

EXPERIMENTAL KINETIC STUDY OF TRANSESTERIFICATION OF ETHYL ACETATE WITH METHANOL CATALYZED BY GEL AND MACROPOROUS ACIDIC ION EXCHANGE RESINS

Evelien Van de Steene^{1,2}, Jeriffa De Clercq^{1*}

*Faculty of Applied Engineering Sciences, University College Ghent,
Schoonmeersstraat 52, B-9000 Ghent, Belgium*

Joris W. Thybaut²

*Laboratory for Chemical Technology, Ghent University,
Krijgslaan 281, B-9000 Ghent, Belgium
(jeriffa.declercq@hogent.be)*

*Corresponding author: [Email: jeriffa.declercq@hogent.be](mailto:jeriffa.declercq@hogent.be)

ABSTRACT

The reaction kinetics of the liquid-phase transesterification of ethyl acetate with methanol to methyl acetate and ethanol, catalyzed by different strong acidic ion exchange resins, Lewatit K1221, K2629, K2649, K2640 and Amberlyst 15, have been investigated. The effect of the initial reactant molar ratio methanol : ethyl acetate and the temperature on the reaction kinetics was studied. Although Lewatit K2629, K2649, K2640 and Amberlyst 15 have approximately the same number of acid sites as Lewatit K1221, their catalytic activity is quite lower than that of K1221. This difference in catalytic activity can be explained by the degree of crosslinking with divinylbenzene (DVB).

Keywords: transesterification, ion exchange resin, kinetics, heterogeneous catalysis.

1. INTRODUCTION/BACKGROUND

Esters are of great significance in various industrial products including fragrances, flavours, solvents, plasticizers, medicinal and surface-active agents¹. Transesterification plays an important industrial role with numerous applications, e.g., the production of biodiesel, polyesters or PET in the polymer². Transesterification has traditionally been catalyzed by homogeneous catalysis such as alkaline bases or mineral acids. However, environmental and economic concerns are such that a continuous process with a heterogeneous catalyst is much more desirable³. The use of a strong acidic ion exchange resins as heterogeneous catalysts for the transesterification is a widely discussed item in literature⁴⁻⁸. These acid resins have inherently low surface areas unless a solvent is used to swell the polymer, thereby exposing additional internal acid sites for reaction⁵. Ali et al.⁶ and Sainio et al.⁹ described the differences in swelling degree between gel and macroporous resins. For the esterification, Ali et al.⁶ and Lee et al.¹⁰ found that a gel-type catalyst is more active than a macroporous, Amberlyst 15, catalyst. These effects were never investigated for transesterification.

2. EXPERIMENTAL

Methanol (Fiers) and ethyl acetate (Fiers) were used as reagents. *n*-Octane (Acros Organics) was used as internal standard. The ion exchange resins Lewatit K1221,

Lewatit K2640, Lewatit K2629, Lewatit K2649 (Lanxess) and Amberlyst 15 (Rohm & Haas) are spherical polystyrene-based resins beads crosslinked with divinylbenzene (DVB), with sulfonic acid groups. Lewatit K2649 is the dried form of Lewatit K2629. The properties of these resins are given in Table 1. Prior to transesterification, the resins were dried under vacuum at 233 K for 24 h to completely remove any moisture.

Table 1: Chemical and physical properties of ion exchange resins

Property	K1221	K2640	K2629 – K2649	Amberlyst 15
Appearance	Dark brown, translucent	Beige opaque	Beige, opaque	Deep grey-beige
Type	Gel	Macroporous	Macroporous	Macroporous
Acid site (eq/kg)	5.3	5.2	4.8	4.8
% DVB	4 %	18 %	18 %	20 %
Surface area ^a (m ² /g)		33	40	53
Pore volume ^a (cm ³ /g)		0.45	0.3	0.40
Bead size (mm)	0.4 – 1.25	0.4 – 1.25	0.4 – 1.2	0.3 – 1.2

