

LIQUID PHASE SYNTHESIS OF ETHYL *TERT*-BUTYL ETHER FROM ETHANOL AND *TERT*-BUTYL ALCOHOL USING MACROPOROUS AND GELULAR ION EXCHANGE RESIN CATALYSTS

*M. UMAR, A. R. SALEEMI and B. SAHA¹

Department of Chemical Engineering, University of Engineering and Technology, Lahore, Pakistan

¹Department of Chemical Engineering, Loughborough University, LE11 3TU, Leicestershire, U.K

Ethyl *tert*-Butyl Ether (ETBE) synthesis using ethanol (EtOH) and *tert*-butyl alcohol (TBA) was studied under atmospheric pressure conditions with different macroporous and gelular ion exchange resin catalysts. The catalysts used were Purolite® (CT-124, CT-145H, CT-151, CT-175, CT-275) and Amberlyst-15 and 35, all in H⁺ form. All catalysts were employed for ETBE synthesis under identical conditions and suitable catalyst was decided on the basis of conversion and selectivity. Among the catalysts studied, CT-124 produced the best results and was used for further studies. Effect of temperature, feed molar ratio of reactants and catalyst loading was studied and the optimum conditions found were: 343 K temperature, 1:2 feed mole ratios and 5 % catalyst loading. Kinetic modeling was performed using various heterogeneous reactions models and it was found that Quasi-Homogeneous model represented the system more adequately.

Keywords: ETBE synthesis, Kinetics, Heterogeneous catalysis, Macroporous, Ion exchange resins

1. Introduction

The use of lead compounds, e.g. tetra ethyl lead and tetra methyl lead as octane boosters and anti-knocking agent is no more in practice in most parts of world due to stringent environmental protection regulations. Therefore, the emphasis is given to alternate sources for increasing octane number as well as the oxygen content of the gasoline fuels. The tertiary ethers like methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME) are considered to be the most suitable and preferred sources over alcoholic oxygenates (e.g. methanol, ethanol and *tert*-butanol) due to their low blending Reid vapor pressure (bRvp), higher octane number and low solubility in water. Among these ethers, ETBE is considered to be the better option due to its characteristics of higher octane rating (111), low bRvp (27.56 KPa) and low oxygen contents (15.7 wt %) [1].

Most of the literature refers to ETBE synthesis using isobutylene (IB) and ethanol (EtOH) as reactants, [2-4]. Recently more emphasis is given to the direct synthesis of ETBE using ethanol (EtOH) and *tert*-butyl alcohol (TBA) in liquid phase.

* Corresponding author : bazaidumar@gmail.com

This is because of the fact that source of IB is limited to steam cracking or catalytic cracking fractions and it is being used as one of the reactants in other chemical industries. Another reason for using TBA instead of IB is that it will be difficult in future to fulfill its requirements for ethers production. TBA is relatively less expensive as it is a major by product in ARCO process for the manufacturing of propylene oxide [5].

Different catalysts have been used for the direct reaction of TBA and ethanol to produce ETBE, these are, heteropoly acid [6]. Potassium hydrogen sulphate [5], Amberlyst-15 ([7], ion exchange resins S-54 and D-72 [1], and β -zeolites [8-9].

The aim of this study was to explore the catalytic efficiency and capacity of different catalysts, which has not been investigated previously for etherification reactions. These new ion exchange resins catalysts include macroporous (Purolite CT-145H, CT-151, CT-175, CT-275) as well as gelular resin (CT 124). TBA conversion and ETBE selectivity with all new catalysts as well as those for Amberlyst -15 (A-15) and Amberlyst-35wet (A-35) are compared. Kinetic

modeling has been performed on the most suitable catalyst, found in batch studies, using heterogeneous models like Langmuir-Hinshelwood-Hougen-Watson (LHHW), Eley-Rideal (E-R) and Quasi Homogeneous (Q-H).

