

## **A reactive poly(styrene sulfonic acid) catalyst preparation and usage for fuel additive ester production**

Filiz Ugur Nigiz, Nilufer Durmaz Hilmioglu

Online Publication Date: 23 Sept 2016

URL: <http://dx.doi.org/10.17515/resm2016.45ma0613.html>

DOI: <http://dx.doi.org/10.17515/resm2016.45ma0613>

Journal Abbreviation: *Res. Eng. Struct. Mat.*

### **To cite this article**

Nigiz FU, Hilmioglu ND. A reactive poly(styrene sulfonic acid) catalyst preparation and usage for fuel additive ester production. *Res. Eng. Struct. Mat.*, 2017; 3(2): 89-97.

### **Disclaimer**

All the opinions and statements expressed in the papers are on the responsibility of author(s) and are not to be regarded as those of the journal of Research on Engineering Structures and Materials (RESM) organization or related parties. The publishers make no warranty, explicit or implied, or make any representation with respect to the contents of any article will be complete or accurate or up to date. The accuracy of any instructions, equations, or other information should be independently verified. The publisher and related parties shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with use of the information given in the journal or related means.



Research Article

## A reactive poly(styrene sulfonic acid) catalyst preparation and usage for fuel additive ester production

Filiz Ugur Nigiz<sup>\*,1</sup>, Nilufer Durmaz Hilmioğlu<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Kocaeli University, Kocaeli, Turkey

### Article Info

Article history:

Received 13 June 2016

Revised 19 Sept 2016

Accepted 23 Sept 2016

Keywords:

Ethyl valerate,

Poly(styrene sulfonic acid),

Reactive polymer,

Fuel additive

### Abstract

The production of new generation fuels from sustainable resource is prominent issue of the current world. A wide range of feedstock can be used to produce first generation liquid fuel from starch to corn. Besides the first one, second generation fuel is considered as fuel additive for increasing the calorific value of gasoline and limiting the hazardous gas emission. Only small amount usage of lignocellulosic based additives such as ethyl valerate (EV) increases the energy density of fuel. Due to the non-hazardous and less irritant properties of ethyl valerate it is defined as "green fuel". It was reported that the 10-20% blend ratio of EV with gasoline causes a significant improvement for engine performance. EV is chemically produced by esterification reaction between ethanol and valeric acid. Reaction can be carried out by means of heterogeneous, homogeneous acid catalyst, lipase and ionic liquids and reactive polymers. In this study, a reactive poly (styrene sulfonic acid) (PSSA) catalyst was prepared and used for ethyl valerate synthesis at different temperature conditions. Effect of alcohol:acid feed molar ratio was also investigated as a function of acid conversion. Better results were obtained as 77.9 % acid conversion at 343 K when alcohol:acid feed molar ratio was 4:1.

© 2016 MIM Research Group. All rights reserved.

## 1. Introduction

Depletion of carbon based fossil fuels, increasing of world's energy demand with increasing number of transportation vehicle and environmental regulations resulted by global warming and climate changes are obligated both producers and consumers to use alternative sustainable energy source [1-3]. Wind energy, solar energy, fuel cells are important instantaneous energy types consumed by different industry. However, the energy intensity of this type of source are relatively low, they are not storable and cannot be used practically. Especially for transportation vehicle, bio based fuels such as diesel or bio alcohols are popular sustainable source due to the large quantity of production capacity. Among them, lignocellulosic biomasses are more abundant.

Biomass based first generation fuels have long been used for transportation and using them as fuel has become mandatory making legal arrangement by governments.

