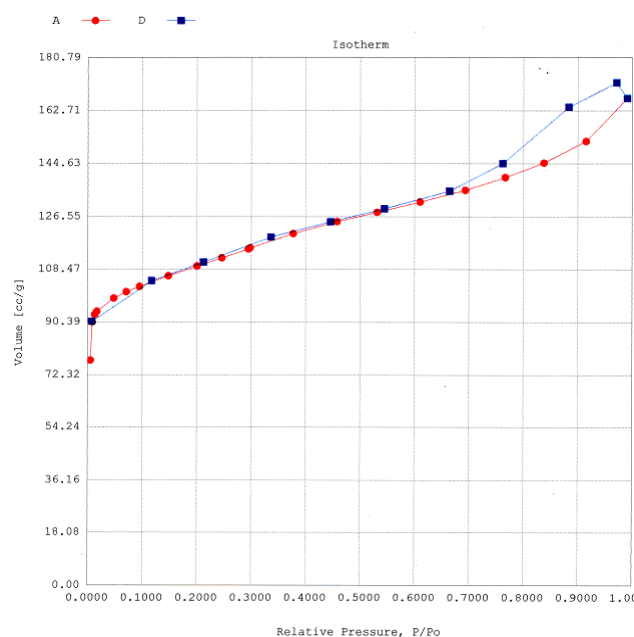


Fig 2. Analysis of zeolite 4A's surface area (isotherm BET)

$$\frac{1}{W\left(\left(\frac{P_0}{P}\right)-1\right)} = \frac{1}{Wm \cdot C} + \frac{C-1}{Wm \cdot C} \left(\frac{P}{P_0}\right) \quad (2)$$

Plotting $\frac{1}{W\left(\left(\frac{P_0}{P}\right)-1\right)}$ against $\left(\frac{P}{P_0}\right)$ will result in a linear

curve. Value of the slope $\left(\frac{C-1}{Wm \cdot C}\right)$ and the intercept

$\left(\frac{1}{Wm \cdot C}\right)$ can be calculated using least square method. Furthermore, the surface area is determined by a formula:

$$S_t = \frac{Wm \cdot N_{av} \cdot A_p}{BM_{N_2}} \quad (3)$$

On the other side, the formula for determining total pore volume of solid material is:

$$\frac{P}{V' \cdot (P - P_0)} = \frac{1}{V'm \cdot C} + \frac{C-1}{V'm \cdot C} \left(\frac{P}{P_0}\right) \quad (4)$$

Plotting $\frac{P}{V'(P - P_0)}$ with $\left(\frac{P}{P_0}\right)$ will yield linear curve.

Value of the slope $\left(\frac{C-1}{V'm \cdot C}\right)$ and the intercept

$\left(\frac{1}{V'm \cdot C}\right)$ can be obtained using *least square*

method. Therefore, total pore volume can be achieved.

The result of BET analysis on zeolite 4A was exhibited in Fig 2. It was revealed that the surface area was 363.2 m^2/g and total pore volume was 1.187E-01 cc/ g. This surface area and pore volume were considered high for conducting adsorption process.

Table 2. Effect of zeolite 4A (1.60 % W/ v) on the concentration of water at various temperatures

Time (t), min	Concentration of Water, g mole/L									
	40 °C		50 °C		60 °C		70 °C		80 °C	
	Cv	Z	Cv	Z	Cv	Z	Cv	Z	Cv	Z
0	1.1863	2.1159	1.2735	2.1564	0.8289	2.3776	0.6565	1.0186	0.3970	1.0933
5	2.8576	4.1986	2.9160	3.7346	3.7515	4.3338	3.8154	4.7265	3.9049	3.9149
10	3.7348	4.2232	3.2406	5.2301	4.1949	5.7152	4.1409	4.5835	4.6330	4.2574
15	3.9229	5.5526	3.6301	4.7819	4.9166	5.6999	4.8378	4.0402	4.7168	3.5962
30	4.4871	4.8479	4.3060	4.8187	5.0728	5.6539	5.1628	3.7726	4.9683	3.1638
45	4.6261	4.7702	5.1715	4.6709	6.2722	5.6519	5.2605	3.5050	5.0558	3.0468
60	4.8951	4.6925	5.6557	4.5230	7.6764	5.6498	5.3583	3.2835	5.1433	2.9769
90	5.0147	4.5371	6.8474	4.2273	8.5446	4.9891	5.5537	3.0103	5.1446	2.8970
120	6.9161	4.3817	7.0520	4.1923	9.4128	4.3284	5.7491	2.7639	5.1661	2.8171