^a Determinated on the dry form of the resin

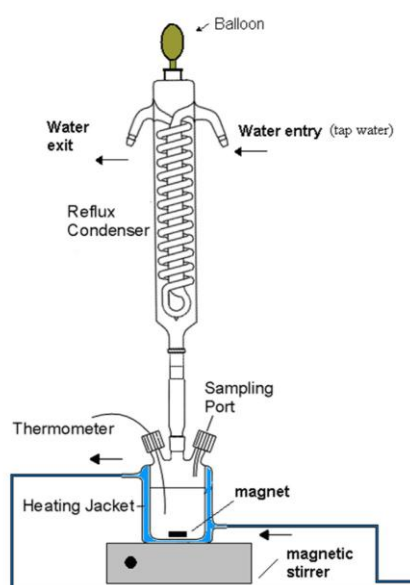


Figure 1: Experimental setup

The transesterification of ethyl acetate with methanol was carried out isothermally in a three-necked glass flask of 180 mL capacity equipped with a reflux condenser, a thermocouple and a sampling port, see Figure 1. The reaction mixture was stirred with a magnetic stirrer at a constant speed. The reactor was loaded first with methanol and catalyst and then heated to the reaction temperature. When this mixture reached the desired temperature, preheated ethyl acetate and *n*-octane were added through the sampling port in order to have a well determined starting point of the experiment without disturbing the reactor temperature. *n*-Octane was used as internal standard for analytical purposes and for obtaining a constant reaction volume. All experiments have been performed at atmospheric pressure. Each experiment was performed at least quadruple with an experimental error below 5%. The range of experimental conditions is given in Table 2.

Samples of the reaction mixture were withdrawn through the sampling port every 1800 s. The samples were analyzed by gas chromatography using a Focus GC, equipped with an AS3000 auto sampler, a Stabilwax capillary column (30 m x 0.32

mm, 0.25 μm thickness) and a flame ionization detector. Conversions were calculated as follows:

$$X_i = \frac{C_{i,0} - C_{i,t}}{C_{i,0}} \quad (1)$$

where X_i is the conversion of reactant i , $C_{i,0}$ the initial concentration of i and $C_{i,t}$ the concentration of i at time t ¹¹.

Table 2. Range of experimental conditions

Temperature (K)	303.15 – 333.15
Pressure (MPa)	0.1
MeOH:EtOAc molar ratio	1:1 – 10:1
Mass of catalyst (10^{-3} kg)	0.5 – 5.0
Batch time* (kg s)	12.6 – 126

* Defined as product of experiment time multiplied by the mass of catalyst

Some independent swelling tests have been performed with the scope to evaluate the swelling factors of the resins in contact with different solvents. The swelling ratio (or swelling factor) of a crosslinked resin is defined as the ratio between the volume of, respectively, the swollen resin, in the presence of a particular solvent, and the volume of the dry resin¹⁵. This parameter was determined at room temperature by using a graduate cylinder of 25.0 mL with 10.0 mL of dry resin. 25.0 mL of solvent was gradually added to the resin. After 5 minutes the volume of the wet resin was examined. From the two volumes (dry and swollen) the swelling ratio can be calculated.

3. RESULTS

3.1 Catalytic activity

The catalytic activity of the 5 ion exchange resins for the transesterification is shown in Figure 2. Lewatit K1221 has a noticeably higher activity than the others, despite the comparable active site concentration, see Table 1. The catalytic activity of K2629, K2640 and K2649 are quite similar. Amberlyst 15 shows the lowest catalytic activity for the transesterification.