2. Experimental

2.1 Materials and methods

All the chemicals, TBA (99.5% GLC), ethanol (99.8%, GC) and ETBE (97% GC) were purchased from Fisher UK and their purity was verified by gas chromatography. Ion exchange resin catalysts of CT brand were provided by M/S Purolite® UK, while Amberlyst-35 was provided by M/S Rohm and Haas® France.

Ion exchange resin catalysts were washed thoroughly with de-ionized water and then with methanol. Washed and dried catalysts were kept in vacuum dryer at 373 K for six hours to remove any residual moisture. Pre-treated resin catalysts were stored in desiccators for further use. Catalysts were characterized using Brunner-Emmett-Teller (BET) surface area and Langmuir surface area measurement, particle size distribution, pore size and pore volume distribution, Scanning Electron Microscopy (SEM) for surface and inner particle structure, bulk and true density measurement and elemental analysis. The characterization and physical properties are presented in our previous work [10].

2.2 Apparatus

A flat bottom 5 necked jacketed reaction vessel of $5.0 \times 10^{-4} \text{ m}^3$ volume was used to carry out experiments. Mechanical stirrer was fixed in the central neck and other necks were used for condenser, thermocouple, catalyst feeding and sampling. A temperature controlled hot water bath was used to keep the contents of reaction vessel at desired temperature.

2.3 Procedure

Pre defined and measured quantities of each reactant (TBA and EtOH) were fed in to reaction vessel and the contents were heated to the desired reaction temperature by circulating hot water through the jacket. When the reaction mixture reached the required temperature, catalyst was added as the weight percent of the reaction mixture and sample was taken. This time was taken as zero for start of the reaction. Samples of

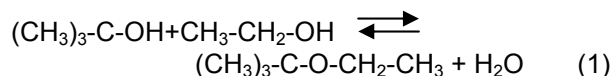
approximately $1.0 \times 10^{-6} \text{ m}^3$ were taken more frequently for initial couple of hours and then half hourly till the equilibrium was attained. The concentration of each component was then measured for all samples.

2.4 Sample analysis

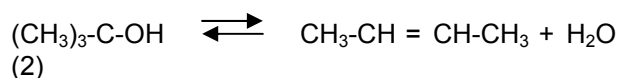
All samples were analyzed by Pye Unicam 104 gas chromatograph equipped with Supelco® PORAPAK-Q (80/100) column of 1.83 m length and $3.175 \times 10^{-6} \text{ m}$ diameter and thermal conductivity detector (TCD). Helium gas of 99.9% purity was used as mobile phase at flow rate of $0.60 \text{ cm}^3/\text{s}$. Injector and detector temperature were set isothermal at 458 K. *iso*-propanol was used as internal standard and separation was achieved for all components. Total duration of sample run was 9 minutes.

2.5 ETBE synthesis reaction

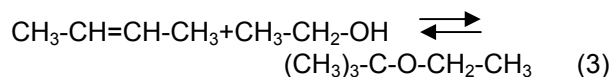
In the direct synthesis of ETBE from TBA and ethanol (EtOH), following sequence of reactions takes place



This main reaction is accompanied by the side reaction, which is dehydration of TBA into IB and water



The third reaction which may take place, is the indirect formation of ETBE by ethanol and IB



The limiting step in this sequence of reactions is supposed to be the surface reaction of ethanol adsorbed in the macro pores of catalyst and TBA to yield ETBE. Under the atmospheric pressure experimental conditions used in this work, IB was not found in liquid phase even up to very less extent, so backward reaction in equation (2) and reaction in equation (3) can safely be neglected.

3. Results and Discussions

3.1 Batch kinetic results

Experiments were carried out in such a way to determine the best catalyst for ETBE synthesis at specified conditions. To overcome the mass transfer resistance, agitation speed of 500 rpm was used after observation that there was no appreciable increase in conversion when speed was increased upto 800. Since higher impeller speed can cause attrition and disintegration of catalyst particles, so impeller speed of 500rpm was considered optimum and maintained through out this study.

