А.А. ГАСПАРЯН, Л.В. ЧАРХИФАЛАКЯН, Г.П. ОГАНЕСЯН

ИССЛЕДОВАНИЕ ФАРМАЦЕВТИЧЕСКОГО РЫНКА РА

Работа посвящена изучению фармацевтической промышленности Армении. Исследованы вопросы расширения фармацевтического рынка, темпов импорта и экспорта лекарственных средств и задач, связанных с урегулированием отрасли. В Армении местное производство удовлетворяет лишь 4…5% спроса внутреннего рынка, а темпы роста импорта в несколько раз превышают темпы отечественного производства.

Ключевые слова: фармацевтическая отрасль, фармацевтический рынок, темпы импорта и экспорта, Союз производителей и импортеров лекарств.

A.A. GASPARYAN, L.V. CHARKHIFALAKIAN, G.P. HOVHANNISYAN

STUDYING THE RA PHARMACEUTICAL MARKET

The work is devoted to the pharmaceutical industry in Armenia, the growth of pharmaceutical market, drug import and export pace, and sectoral issues. The Domestic production in Armenia satisfies only 4…5% of domestic demand, while the import growth rates are higher than the domestic production

Keywords: pharmaceutical industry, pharmaceutical market, import and export rates, Drug Manufacturers and Importers Union (DMIU).

UDC 665.11

A.A. TADEVOSYAN, A. QUEIROZ, A. RIBEIRO, P. BRITO, N.R. HOVHANNISYAN

CHARACTERIZATION OF BIODIESEL SAMPLES USING DIFFERENT AMOUNTS OF IONIC LIQUID

The biodiesel production through Ionic Liquid (IL) catalyzed esterification is studied. The recovery of IL 1-butyl-3-methylimidazolium hydrogen sulphate ([BMIM] [HSO_4]) is studied. Several esterification reactions of oleic acid were carried out, using a quantity of catalyst of 10 wt%, 15 wt% and 20 wt% relative to the mass of the oleic acid. The results obtained confirm that it is possible to reuse this IL in successive reactions of esterification without a great loss of yield and, with this, to significantly reduce the costs associated with the purchase of these compounds that are quite expensive.

Keywords*:* biodiesel, esterification, ionic liquid, recovery.

Introduction. Biodiesel is an alternative fuel diesel that can be produced from vegetable oils and animal fats [1]. There is a recent growing interest in the development of alternative technologies to the oil economy based on renewable

energy sources. A possible solution is a biofuel usable in compression-ignition engines produced from biomass rich in fats and oils. A wide range of raw materials can be used in the production of biodiesel. Nevertheless, the use of sources that do not compete with the food market like waste cooking oils which usually feature high levels of free fatty acids (FFA's), can put problems in the process of production of biodiesel through alkaline transesterification [2]. These problems are partially overcome by the use of catalysts, such as ionic liquids (IL's) that also promote reactions of esterification of FFA's to biodiesel [3,4]. Thus, the objective of this work consists in the study of the influence of IL's application in the catalysis of - esterification reactions of organic acids to the corresponding methyl esters.

Experimental analysis. Several esterification reactions were performed using three different amounts (%) of ionic liquid. After each reaction, the obtained samples were separated in aqueous and organic phases by decantation and centrifugation. Both organic (biodiesel) and aqueous (with ionic liquid) samples were dried and stored in the refrigerator ($4^{o}C$) for further analysis. After each reaction test, the reaction yield was determined, using the acidity of the organic phase measured by volumetric titration. The characterization of the produced biodiesel samples was measured qualitatively and quantitatively for the determination of Fatty Acidy Methyl Ester (FAME) content of all biodiesel samples, a VARIAN CP-3800 gas chromatography equipment was used. The system has a Flame Ionization Detector (FID) and a Supelcowax-10 capillary column ($30m$ x $0.25mm$ x $0.25\mu m$). Additionally, initial and final samples of the selected ionic liquid were characterized by UV-Vis (VARIAN Cary 50) and Fourier Transform Infra-Red (FTIR) spectroscopy (ABB MB300).