Second generation fuels such as valeric acid esters has been also considered as fuel additive for increasing the calorific value of gasoline since 2004. Beside them, ethyl valerate (EV) –ethyl pentanoate- is a high performance fuel additive candidate that can be fully compatible both with gasoline and diesel [4, 5]. EV has seven carbon numbers so the calorific value is higher than ethanol. Due to the low vapor pressure compared to gasoline and ethanol, it reduces the carbon emissions [5-7]. Different from the ethanol, EV does not form an azeotrope with water. Hence, the cost of production and separation process of EV is relatively low. Fuel performance of 15 % vol. In the literature, exhaust

\*Corresponding author: [filiz.ugur@kocaeli.edu.tr](mailto:filiz.ugur@kocaeli.edu.tr)

DOI: <http://dx.doi.org/10.17515/resm2016.45ma0613>

Res. Eng. Struct. Mat. Vol. 3 Iss. 2 (2017) 89-97

emission, fuel performance and drivability of EV-gasoline mixture has been tested. Researchers have reported that the blend fuel significantly increases the engine performance without negative effect on engine equipments (pipe, valve, storage tank) [5,6].

Ethyl valerate is produced by esterification of bio based valeric acid and ethanol. It can be synthesized automatically or different catalysts are used to increase reaction yield and decrease time period. Homogeneous catalyst such as Bronsted solutions, heterogeneous catalyst such as metal oxide, SiO<sub>2</sub>, HZSM-5, and lipases are used to catalysis ethyl valerate production [6-12]. Although homogeneous catalysts have high performance for this reaction, they cause corrosion in engine storage when they react by trace amount of water and H<sub>2</sub>S. Additionally, recovering of these catalysts from the reaction media is difficult [7]. Heterogeneous catalysts have many advantages over the homogeneous ones such as lack of corrosive properties, easy reuse and recovery. They can be divided into groups such as zeolites, clays, heteropoly acids, composites, ion exchange resins and reactive polymers. Reactive polymers are the smart organic materials that have many catalytic sites to catalyze different type of reactions [13-15]. Among them, poly (styrene sulfonic acid) (PSSA) plays an important role owing to the homogeneously distributed high concentrations of acid sites [16-20]. Owing to the high proton conductivity it is used as conductive polymer in fuel cells. Additionally, it has high ion exchanging capacity so it is formed as catalytic resin (Amberlyst XN10) and used in chemical reactions process [21-23].

In this study, PSSA polymeric catalyst was prepared to catalysis the ethyl valerate esterification. In order to enhance the mechanical durability of reactive polymer, it was blended with carboxy methylcellulose (CMC). Reactions were carried out for seven hours. Equal molar ratio of ethanol and valeric acid were used. Small pieces of blend membrane were used as heterogeneous catalyst. And the activity of polymer was compared with a homogeneous catalyst (sulfuric acid). Both CMC and PSSA were hydrophilic polymer and to prevent the dissolution of PSSA into aqueous media, a cross-linking method was applied. Effect of temperature, initial feed molar ratio on valeric acid conversion were evaluated. The structural properties of catalytic membrane were analyzed by using scanning electron microscope (SEM). The thermal behavior of membrane was evaluated by means of thermal gravimetric analysis (TGA). In order to increase the mechanical strength of PSSA, it was blended with CMC. Both of them were hydrophilic and a cross-linking procedure was applied to prevent dissolving into aqueous reaction media. To determine the cross-linking efficiency FTIR analysis was also applied.

## **2. Material and Method**

### **2.1. Materials**

Poly(styrene sulfonic acid), carboxymethyl cellulose, sulfuric acid and ethanol (99% purity) were purchased from Aldrich Chemicals. Glutaraldehyde (GA), hydrochloric acid (HCl), acetone was supplied from Merck Chemicals in Turkey.

### **2.2 Catalyst Preparation**

In this study a reactive polymer was prepared and used for ethyl valerate synthesis. Reactive polymer catalyst was formed as thin membrane film to prevent the mass transfer limitation. The sulfonic acid groups in polymer were responsible for the catalytic activity of polymer. Therefore, prepared film should be as thin as possible to allow contact of substrate and sulfonic groups. For the preparation of reactive-catalytic polymer solution 2.5 wt. % PSSA and 1.5 wt. % CMC polymer was added to 100 ml distilled water. This solution was stirred for 10 hours at room temperature. After a

homogeneous polymer solution was obtained, the solution was cast onto a poly(methyl methacrylate) plate. Catalyst film was dried for three days at room temperature and it was kept in a cross-linking bath (consisted of 25 vol. % water, 75 vol. % acetone and 1 vol. % HCl and glutaraldehyde) for four hours to prevent dissolving of polymers in the reaction media. Catalytic polymeric film has been shown in Fig. 1.