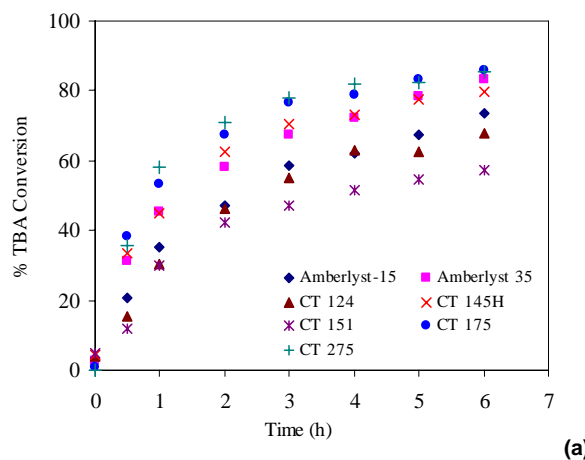
3.1.1 Effect of catalyst type

All seven catalysts were tested under same condition of temperature, feed mole ratio of reactants, agitation speed and catalyst loading. TBA Conversion and ETBE selectivity were determined for each catalyst. Following equations were used to calculate conversion and selectivity.

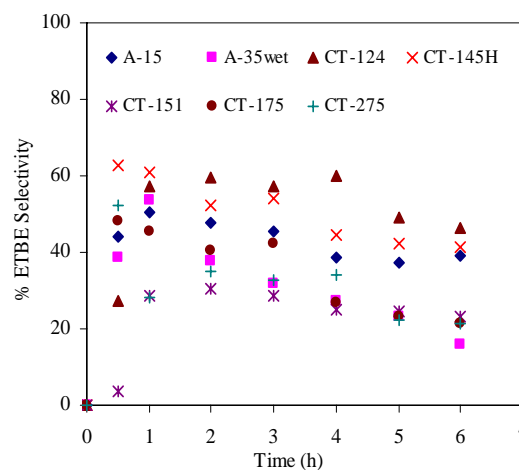
$$\% \text{ TBA Conversion} = \frac{(C_{\text{TBA},0} - C_{\text{TBA},t}) * 100}{C_{\text{TBA},0}} \quad (4)$$

$$\% \text{ ETBE selectivity} = \frac{(C_{\text{ETBE},t}) * 100}{(C_{\text{TBA},0} - C_{\text{TBA},t})} \quad (5)$$

where $C_{\text{TBA},0}$ and $C_{\text{TBA},t}$ are concentrations [K-mol/m^3] of TBA at time zero and time $t(h)$ respectively, while $C_{\text{ETBE},t}$ is concentration [K-mol/m^3] of ETBE at any time t . TBA conversion and ETBE selectivity of various catalysts are shown in Fig. 1 (a & b). It is evident from the figures that CT-175 and CT-275 yielded the maximum conversion but they resulted in poor selectivity, while CT-124 and CT-145H resulted in conversion upto 70 % but they gave selectivity around 60%. Amberlyst-15, Amberlyst-35 and CT-151 were not found suitable from selectivity standpoint. Therefore, it can be inferred that CT-124 and CT-145H are better than the rest of catalysts used in this study. Keeping in view the above results, these two catalysts were further investigated at different operating condition. Details about CT-145H are reported separately [10].



(a)



(b)

Figure 1. TBA conversion (a) and ETBE selectivity (b) for different catalysts at 343 K, 1:2 feed molar ratio and 5 % catalyst loading.