Result and discussion. For the experiments carried out with ionic liquids as catalysts, the molar ratio between oleic acid and methanol was 1/10 and the quantity of IL was 10%, 15%, 20% of the oleic acid. In the first experiment [BMIM][HSO_4] was used as a catalyst. Several experiments were made using [BMIM][HSO_4] as a catalyst and the percentage of IL was varied (10%, 15% and 20%). The reaction time was 6 h, the reaction temperature - $90^{o}C$. In Table 1 the results are presented.

Table 1

Effect of quantity of [BMIM][HSO_4]on production conversions

Quantity of ILs, %	$m_{ionic\ liquid}$ g	$m_{oleic\ acid}$, g	V_{MeOH}, ml	Conversion, %
10	1.1560	11.3239	16.20	76.6
15	1.7383	11.3474	16.23	83.3
20	2.2312	11.2969	16.23	84.9

Characterization of biodiesel samples by using different amounts of ionic liquid. To study the effect of recovery of [BMIM][HSO_4] in the performance of the next esterification step, which is presented in Table 2, 1-3 esterification reactions (with 10%, 15% and 20% amounts of ILs) were carried out followed by 4 (10% amount of IL) and 5 (15%, 20% amounts of IL) recovery steps. 4 reactions were discussed because after the fourth recovery of IL, the mass was very small. The yields obtained for the reactions carried out with higher amounts of IL (15 wt% and 20 wt%) were higher than those obtained for the reactions with 10 wt% of IL.

Table 2

Number of runs (recovery) ILs 10%, 15%, 20% and reaction conversions

Number of runs	Conversion, %					
	ILs 10 wt, %	Name	ILs 15 wt, %	Name	ILs 20 wt, %	Name
1	76.6	REC 10.1	83.3	REC 15.1	84.9	REC 20.1
2	73.7	REC 10.2	79.9	REC 15.2	81.5	REC 20.2
3	67.4	REC 10.3	77.0	REC 15.3	81.8	REC 20.3
4	58.3	REC 10.4	---	---	---	---
5	---	---	75.3	REC 15.5	77.1	REC 20.5

In Fig. 1 biodiesel conversion dependencies on the amount of the catalyst and recovery runs is presented. It is possible to verify that when the amount of ILs increases, the biodiesel conversion also increases.

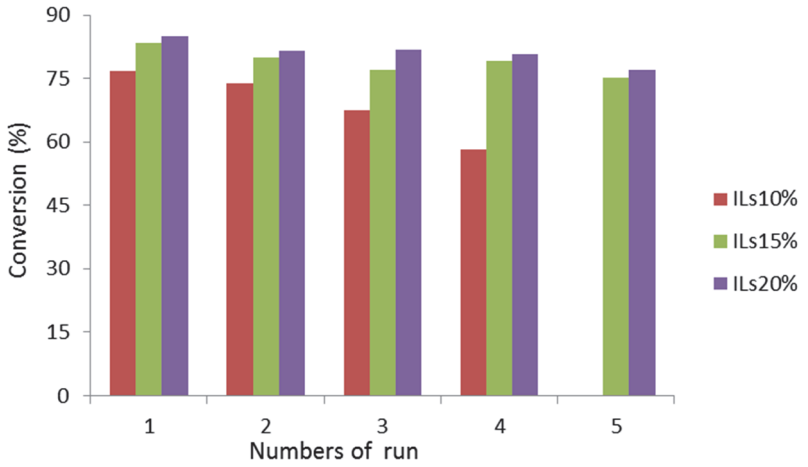


Fig. 1. The reaction conversions dependency on the amount of the catalyst and the number of runs (recovery) ILs 10%, 15%, 20%

For carrying out the recovery, the flask containing a water phase, was weighted, after the added water phase. After the recovery, the flask and ILs were measured together. After four successive reactions, the mass of IL decreased by about 60.8% (reaction with ILs 10%), in the reaction with 20%, 15% IL after 5 runs the mass of IL decreased about 28% and in the reaction with 20% of IL, the IL mass decreased 23.8%.