### 2.3 Catalyst Characterization

CMC-PSSA blend polymeric catalyst was screened by using a JEOL JSM-6335 F Field Emission Scanning Electron microscope. Liquid nitrogen was used to prepare the membrane sample. Thermogravimetric analysis (TGA) of catalyst was taken at Tubitak Marmara Research. A Perkin Elmer Furrier Transform Infrared Spectroscopy was used to characterize the cross-linking efficiency of polymeric thin film catalyst.

### 2.4 Experimental Setup

Reactions between the ethanol and valeric acid were carried out in three-necked glass flask reactor at different temperature (323 K, 333 K and 343 K) and initial alcohol:acid molar ratio (M) (M=1, M=2, M=4). Reaction set-up has been shown in Fig. 1.

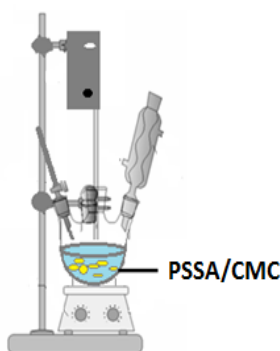


Fig. 1. Experimental reaction set-up

Catalyst film was cut into equal pieces and settled in the reactor. With an hourly interval, 0.2 µm samples were taken from the reactor and analyzed by using titration method and Gas chromatography. In this study, thermal conductivity detector (TCD) and HP-FFAP column equipped with GC (Agilent 7980) was used. The carrier gas was nitrogen. Detector temperature was arranged to 280 °C, oven temperature was 220 °C and injector temperature was 240 °C.

Free valeric acid content was calculated as equation 1, conversion was calculated as shown in equation 2.

$$F(\text{wt.}\%) = \frac{N_{\text{KOH}} \cdot V_{\text{KOH}} \cdot MW_{\text{VA}}}{1000 \cdot W_{\text{sample}}} \cdot 100 \tag{1}$$

$$X = \frac{n_{A_0} - n_A}{n_A} * 100 \tag{2}$$

F; free valeric acid concentration,  $N_{\text{KOH}}$ ; normality of consumed KOH solution,  $V_{\text{KOH}}$ ; volume of consumed KOH solution,  $MW_{\text{VA}}$ ; molecular weight of valeric acid,  $W_{\text{sample}}$ ; weight of analyzed sample,  $n_{\text{A0}}$  and  $n_{\text{A}}$ ; initial and final moles of valeric acid respectively.

### 3. Results and Discussions

#### 3.1 Characterization of Catalyst Film

Fig. 2 shows the microscope shots of PSSA-CMC catalyst. Fig. 2a represents the circular PSSA powder. Homogeneous PSSA distribution in catalytic film was seen in Fig. 2b, 2c and 2d.

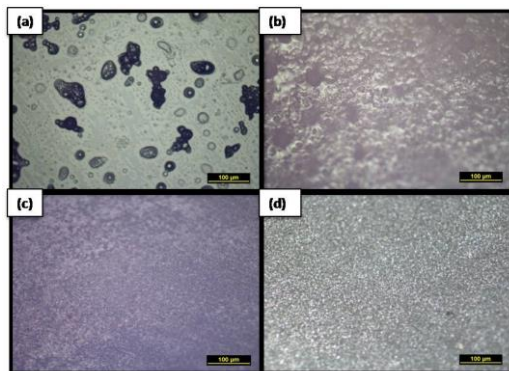


Fig. 2. Photomicrographs of PSSA catalyst

PSSA-CMC layer can be seen in Fig. 3 clearly. The dark side represents the PSSA polymer and the light region is attributed to CMC polymer.