3.1.2 Effect of temperature

Experiments were carried out at 343, 348 and 353 K to find the TBA conversion and ETBE selectivity using CT-124. Results are shown in Fig. 2 (a, b, and c) respectively. These figures suggest that temperature of 343 K yielded best set of conversion and selectivity. Although the maximum value of selectivity is almost equal for all three temperatures but it becomes consistent after 4 hours at 343 K temperature while decreases with time for other two temperatures. The reason of decrease in selectivity at higher temperature can be attributed to the formation of IB, which reduces the selectivity towards ETBE. Same behavior was noticed for other catalysts at higher temperatures. Experiments were also conducted at lower temperatures (323 and 333 K) but those resulted in poor conversion. Based on the experimental

evaluation, 343 K was considered optimum temperature therefore; remaining experiments were conducted at this temperature.

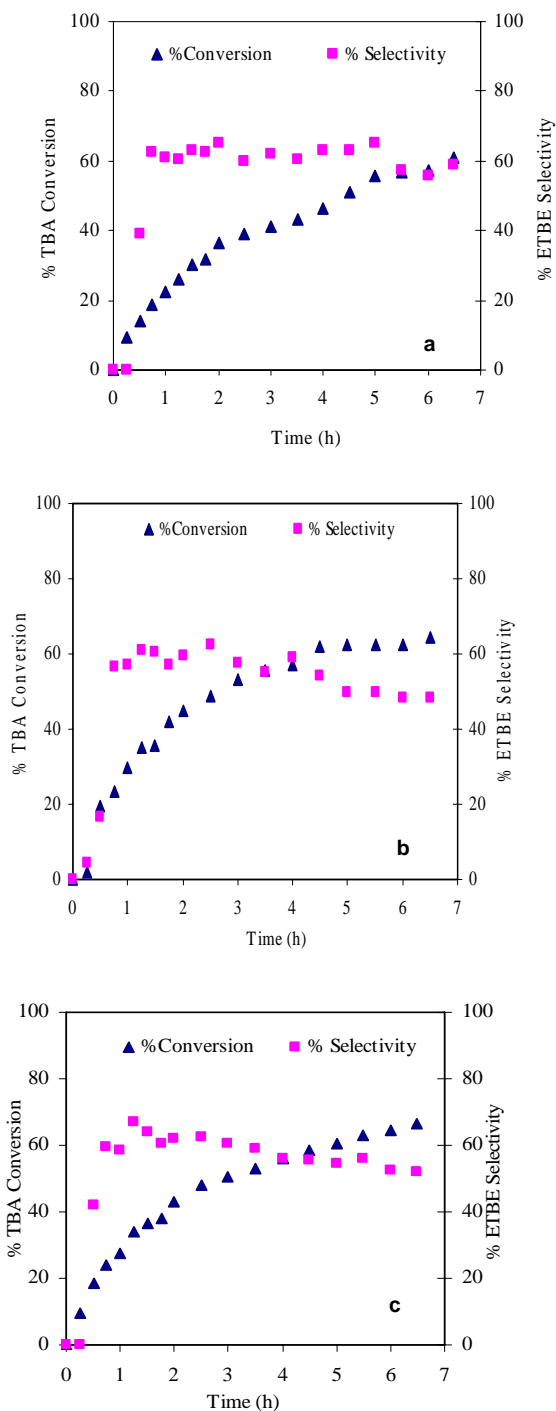


Figure 2. TBA conversion and ETBE selectivity at 1:2 FMR, 5 % catalyst loading and different temperatures (a) 343 K, (b) 348 K, (c) 353 K.

3.1.3 Effect of feed molar ratio (FMR)

Three different feed mole ratios were investigated to find their effect on conversion and selectivity. These ratios were 1:1, 1:2 and 1:4. Figures 3(a), 2(a) and 3(b) show the effect of feed mole ratios 1:1, 1:2 and 1:4 respectively on TBA conversion and ETBE selectivity using CT-124 catalyst. The 1:1 ratio did not produce appreciable conversion and selectivity as compared to those with higher ethanol concentration. It can be seen from these figures that 1:4 ratio gave better selectivity than that at 1:2 ratio but the conversion approximately followed the same trend. So it can be inferred that excess of ethanol beyond twice the limiting reactant is not so much beneficial in terms of selectivity and conversion. Therefore 1:2 mole feed ratio was considered optimum in this study.