ILs analysis by UV-VIS. The effect of the recovery steps in the quality of the IL was studied by UV-VIS spectroscopy. The spectrum of the original IL and the ILs recovered after the final esterification reaction, for each % IL is presented in Fig. 2. The original ILs have a yellow colour, but the recovered the ILs sample is of a little bit dark colour. In Fig. 2, the absorption spectra of samples of the ionic liquid [BMIM][HSO_4] are shown. The spectra were recorded in a 1 *cm* quartz cell. The absorption spectrum of the original IL (red, solid line) shows an absorption maximum around 260 *nm*.

The original ionic liquid [BMIM][HSO_4] 0.11 absorbance threshold shifts for the original ILs sample from 200 *nm* to about 260 *nm*, the spectra of the recovered ILs does not differ from each other and show the absorption bands for ILs (REC20) 200 *nm* to 250 *nm*, for ILs (REC15) 200 *nm* to 264, for ILs (REC10) 200 *nm* to about 255. Spectroscopic results prove the [BMIM][HSO_4] after the recovery retained stable catalytic performance.

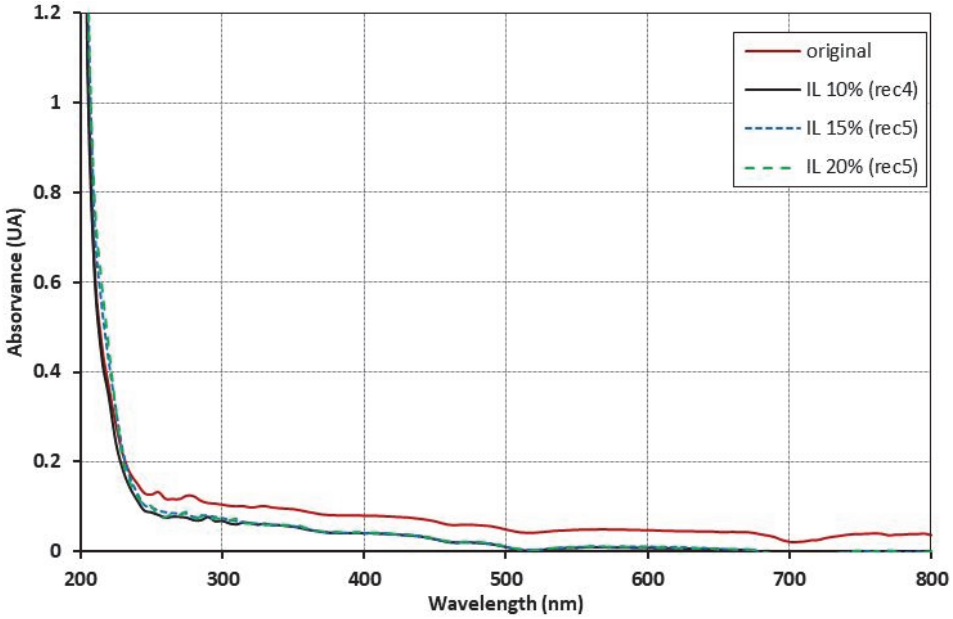


Fig. 2. UV-Vis spectrum obtained for original and the recovered ILs obtained for different amount of ILs (10, 15 and 20%)

ILs analysis by FTIR. The effect of the recovery steps in the quality of the IL was studied by FTIR spectroscopy. The molecular formula for the IL 1-Butyl-3-methylimidazolium hydrogen sulphate is [BMIM][HSO_4]. Fig. 3 shows the structural formula of the sample.