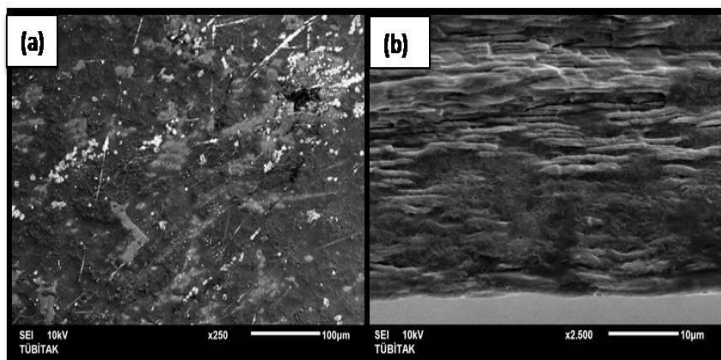


Fig. 3. SEM micrographs of catalytic film

Water is also formed by valeric acid-ethanol esterification. Because of the hydrophilic characters of PSSA and CMC, catalytic film shows a swelling and decomposition tendency in aqueous reaction media. Hence, a cross-linking procedure should be applied to reinforce the polymeric film. In order to comprehend the cross-linking reaction between the GA and CMC-PSSA, FTIR analyze was done after the reaction. As seen in Fig. 4, the peaks were seen in  $1370 \text{ cm}^{-1}$  -  $1410 \text{ cm}^{-1}$  and  $1120 \text{ cm}^{-1}$  regions were corresponding to  $\text{cm}^{-1}$  cross-linking formation between the GA and polymer. Additionally, it was obtained

that the cross-linking bonds were not destroyed after the reaction. Hence, it was proved the reusability of polymeric catalyst without a cross-linking degradation.

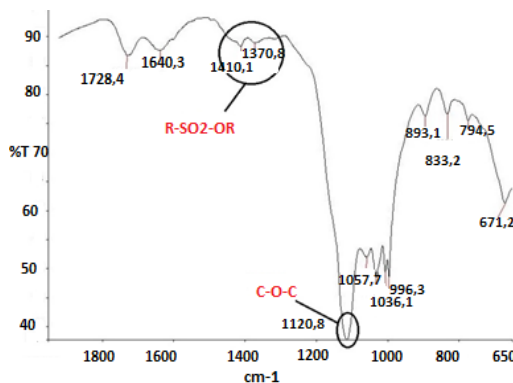


Fig. 4. FTIR spectra of cross-linked catalytic film after the reaction

TGA measures the amount of weight loss of the membrane as a function of increasing temperature. TGA analysis is very important to determine thermal behavior of membrane material under the different temperature. It is also important to determine membrane stability during the numerous of experiments under the harsh operating conditions. In this study a method was identified that the temperature changed from 25°C to 600°C routinely and the weight loss was recorded. TGA results of blend membrane and CMC polymer is seen in Fig. 5. As can be seen at spectra, there is no thermal degradation at operating temperature range (323 K – 343 K) of PSSA added CMC membrane after the reaction.

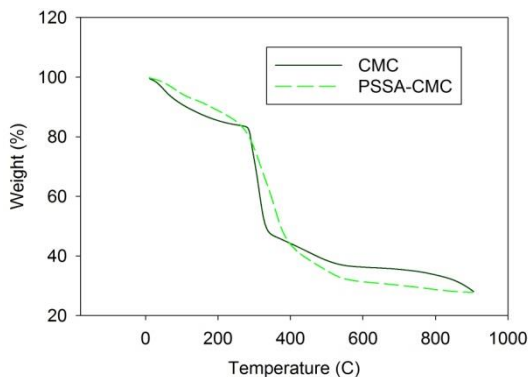


Fig. 5. TGA curves of CMC and PSSA-CMC composite catalytic membrane after the reaction

### 3.2 Determination of Reaction Time

Fig. 6 shows the conversion trend of esterification at 343 K when alcohol:acid initial feed molar ratio is 1.