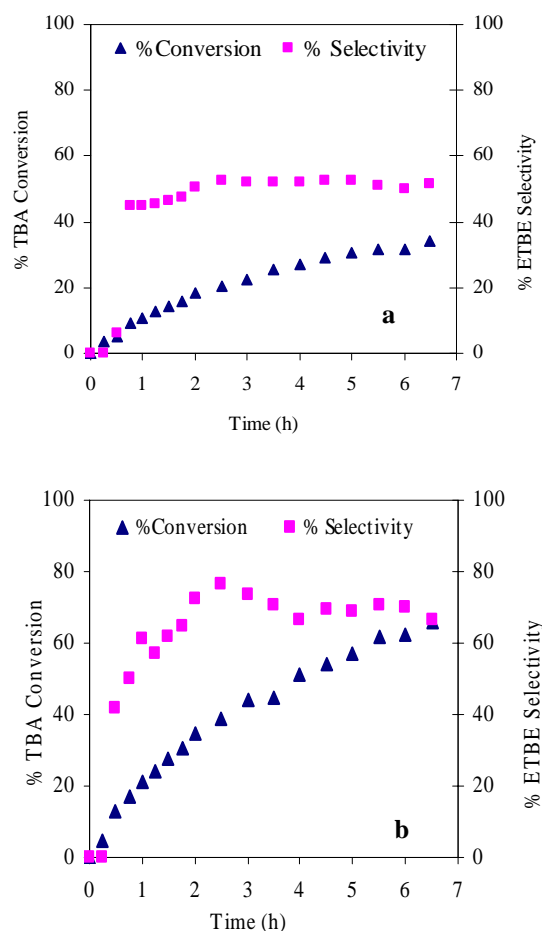


Figure 3. TBA conversions and ETBE selectivity at 1:1(a) and 1:4(b) FMR, 5 % catalyst loading, 343 K temperature and 5 % catalyst loading.

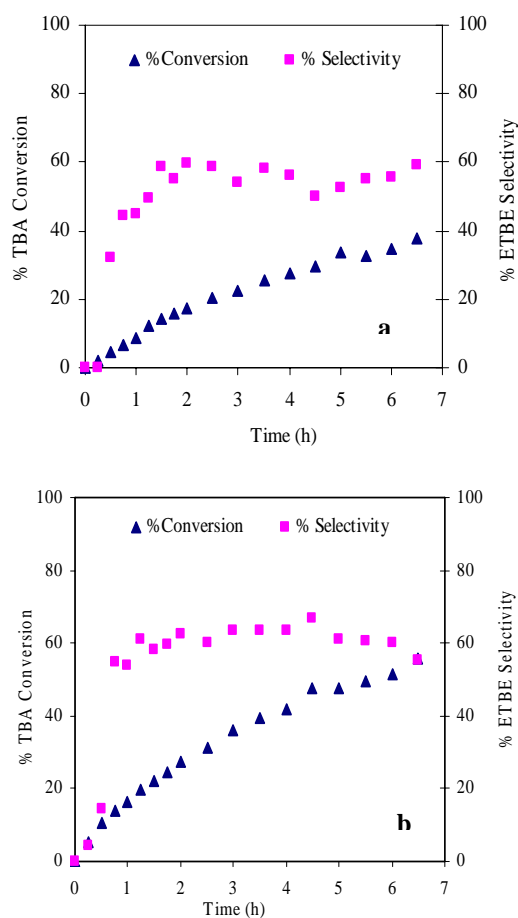


Figure 4. TBA conversion and ETBE selectivity at 2.5 w/w % (a) and 10 w/w % (b) catalyst loading of CT-124, 1:2 FMR and 343 K temperature.