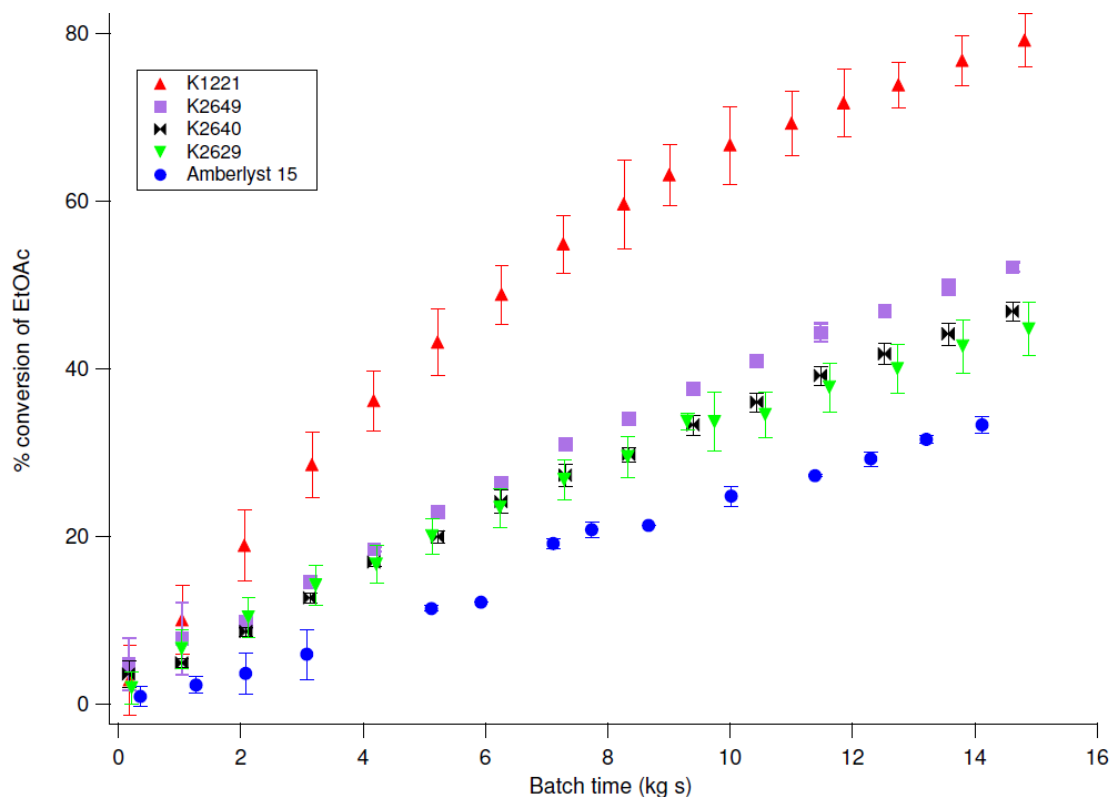


Figure 2: Experimental conversion of ethyl acetate versus batch time catalyzed by different ion exchange resins (legend). (Molar ratio of MeOH:EtOAc = 10:1, Temperature = 333 K)