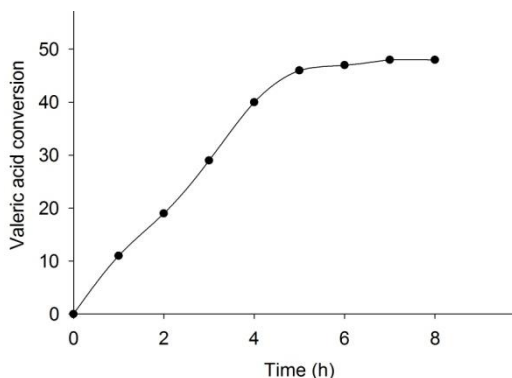


Fig. 6. Determination of reaction time (M=1, 343 K)

It was observed from the figure that the conversion results are almost same after eight hours. Then it was considered that the eight hours was enough to evaluate the effect of operation conditions on valeric acid conversion.

### 3.3 Effect of Temperature on Acid Conversion

Ethyl valerate production is an endothermic reversible reaction so the performance of the reaction is directly related to temperature. Temperature increases the rate of reaction and conversion enhances as can be seen in Fig. 7. When temperature changed from 323 K to 343 K, valeric acid conversion increased from 28 % to 48 % when the initial feed molar ratio was 1. Alter from the other homogeneous and heterogeneous catalyst, PSSA/CMC film absorbs the formed water. According to the Le Chatelier's principle, removal of the water from reaction media increases the overall reaction yield. Due to the swelling tendency of polymeric film, water uptake capacity increases with temperature. Hence, the temperature shows double effect on the conversion of valeric acid when a reactive polymer is used as catalyst. After the reaction is completed, swollen film is removed from reaction media. After a simply desorption process, it can be used over a long time period.

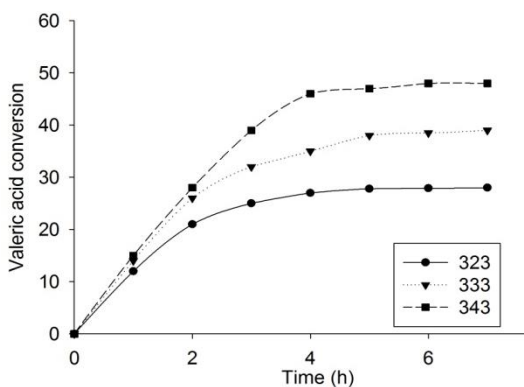


Fig. 7. Effect of temperature on conversion (M=1)

### 3.4 Effect of Initial Molar Ratio on Acid Conversion

In order to determine the reaction behavior at different conditions, effect of initial feed molar ratio on conversion was also investigated. In this reaction, valeric acid is the

limiting reactant, so excess mole of alcohol was used to determine conversion change. As seen in Fig. 8, conversion increased from 48 % to 77.9 % when initial molar ratio increased from 1 to 4 at 343 K.

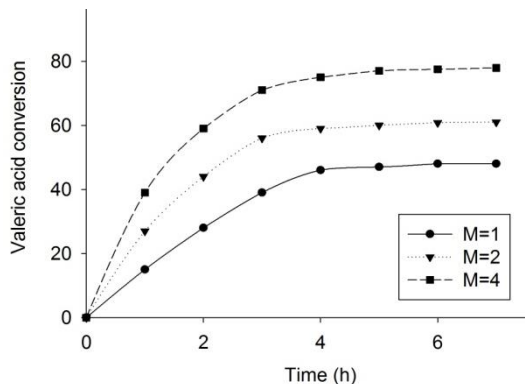


Fig. 8. Effect of initial molar ratio on conversion (T=343 K)

### 3.5 Determination of Reusability of The Reactive Polymer

Fig. 9 shows the reusability experiments of reactive polymer at 343 Kelvin when the initial alcohol:acid molar ratio is four. Experiments showed that the catalytic polymer was preserved approximately 94 % of its reactivity during the six reaction period under the same operating conditions. This result was a promising in terms of catalyst reusability. Thereby, it is possible to predict the using of reactive polymer as a heterogeneous catalyst can reduce the overall catalyst cost.