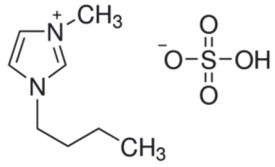
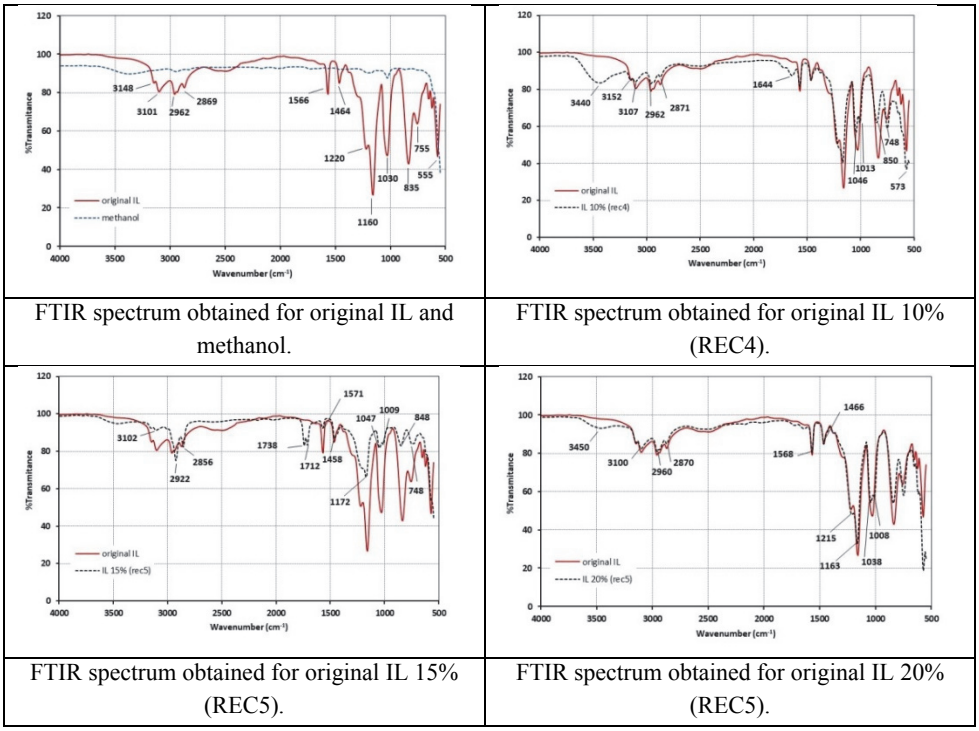


Fig. 3. Formula 1-Butyl-3-methylimidazolium hydrogen sulphate

The spectrum of the original IL, methanol and the ILs recovered after the final esterification reaction, for each %IL is presented in Fig. 4.



FTIR spectrum obtained for original IL and methanol.	FTIR spectrum obtained for original IL 10% (REC4).
FTIR spectrum obtained for original IL 15% (REC5).	FTIR spectrum obtained for original IL 20% (REC5).

Fig. 4. FTIR spectrum obtained for methanol and ILs (10%,15%,20%)

Conclusion. In this study, the reaction yield was found to be 76.6% to 10% IL, 83.3% to 15% IL and 84.8% to 20% IL. These yields decreased to 58.2% (10% IL) with 4 cycles of recycling, 75.2% (15% IL) with 5 cycles of recycling and 77.1% (20% IL) with 5 cycles of recycling. In this work the FAME content was calculated: values of around 50-60% of FAMEs / g biodiesel sample. Another 40-50% could be in the organic phase (as acids) or in the aqueous phase.

For analyzing the Ils, UV-VIS and FTIR were used. It was found that it retained stable catalytic performance after recovery.

Acknowledgement:
We have acknowledged to professor G.H. Torosyan for his support for this work.