Note : Z = Reaction in the Presence of Zeolite 4A (1.6 % W/ v) ; Cv = Conventional Reaction

Effect of Zeolite 4A on Water Concentration at Various Reaction Temperatures

Esterification experiments with and without the addition of Zeolite 4A are given in Table 2 and Fig 3. The influence of zeolite 4A on the water concentration was clearly visible. In the conventional reactions, concentration of water tended to sharply increase on the initial reaction then the increase went slower until it reached equilibrium. In the presence of Zeolite 4A, initially the water concentration increased but it then decreased, subsequently it reached the constant concentration.

Effect of zeolite 4A was not significant at the initial time of reaction since the reaction rate was still faster than the rate of water adsorption. Thus, the rate of water formation is higher than the rate of water removal. However, the reaction rate then grew slower while the adsorption of water proceeded. Hence, water concentration on the system decreased. At the end of the process, reaction had reached equilibrium and the adsorbent got its maximum capacity, therefore the water concentration would be constant.

Advanced study showed that concentration of water affected the conversion obtained. With water removal the conversion was higher. Removal of water shifted the reaction towards the product, consequently the conversion was then enhanced beyond equilibrium. However, the increase of the temperature provided less significant effect in improving the reactor conversion. It was due to the exothermic property of the water adsorption.

Referring to the *Le Chatelier* Principle, for the exothermic process, the increase of the temperature will reduce the total molecules adsorbed [19]. Physical bond between adsorbates (water) and the adsorbent active sites (zeolite 4A) becomes weak as the increasing temperature. This phenomenon was previously studied by Carmo and Gubulin [20], investigating the water adsorption in the mixture of water-ethanol on Zeolite 3A.

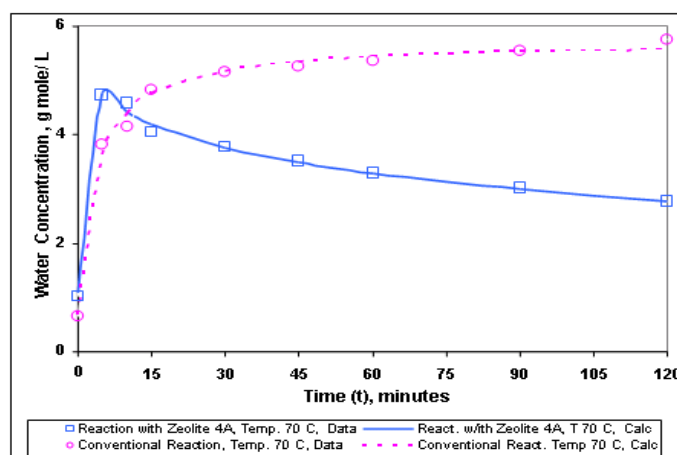


Fig 3. Effect of zeolite 4A (1.60 % W/ v) on the concentration of water at temperature of 70 °C

Based on that theory, in this work, the higher temperature caused the less water molecules to be adsorbed. Hence the effect on improving the conversion should be less significant.