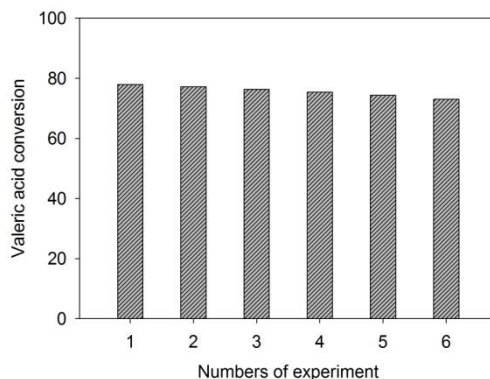


Fig. 9. Reusability experiments of reactive polymer (T=343 K, M=4)

### 4. Conclusions

In this study, a reactive polymeric PSSA/CMC film catalyst was prepared and used to ethyl valerate synthesis at different reaction and feed molar ratio. At the end of the eight hours, 80 % acid conversion was achieved at 343 K when the feed molar ratio was 4. This result is quite good. Also, it was seen that there was no degradation in polymer film



catalyst after the reaction. Hence, characterization and conversion results proved the availability of catalyst film for efficient valeric acid-ethanol esterification.

## **Acknowledgements**

This research was supported by the Scientific Research Project Center of Kocaeli University (Grant Number: 040/2016).

## **References**

- [1] Luo L, Van der Voet E, Huppel G, Udo de Haes HA. Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol. *Int J Life Cycle Assess.* 2009; 14: 529–539. <http://dx.doi.org/10.1007/s11367-009-0112-6>
- [2] VonBlottnitz H, Curran MA. A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. *Journal of Cleaner Production.* 2007;15: 607-619. <http://dx.doi.org/10.1016/j.jclepro.2006.03.002>
- [3] Balat M, Balat H. Recent trends in global production and utilization of bio-ethanol fuel. *Applied Energy.* 2009; 86: 2273–2282. <http://dx.doi.org/10.1016/j.apenergy.2009.03.015>
- [4] Pan T, Deng J, Xu Q, Xu Y, Guo QX, Fu Y. Catalytic conversion of biomass-derived levulinic acid to valerate esters as oxygenated fuels using supported ruthenium catalysts. *Green Chem.* 2013; 15: 2967-2974. <http://dx.doi.org/10.1039/c3gc40927a>
- [5] Lange J, Price R, Ayoub PM, Louis J, Petrus L, Clarke L, Gosselink H. Valeric Biofuels: A Platform of Cellulosic Transportation Fuels. *Angewandte Chemie International Edition.* 2010; 49: 4479–4483. <http://dx.doi.org/10.1002/anie.201000655>
- [6] Climent MJ, Corma A, Iborra S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem.* 2014; 16: 516-547. <http://dx.doi.org/10.1039/c3gc41492b>
- [7] Dong L, He L, Tao G, Hu C. High yield of ethyl valerate from the esterification of renewable valeric acid catalyzed by amino acid ionic liquids. *RSC Advances.* 2013; 3; 4806-4813. <http://dx.doi.org/10.1039/c3ra23034a>
- [8] Giovana SP, Barros M, Ranulfo MA, Elias BT. Production of Ethyl Valerate from Burkholderia cepacia Lipase Immobilized in Alginate. *Chemical Engineering Transactions.* 2013; 32: 1063-1068
- [9] Alonso DM, Wettstein SG, Dumesic JA. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. *Green Chem.* 2013; 15: 584-595. <http://dx.doi.org/10.1039/c3gc37065h>
- [10] Chan-Thaw CE, Marelli M, Psaro R, Ravasio N, Zaccheria F. New generation biofuels:  $\gamma$ -valerolactone into valeric esters in one pot. *RSC Adv.* 2013; 3: 1302-1306. <http://dx.doi.org/10.1039/C2RA23043G>
- [11] Raghavendra T, Sayania D, Madamwar D. Synthesis of the 'green apple ester' ethyl valerate in organic solvents by Candida rugosa lipase immobilized in MBGs in organic solvents: Effects of immobilization and reaction parameters. *Journal of Molecular Catalysis B: Enzymatic.* 2010; 63: 31–38. <http://dx.doi.org/10.1016/j.molcatb.2009.11.015>
- [12] Bayramoglu G, Hazer B, Altintas B, Arica MY. Covalent immobilization of lipase onto amine functionalized polypropylene membrane and its application in green apple flavor (ethyl valerate) synthesis. *Process Biochemistry.* 2011; 46: 372–378. <http://dx.doi.org/10.1016/j.procbio.2010.09.014>
- [13] Ozdemir S, Buonomenna MG, Drioli E. Catalytic polymeric membranes: Preparation and application, *Applied Catalysis A: General.* 2006; 307:167–183. <http://dx.doi.org/10.1016/j.apcata.2006.03.058>