REFERENCES

1. **Ahmia A.C., Danane, Bessah F.R., Boumesbah I**. Raw material for biodiesel production. Valorization of used edible oil // Revue des Energies Renouvelables. -2014. -17. –P. 335-343.
2. **Md Ehsana, Md Tofajjal Hossain Chowdhury.** Production of Biodiesel Using Alkaline Based Catalysts From Waste Cooking Oil: A Case Study // Procedia Engineering. -2015. -105. -P. 638-645.

3. **Abbaspour-Gilandeha E., Azim S.C.** Bronsted acidic ionic liquid ([BMIM]HSO_4) as an efficient catalysts for the one-pot synthesis of 2H-indazolo[2,1-b] phthalazine-trione derivatives // Iranian Journal of Catalysis. -2014. -4(3). -P.175-180.
4. **Andreani L., Rocha J.D.** Use of Ionic Liquids in biodiesel production: A Review// Brazilian Journal of Chemical Engineering. -2012. -V.29, №1. -P.1-13.

Ա.Ա. ԹԱԴԵՎՈՍՅԱՆ, Ա. ՔՈՒԵՅՐՈՋ, Ա. ՌԻԲԵՅՐՈ,
Պ. ԲՐԻՏՈ, Ն.Ռ. ՀՈՎՀԱՆՆԻՍՅԱՆ

ԿԵՆՍԱԴԻԶԵԼԻ ՆՄՈՒՇՆԵՐԻ ԲՆՈՒԹԱԳՐՈՒՄԸ ՏԱՐԲԵՐ ՔԱՆԱԿՈՒԹՅԱՄԲ ԻՈՆԱՅԻՆ ՀԵՂՈՒԿՆԵՐԻ ԿԻՐԱՌՄԱՄԲ

Ուսումնասիրվել է կենսադիզելի ստացումն իոնային հեղուկով (ԻՀ) կատալիզվող եթերացմամբ: Հետազոտվել է 1-բութիլ-3-մեթիլիմիդազոլիումի հիդրոսուլֆատ ([BMIM][HSO_4]) ԻՀ-ի վերականգնումը, և իրականացվել են օլեինաթթվի եթերացման մի քանի ռեակցիաներ՝ կիրառելով կատալիզատորի 10 զանգվ.%, 15 զանգվ.% և 20 զանգվ.% քանակություն՝ ըստ օլեինաթթվի: Արդյունքները հաստատում են, որ այս ԻՀ-ը կարելի է կրկնակի օգտագործել եթերացման հետագա ռեակցիաներում՝ առանց արգասիքի մեծ կորստի, դրանով զգալիորեն իջեցնելով ծախսերը, որոնք կապված են այս բավականին թանկ միացությունների ձեռքբերման հետ:

Առանցքային բառեր. կենսադիզել, եթերացում, իոնային հեղուկ, վերականգնում:

А.А. ТАДЕВОСЯН, А. КУЕЙРОС, А. РИБЕЙРО,
П. БРИТО, Н.Р. ОГАНЕСЯН

ХАРАКТЕРИСТИКА ОБРАЗЦОВ БИОДИЗЕЛЯ С ИСПОЛЬЗОВАНИЕМ РАЗЛИЧНЫХ КОЛИЧЕСТВ ИОННОЙ ЖИДКОСТИ

Изучено получение биодизеля с помощью этерификации катализируемой ионной жидкостью (ИЖ). Исследовано восстановление ИЖ 1-бутил-3-метилимидазолиум гидросульфат [BMIM][HSO_4] и проведено несколько реакций этерификации олеиновой кислоты с использованием количеств катализатора 10 мас.%, 15 мас.% и 20 мас.% относительно массы олеиновой кислоты. Результаты подтверждают, что можно повторно использовать эту ИЖ в последовательных реакциях этерификации без большой потери продукта и тем самым значительно снизить затраты, связанные с приобретением этих довольно дорогих соединений.

Ключевые слова: биодизель, этерификация, ионная жидкость, восстановление.