3.2 Temperature and molar ratio effect

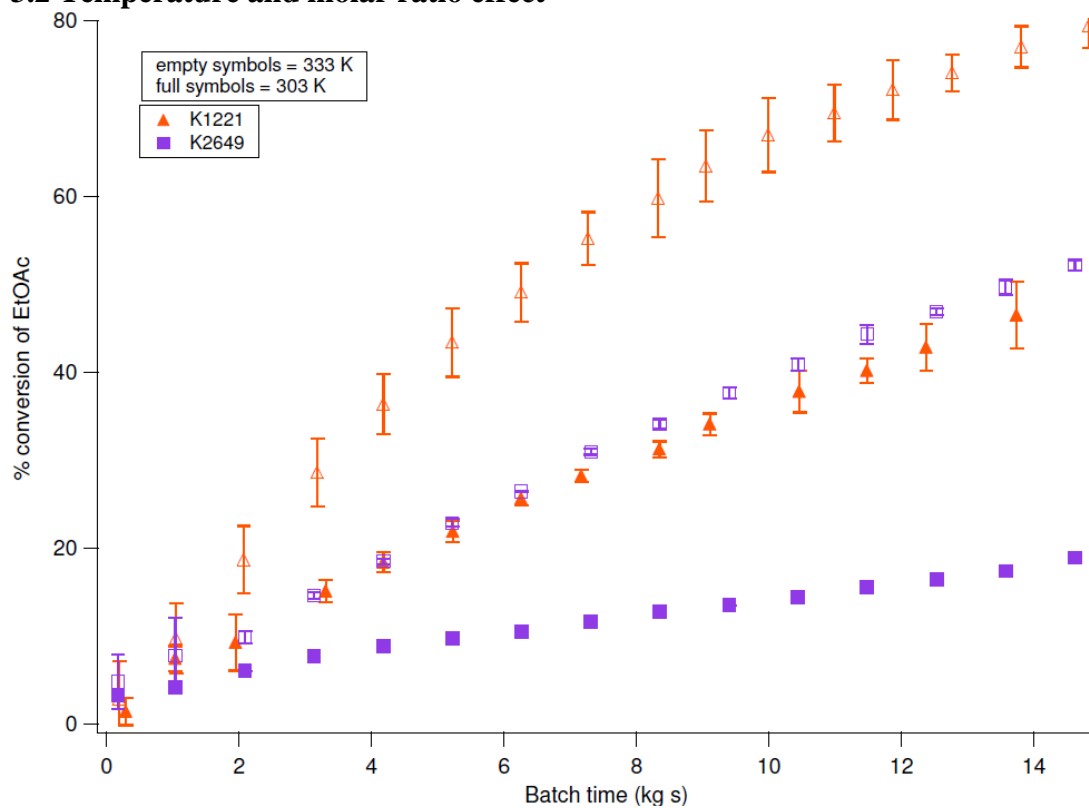


Figure 3: Experimental conversion of ethyl acetate as function of the batch time catalyzed by gel (K1221) and macroporous (K2649) ion exchange resins (legend) and at different temperatures (legend) (initial molar ratio MeOH:EtOAc = 10:1)

The effect of temperature (303 - 333 K) was investigated for both gel and macroporous resins. In accordance with the Arrhenius law, a higher temperature results in a higher reaction rate and a correspondingly higher ethyl acetate conversion at the same batch time, see Figure 3.

Also the effect of the initial methanol to ethyl acetate ratio (1:1 – 10:1) on the transesterification of ethyl acetate and methanol catalyzed with both gel or macroporous resins was investigated. Higher molar ratios result in higher ethyl acetate conversions, see Figure 4. Because the ethyl acetate/catalyst amount ratio was kept constant in these experiments, this also corresponds to higher reaction rates. If the initial molar ratio increases from 1:1 to 5:1, an increase in conversion for K1221 and K2649 of respectively 41% and 25% is obtained. If the initial molar ratio increases from 5:1 to 10:1 a respectively increase in conversion of 14% and 5% is observed.