- [14] Mathias U. Advanced functional polymer membranes. *Polymer*. 2006; 47: 2217-2262. <http://dx.doi.org/10.1016/j.polymer.2006.01.084>
- [15] Shi W, He B, Li J. Esterification of acidified oil with methanol by SPES/PES catalytic membrane. *Bioresource Technology*, 2011; 102:5389-5393. <http://dx.doi.org/10.1016/j.biortech.2010.09.074>
- [16] Zhu M, He B, Shi W, Feng Y, Ding J, Li J, Zeng F. Preparation and characterization of PSSA/PVA catalytic membrane for biodiesel production. *Fuel*, 2010; 89: 2299-2304. <http://dx.doi.org/10.1016/j.fuel.2010.02.001>
- [17] Shevchenko VV, Stryutskii AV, Bliznyuk VN, Synthesis, structure, and properties of anhydrous organic-inorganic proton-exchange membranes based on sulfonated derivatives of octahedral oligosilsesquioxanes and  $\alpha,\omega$ -di(triethoxysilyl) oligo(oxyethylene urethane urea), *Polym. Sci. Ser. B*, 2014; 56: 216-228. <http://dx.doi.org/10.1134/S1560090414020158>
- [18] Kim DS, Cho H, Kim DH, Lee BS, Yoon S, Kim Y, Moon G, Byun H, Rhim J, Surface fluorinated poly(vinyl alcohol)/poly(styrene sulfonic acid-co-maleic acid) membrane for polymer electrolyte membrane fuel cells Origin, *Journal of Membrane Science*, 2009; 342: 138-144. <http://dx.doi.org/10.1016/j.memsci.2009.06.034>
- [19] Lin CW, Huang YF, Kannan AM, Semi-interpenetrating network based on cross-linked poly(vinyl alcohol) and poly(styrene sulfonic acid-co-maleic anhydride) as proton exchange fuel cell membranes, *Journal of Power Sources*, 2007; 164: 449-456. <http://dx.doi.org/10.1016/j.jpowsour.2006.10.081>
- [20] Sahu AK, Selvarani G, Bhat SD, Pitchumani S, Sridhar P, Shukla AK, Narayanan N, A. Banerjee, N. Chandrakumar, Effect of varying poly(styrene sulfonic acid) content in poly(vinyl alcohol)-poly(styrene sulfonic acid) blend membrane and its ramification in hydrogen-oxygen polymer electrolyte fuel cells, *Journal of Membrane Science*, 2008; 319: 298-305. <http://dx.doi.org/10.1016/j.memsci.2008.04.004>
- [21] Yang CC, Chiu SJ, Kuo SC. Preparation of poly(vinyl alcohol)/montmorillonite/poly(styrene sulfonic acid) composite membranes for hydrogen-oxygen polymer electrolyte fuel cells. *Curr. Appl. Phys.* 2011; 11: 229-237. <http://dx.doi.org/10.1016/j.cap.2010.11.043>
- [22] Patel R, Im SJ, Ko YT, Kim JH, Min BR. Preparation and characterization of proton conducting polysulfone grafted poly(styrene sulfonic acid) polyelectrolyte membranes. *J. Ind. Eng. Chem.* 2009; 15: 299-303. <http://dx.doi.org/10.1016/j.jiec.2008.12.011>
- [23] Benedict DJ, Satish JP, Shih-Perng T. Esterification of Lactic Acid and Ethanol with/without Pervaporation, *Ind. Eng. Chem. Res.* 2003; 42: 2282-2291 <http://dx.doi.org/10.1021/ie020850i>