Effect of Zeolite 4A Loading

Effect of Zeolite 4A loading was investigated in this work. It was observed that the increase of zeolite 4A loading led to the higher amount of water to be removed. The result on the Table 3 and Fig 4 showed that water concentration in the system decreased as the increasing of zeolite 4A loading. This phenomenon took place since the higher amount of zeolite 4A to be employed meant the higher surface area provided for the adsorption process. Referring to the theory, total adsorptive capacity of an adsorbent depends on its surface area. The increase of the surface area of the adsorbent leads to the increase of the total molecules adsorbed [21]. Besides, surface area of the adsorbent also has significant influence on the adsorption rate.

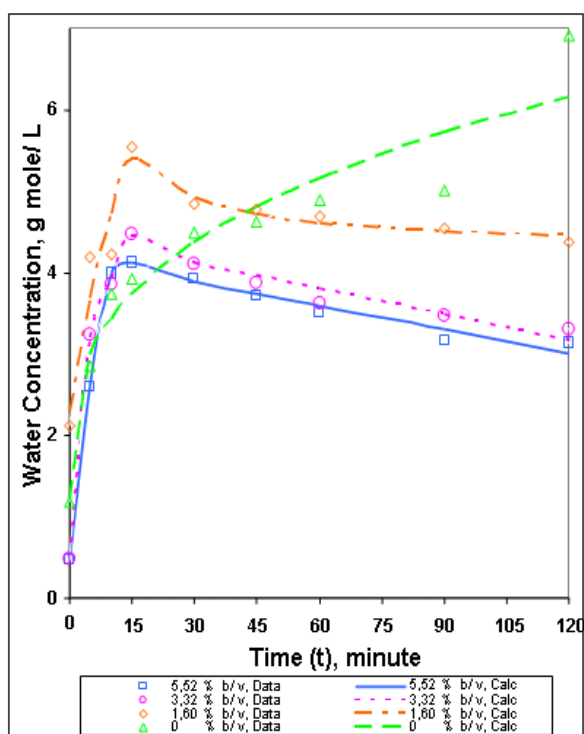


Fig 4. Effect of zeolite loading on the concentration of water (at reaction temperature of 40 °C)

Table 3. Effect of zeolite loading on the concentration of water (at reaction temperature of 40 °C)

Time of Reaction, min	Concentration of Water, g mole / L			
	Zeolite 4A loading (% g Zeolite 4A/ mL liquid)			
	0	1.60	3.36	5.52
0	1.1863	2.1159	0.4899	0.4754
5	2.8576	4.1986	3.2346	2.6117
10	3.7348	4.2232	3.8577	4.0010
15	3.9229	5.5526	4.4809	4.1281
30	4.4871	4.8479	4.1039	3.9231
45	4.6261	4.7702	3.8793	3.7181
60	4.8951	4.6925	3.6335	3.5131
90	5.0147	4.5371	3.4716	3.1745
120	6.9161	4.3817	3.3098	3.1356

The higher surface area, the higher adsorption rate should occur [22]. Surface area plays important role in an adsorption process. The extent of adsorption is proportional to the specific area, which is defined as that portion of the total area that is available for adsorption. Surface area is also closely related to the pore volume of the solid. Porous solid provides a very high surface area or high micropore volume that high adsorptive capacity can be achieved [18].

The influence of zeolite 4A loading on the conversion was also visible. It was revealed that the higher loading of zeolite 4A led to the higher conversion obtained. The higher amount of zeolite 4A to be added, the higher amount of water to be adsorbed would be. Hence, it more significantly shifted the equilibrium to the