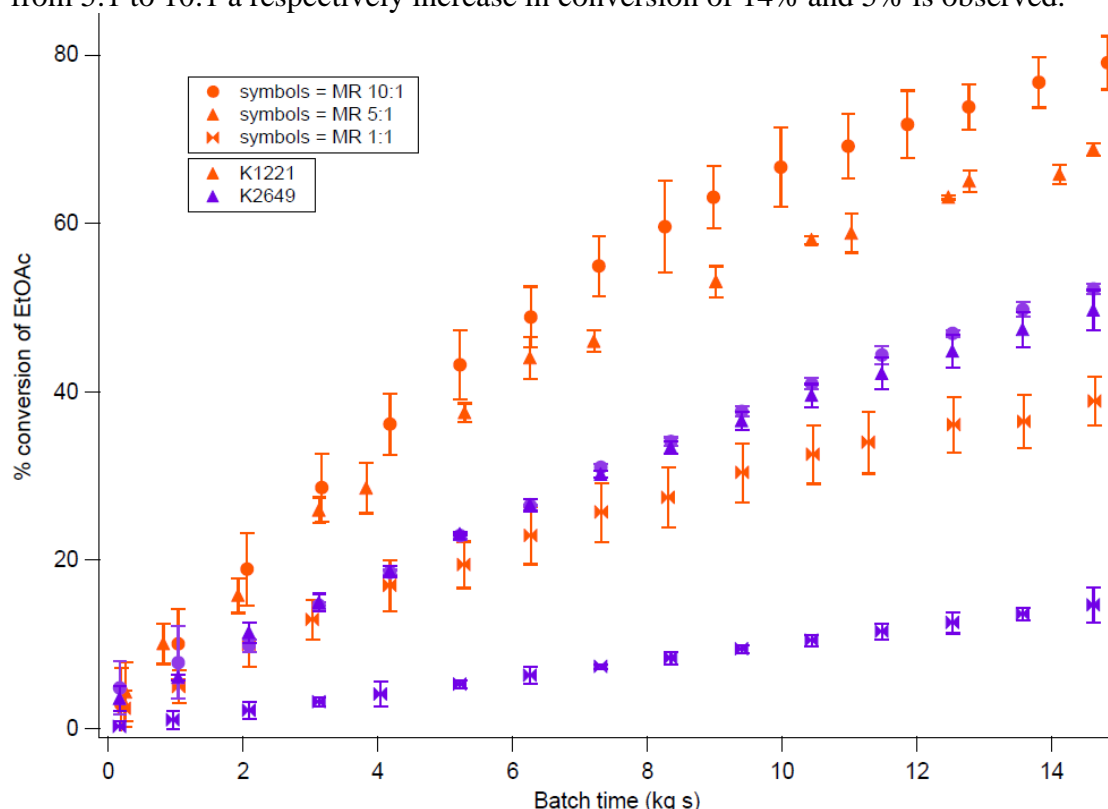


Figure 4: Experimental conversion of ethyl acetate as function of the batch time catalyzed by gel (K1221) and macroporous (K2649) ion exchange resins (legend) and at different initial molar ratios MeOH:EtOAc (legend) (temperature = 333 K)

3.3 Volumetric swelling experiments

The results obtained from the swelling tests are shown in Figure 5 and Figure 6. All the components swell both gel and macroporous resins. Figure 5 shows that the swelling ratio of the catalyst K1221, is found to decrease in the order of methanol > ethanol > ethyl acetate = methyl acetate. The affinity order of the solvents for the polymer is the same for all resins, as is expected due to the chemical similarity of the resins. From Figure 6 it can be appreciated that the gel type resin, K1221 shows obviously a higher swelling ratio than the macroporous resins, K2640 and K2649. K2649 shows a slightly higher swelling ratio than K2640, although both resins have the same amount of crosslinking (18%). Increase in the crosslinking density is found to decrease the swelling ratio, hence the sorbed amount of each solvent will decrease.

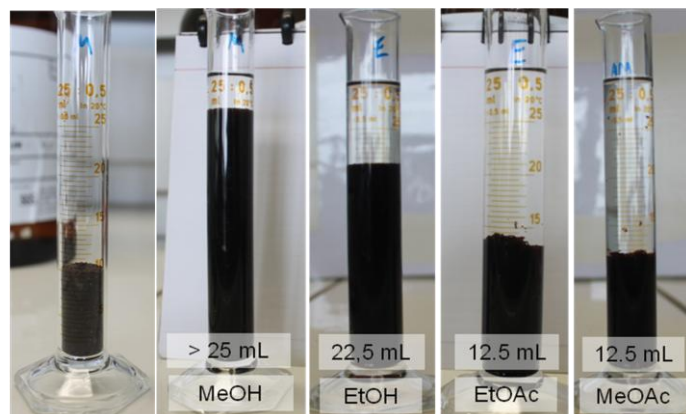


Figure 5: Experimental determination of the swelling behavior of Lewatit K1221 in different reaction medium (Legend). Left: 10 mL of dry K1221, Right: volume of wet K1221.

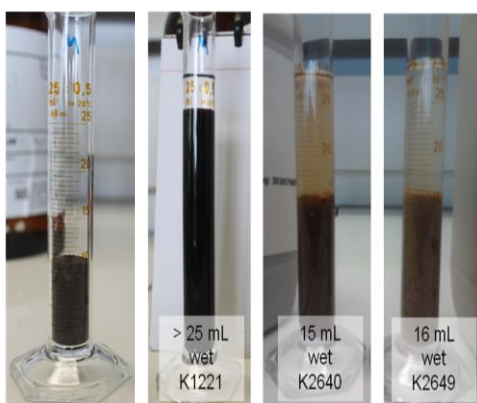


Figure 6: Experimental determination of the swelling behavior of different resins (Legend) in methanol. Left: 10 mL of dry resin, Right: amount of wet, swollen resin.