3.1.4 Effect of catalyst loading

To find the effect of amount of catalyst added to the reaction system, conversion and selectivity were measured for three catalyst loadings, these are 2.5(w/w %), 5 (w/w %) and 10(w/w %) of the reaction mixture. Figures 4(a), 2(a) and 4 (b) shows how conversion and selectivity varies with increasing the amount of catalyst. It is observed that catalyst loading of 2.5% though yielded reasonably good selectivity but gave poor conversion. The 5% and 10% loading produced similar results in terms of conversion but selectivity was observed to be about 5% more in case of 10% catalyst loading. Since doubling the amount of catalyst did not yielded appreciable benefit in terms of conversion and selectivity therefore, 5% catalyst loading was considered optimum.

3.2 Kinetic modeling

The two models covering heterogeneous catalytic reaction namely Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Eley Riedel (E-R) models were applied to the experimental data obtained. Reaction rate expression for LHHW model can be expressed as

$$-r_A = \frac{k_1[a_A a_B - a_C a_D / K_{eq}]}{(1 + K_A a_A + K_B a_B + K_C a_C + K_D a_D)^2} \quad (6)$$

The reaction rate for E-R model is written as

$$-r_A = \frac{k_1[a_A a_B - a_C a_D / K_{eq}]}{(1 + K_A a_A + K_B a_B + K_C a_C + K_D a_D)} \quad (7)$$

where $-r_A$ is rate of reaction for limiting reactant [$K\text{-mol/m}^3$], k_1 is rate constant of reaction 1, K is equilibrium adsorption constant for each component, k_{eq} is equilibrium constant of reaction and a represents the activity of particular component. The subscripts A, B, C and D refer to TBA, EtOH, ETBE and water respectively. Activity coefficients were calculated using modified UNIFAC group contribution method [11].

When all experimental values were incorporated into model equations, both models gave very much analogous results. Multiple linear and non-linear regression techniques were used to find out the constants of equations 6 and 7 [12]. Both models were found to be non-coherent and inconsistent. The calculated values of adsorption constants as well as reaction rate constant were scattered and some negative values which of course is not plausible.

Since both the heterogeneous models were not found coherent therefore, Quasi-Homogeneous (Q-H) model was used to interpret the data. Equation for the Q-H model is

$$-r_A = k_1[a_A a_B - (a_C a_D / K_{eq})] \quad (8)$$

This model fitted well to the experimental data. Experimentally found conversions and those calculated using Q-H model at various temperatures is presented in Fig. 5

This figure depicts that Q-H model describes the system more adequately than the other heterogeneous models. Although the system is heterogeneous originally but it can be supposed that contents of reaction vessel are so intimately mixed that it almost approaches to homogeneous system.

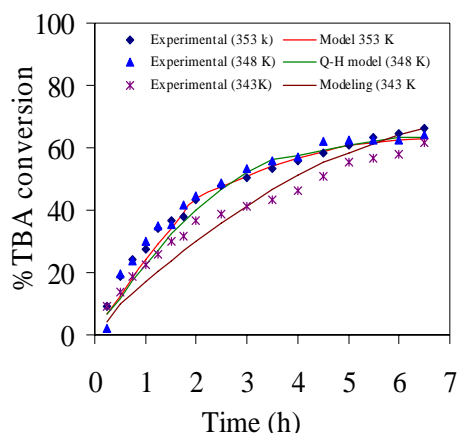


Figure 5. Experimental and Q-H model calculated TBA conversion for ETBE synthesis at various temperatures, 1:2 FMR and 5% catalyst loading.

Expression obtained for rate constant k_1 using Arrhenius equation for this system is given in following equation.

$$k_1 = \exp(11.827 - 6429.6/T) \quad (9)$$

Arrhenius plot was drawn for this system which is presented in Fig. 6. Arrhenius coefficient and activation energy are 1.8×10^5 and 53.4556 KJ respectively. These values are in agreement with the published literature [1].