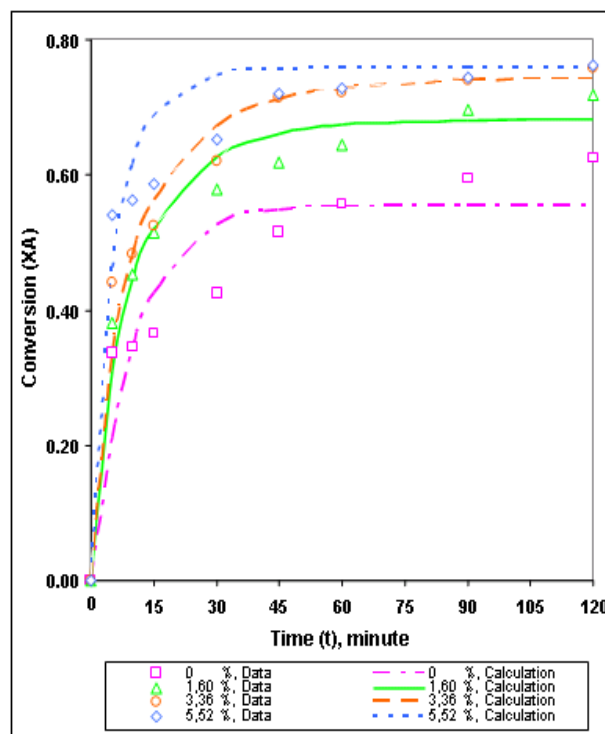


Fig 5. Effect of zeolite 4A on the conversion (at temperature of 40 °C)

right, resulting in the higher conversion. Among all the experiments conducted, the highest enhancement of conversion was 13.6 %, achieved on the reaction performed at 40 °C with zeolite 4A loading of 5.52 % w/v. At this condition, the reactor conversion was 76.11 %. As comparison, in the absence of zeolite 4A, the conversion of the reaction carried out on the same temperature was only 62.5 %. Enhancement of the conversion obtained in this research was more significant than that achieved by Gulati *et al.* [9] in on their work of sorbitol 1(6)-monostearate synthesis, in the presence of zeolite 4A to the amount of 10 % w/v.

The equation illustrating the effect of zeolite 4A loading on the conversion obtained at the equilibrium condition was then found using *Signaplot* software.

$$X_{Ae} = 0.6248 + 0.0868 C_{4A}^{0.2848} \quad (5)$$

X_{Ae} represented equilibrium conversion of Acetic Acid and C_{4A} was Zeolite 4A loading (g/ 100 mL liquid).

CONCLUSION

Based on the analysis using BET Methods, it was obtained that the surface area of zeolite 4A was 363.2 m²/g and the pore volume was 1.187e-1 cc/g..The increase of the temperature led to the lower amount of water to be adsorbed, and the less significant effect on the conversion enhancement.

The amount of water removed and the conversion achieved were proportional to the amount of the zeolite 4A to be employed. The equation illustrating the effect

of zeolite 4A loading on the conversion obtained at the equilibrium condition was:

$$X_{Ae} = 0.6248 + 0.0868 C_{4A}^{0.2848}$$

NOMENCLATURE

A_p = Projection area of N molecule = 16.2 Å
 BM_N = Molecular mass of nitrogen, g/ g mole
 C = BET constant, associated with the adsorption energy on the monolayer
 C_{4A} = Zeolite 4A loading, g/ 100 ml cairan
 k_1 = esterification reaction rate constant to the right, L/ g mole-min
 k_2 = esterification reaction rate constant to the left, L/ g mole-min
 N_{av} = Avogadro number = 6.023×10^{23} molecule/ g mole
 P, P_o = Vapor pressure of adsorbate, atm
 S_t = Surface area of solid, Å
 T = Absolute temperature, K
 V' = Volume of N_2 adsorbed on the pore, L
 V'_m = Pore Volume, L
 W = Weight of N_2 gas adsorbed on the pore at the relative temperature (P/P_o), g
 W_m = Weight of adsorbate forming monolayer on the solid surface, g

ACKNOWLEDGEMENT

The financial support from BPPS Scholarship, Indonesia, is gratefully acknowledged. Acknowledgments are also expressed to Prof. I. M. Bendiyasa, Dr. Imam Prasetyo, Prof. W. B. Sediawan and Dr. Arief Budiman of their advices on this work.