4. DISCUSSION

The reaction rate of the resin-catalyzed transesterification is clearly dependent on the number of active sites and their accessibility. Since the initial reaction rate, i.e. the slope of the concentration profile at time zero, is not proportional with the number of active sites, especially their accessibility needs to be considered. The latter is affected by the divinylbenzene (DVB) content, e.g., a higher content will reduce the swelling ability of the resin and therefore reduce the accessibility of the active sites. The gel resin K1221 is on a microscopic scale a homogeneous matrix with no discontinuities⁵, see Figure 7(left). If the totally dry gel beads are placed in a polar reaction medium, e.g., pure methanol, swelling with ca. 110 % of its initial volume will occur, hence all the active sites in the body of the bead and on the bead's surface are available for the reactants, see Figure 7. The macroporous resins K2649, K2640, K2629 and Amberlyst 15, consist of agglomerates of very small microspheres interspersed with macropores^{12, 13}, see Figure 7(right). If these dry macroporous resins are placed in a polar reaction medium, e.g., pure methanol, swelling of ca. 55 % will occur. The reactants may move easily through the macropores into the interior of the bead¹³. The sorption of the reactants in the microspheres generates an osmotic pressure that turns out to be balanced by the elastic counter-forces which are due to the existence of the cross-linking effect^{14, 15}. Hence, only the active sites on the surface, in the macropores and in the swollen part of the microspheres are available for reactants, see Figure 7.

The osmotic pressure will increase with an increase of cross linking density^{6, 9}, resulting in the lowest catalytic activity for Amberlyst 15.

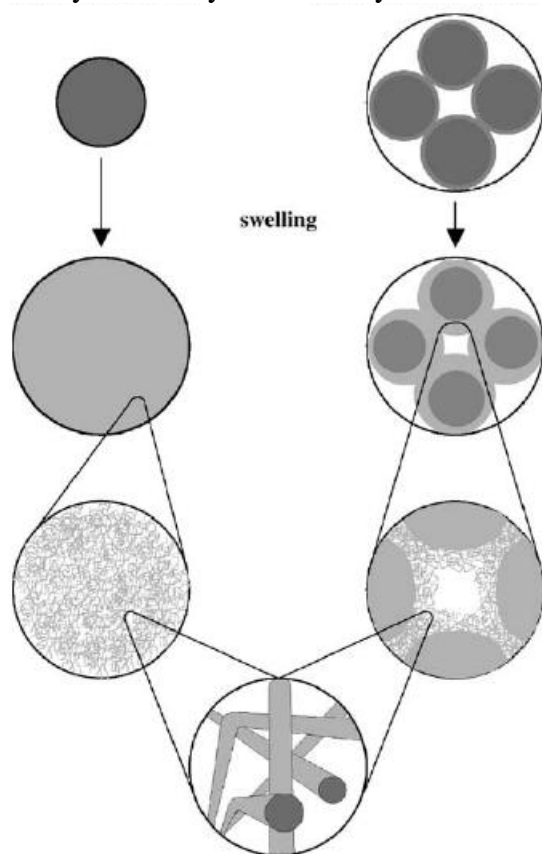


Figure 7. Schematic representation of the micro- and nanoscale morphology of gel (left) and macroporous (right) resins¹⁶.

The DVB content of K2649, K2640 and K2629, is the same, nevertheless the catalytic activity is not comparable. K2649 is the dry form of K2629, both should have the same catalytic activity up to 5.0 kg_{cat} s. K2640 is a polysulfonated resin, c.q. more than 1 sulfonic acid groups are on one aromatic ring, hence sulfone bridging will occur¹⁷. Although these higher acid concentration, the sulfone bridging will decrease the swelling ability and reduce the catalytic activity of these resin, see Figure 6.

The differences in reaction rate, obtained as an effect of the initial molar ratio (Figure 4) are a combination of a different swelling degree and an excess of the reactant, c.q., methanol. At a molar ratio of 1:1 the reaction medium is, due to the small amount of methanol, less polar than at higher molar ratios. With more polar components, the swelling of the resin is higher and, hence, the accessibility of the active sites is improved⁵. Swelling experiments, Figure 5, show a higher wet volume of the resin in a more polar solvent. Figure 6 shows a higher swelling ratio for the gel type resin (K1221) than the macroporous (K2649 and K2640). Hence, with an increase in initial molar ratio, the increase in reaction rate for the transesterification, catalyzed by Lewatit K1221, is higher than if the reaction is catalyzed by Lewatit K2649.

5. CONCLUSIONS

Acid ion exchange resins can be used as catalysts for the transesterification. The catalytic activity is function of the active sites and inversely proportional with the

amount of cross-linking by DVB. Increasing the temperature or the molar ratio will increase the reaction rate. The degree of swelling explain the differences in catalytic activity between gel and macroporous resins. Highest reaction rates are obtained with gel type resins in a polar reaction medium.