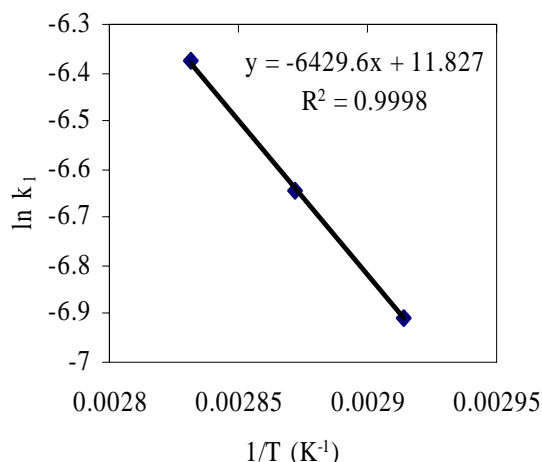


Figure 6. Arrhenius plot for ETBE synthesis on CT-124 catalyst.

4. Conclusions

Among the seven catalysts used for etherification of two alcohols in liquid phase to synthesize ETBE, two catalysts namely CT-124(gel based) and CT-145-H (macro porous) were found superior to others in terms of TBA conversion and ETBE selectivity. Among these two, CT-124 produced better results at 343 K as it yielded consistent selectivity with time while in case of CT-145H selectivity decreased after three hrs of reaction time. Feed mole ratio of 1:2 and catalyst loading of 5% were considered optimum for the system studied. Heterogeneous reaction models LHHW and E-R did not give the best fit while the Quasi-Homogeneous model portrayed the system more closely. Values for activation energy and Arrhenius coefficient for Q-H model are in range to those already published. In next phase of the study, these catalysts will be used for ETBE synthesis via reactive distillation in packed column.

Acknowledgements

MU is grateful to the Higher Education Commission (HEC) Pakistan for funding this research under International Research Support Initiative Program. Support of Dr. Krzysztof Ambroziak and the laboratory staff at Loughborough University is thankfully acknowledged.

References

- [1] B. Yang, S. Yang and R. Yao, *Reactive and Functional Polymers* **44** (2000) 167.
- [2] B. H. Bisowarno and M. O. Tade, *Industrial and Engineering Chemistry Research* **39** (2000) 1950.
- [3] C. Fite, M. Iborra, J. Tejero, J. F. Izquierdo and F. Cunnil, *Industrial and Engg. Chem. Res.* **33**, (1994) 581.
- [4] M.G. Sneesby, M.O. Tade', R. Datta and T.N. Smith, *Industrial and Engineering Chemistry Research* **36** (1997) 1855.
- [5] M. Matouq, A. T. Quitain, K. Takahashi and S. Goto, *Industrial and Engineering Chemistry Research* **35** (1996) 982.
- [6] X. Yin, B. Yang and S. Goto, *International Journal of Chemical Kinetics* **27** (1995) 1065.
- [7] A. Quitain, H. Itoh and S. Goto, *Journal of Chemical Engineering, Japan* **32** (1999) 280.

- [8] S. Assabumrangrat, W. Kiatkittipong, N. Sevitoon, P. Prasertdam and S. Goto, *Inter. J. of Chemical Kinetics* **34** (2002) 292.
- [9] S. Assabumrangrat, D. Wongwattanasate, V. Pavarajarn, P. Prasertdam, A. Arpornwichanop and S. Goto, *Korean Journal of Chemical Engineering* **21**, No. 6 (2004) 1139.
- [10] M.Umar, A R. Saleemi and S. Qaiser, *Catalysis Communications* **9** (2008) 721.
- [11] B.G. Kyle, *Chemical and Process Thermodynamics*, 3rd Ed. Prentice Hall PTR, 270, 2000.
- [12] M. B Cutlip and M. Shacham, "Problem Solving in Chemical Engineering with Numerical Methods", Prentice Hall International Series, **77** (1999) 357.