REFERENCES

- Prasetyo, I., 2001, *Pemisahan CO₂ dengan Adsorpsi*, Fakultas Teknik, Universitas Gadjah Mada, Yogyakarta.
- Yadav, G.D. and Thathagar, M. B., 2002, *React. Funct. Polym.*, 52, 99-110.
- Kenig, E. Y., Bäder, H., Górak, A., Beßling, B., Adrian, T., and Schoenmakers, H., 2001, *Chem. Eng. Sci.*, 56, 6185-6193.
- Nijhuis, T. A., Beers, A. E. W., Kapteijn, F., and Moulijn, J. A., 2002, *Chem. Eng. Sci.*, 57, 1627-1632.
- Beers, A. E. W., Spruijt, R.A., Nijhuis, T. A., Kapteijn, F., and Moulijn, J. A., 2001, *Catal. Today*, 66, 175-181.
- Lim, S. Y., Park, B., Hung, F., Sahimi, M., Tsotsis, T. T., 2002, *Chem. Eng. Sci.*, 57, 4933-4946.
- Bernal, M. P., Coronas, J., Menendez, M., and Santamaria, J., 2002, *Chem. Eng. Sci.*, 57, 1557-1562.
- Sekeroglu, G., Fadiloglu, S., and Ibaloglu, I., 2004, *Turkish J. Eng. Env. Sci.*, 28, 241-247.
- Gulati, R., Arya, P., Malhotra, B., Prasad, A. K., Saxena, R. K., Kumar, J., Watterson, A. C., and Parmar, V. S., 2003, Novel Biocatalytic Esterification Reactions on Fatty Acids: Synthesis of Sorbitol 1(6)-monostearate, http://arkat-usa.org/ark/publication/new_may03-pdf.
- Carr, R. W. and Dandekar, H. W., 2001, *Adsorption with Reaction*. In S. Kulprathipanja (Ed.), *Reactive Separation Process*, Taylor & Francis, Philadelphia
- Sharma, A. and Chattopadhyay, S., 2000, *J. Molec Catal. B: Enzymatic*, 10, 531-534.
- Östman, M., 2003, *Information on Substances: n-Butyl Acetate*, www.kemi.se/kemamne_eng/n-butylacetate_eng.Htm.
- Kirk, R. E. and Othmer, D. F., 1992, *Encyclopedia of Chemical Technology*, The Interscience Encyclopedia Inc., New York.
- Chaplin, M., 2004, *The Water Molecule*, <http://www.isbu.ac.uk/water/molecule/html>
- Anonim, 2003, *Molecular Sieve Desiccant Dehydrator for Natural Gas*, <http://www.emersonprocess.com>.
- Grimes, B., Hallick, R., Williams, K., and Wells, M., 1997, *Chemistry Tutorial: The Chemistry of Water*, <http://www.biology.arizona.edu/biochemistry/tutorials/Chemistry/page3.html>.
- Slichter, 2003, *Covalent Bonding and Polarity in Water Molecule*, <http://ghs.gresham.k12.or.us/science/ps/sci/ibbio/chem/notes/chpt2/water.htm>.
- Do, D. D., 1998, *Adsorption Analysis: Equilibria and Kinetic*, p. 61, Imperial College Press, London.
- Seader, J. D. and Henley, E. J., 1998, *Separation Process Principles*, pp. 777-789, John Wiley and Sons, Inc., New York.
- Carmo, M. J. and Gubulin, J. C., 1997, *Braz. J. Chem. Eng.*, 3, 1-12.
- Visvanathan, C., 1998, *Adsorption Isotherm*, www.courses.ait.ac.th/ED08.13/Chapter7-8.htm.
- Kumar, K. V., Subanandam, K., Ramamurthi, V., and Sivanesan, S., 2004, *Solid Liquid Adsorption for Wastewater Treatment: Principle Design and Operation*, www.eco-web.com/cgi-local/stc?a=editorial/index.html&b=/editorial/040201.Html.