Acknowledgements

The Research Fund of the University College Ghent and the faculty of Engineering and Architecture of Ghent University are acknowledged for their financial support. Lanxess is acknowledged for providing the ion exchange resins. Jean Moriau and Rudolf Wagner are acknowledged for their scientific knowledge about ion exchange resins.

REFERENCES

1. Ali SH. Kinetics of Catalytic Esterification of Propionic Acid with Different Alcohols over Amberlyst 15. *International Journal of Chemical Kinetics* Jun;**41**(6):432-48.(2009).
2. Dossin TF, Reyniers MF, Berger RJ, Marin GB. Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. *Applied Catalysis B-Environmental* Sep;**67**(1-2):136-48.(2006).
3. Van de Steene E, De Clercq J, Thybaut JW. Adsorption and reaction in the transesterification of ethyl acetate with methanol on Lewatit K1221. *Journal of Molecular Catalysis A: Chemical*;**359**(0):57-68.(2012).
4. Sert E, Atalay FS. Determination of Adsorption and Kinetic Parameters for Transesterification of Methyl Acetate with Hexanol Catalyzed by Ion Exchange Resin. *Industrial & Engineering Chemistry Research* May;**51**(18):6350-5.(2012).
5. Chakrabarti A, Sharma MM. CATIONIC ION-EXCHANGE RESINS AS CATALYST. *React Polym.* [Article] Jul;**20**(1-2):1-45.(1993).
6. Ali SH, Al-Rashed O, Azeez FA, Merchant SQ. Potential biofuel additive from renewable sources - Kinetic study of formation of butyl acetate by heterogeneously catalyzed transesterification of ethyl acetate with butanol. *Bioresour Technol* Nov;**102**(21):10094-103.(2011).
7. Zanette AF, Barella RA, Pergher SBC, Treichel H, Oliveira D, Mazutti MA, et al. Screening, optimization and kinetics of *Jatropha curcas* oil transesterification with heterogeneous catalysts. *Renewable Energy* Feb;**36**(2):726-31.(2011).
8. Zielinska-Nadolska I, Warmuzinski K, Richter J. Zeolite and other heterogeneous catalysts for the transesterification reaction of dimethyl carbonate with ethanol. *Catalysis Today* May;**114**(2-3):226-30.(2006).
9. Sainio T, Laatikainen M, Paatero E. Phase equilibria in solvent mixture-ion exchange resin catalyst systems. *Fluid Phase Equilib.* [Article] Apr;**218**(2):269-83.(2004).
10. Lee MJ, Wu HT, Lin HM. Kinetics of catalytic esterification of acetic acid and amyl alcohol over Dowex. *Industrial & Engineering Chemistry Research* Nov;**39**(11):4094-9.(2000).
11. Froment GF, Bischoff KB. *Chemical Reactor Analysis and Design*. second edition ed: Wiley; 1990.
12. Silva V, Rodrigues AE. Kinetic studies in a batch reactor using ion exchange resin catalysts for oxygenates production: Role of mass transfer mechanisms. *Chemical Engineering Science* Jan;**61**(2):316-31.(2006).
13. Ihm SK, Ahn JH, Jo YD. Interaction of reaction and mass transfer in ion-exchange resin catalysts. *Industrial & Engineering Chemistry Research* Sep;**35**(9):2946-54.(1996).
14. Christensen SG, Thomsen K. Experimental measurement and modeling of the distribution of solvent and ions between an aqueous phase and an ion exchange resin. *Fluid Phase Equilib* Feb;**228**:247-60.(2005).

15. Tesser R, Di Serio M, Casale L, Carotenuto G, Santacesaria E. ABSORPTION OF WATER/METHANOL BINARY SYSTEM ON ION-EXCHANGE RESINS. *Canadian Journal of Chemical Engineering* Dec;**88**(6):1044-53.(2010).
16. Corain B, Centomo P, Lora S, Kralik M. Functional resins as innovative supports for catalytically active metal nanoclusters. *Journal of Molecular Catalysis a-Chemical Sep*;**204**:755-62.(2003).
17. Martins CR, Ruggeri G, De Paoli MA. Synthesis in pilot plant scale and physical properties of sulfonated polystyrene. *J Braz Chem Soc Sep-Oct*;**14**(5):797-802.(2003).