

Досліджено пряме амідкування низькоякісної ріпакової олії аміноетилетаноламіном. Встановлено, що зниження тиску в системі впливає на перетворення вільних жирних кислот і ацилгліцеринів. Розраховані кінетичні параметри взаємодії компонентів ріпакової олії з аміном і встановлено, що константи швидкості взаємодії низькоякісної ріпакової олії з аміном на $\approx 15\%$ менше цих показників для рафінованої ріпакової олії. Зниження тиску сприяє прискоренню отримання алкілімідазолінов

Ключові слова: амідкування, низькоякісна ріпакова олія, алкілімідазоліни, поверхнево-активні речовини, константи швидкості

Исследовано прямое амидирование низкокачественного рапсового масла аминоэтилэтанолламином. Установлено, что снижение давления в системе оказывает влияние на превращение свободных жирных кислот и ацилглицеринов. Рассчитаны кинетические параметры взаимодействия компонентов рапсового масла с амином и установлено, что константы скорости взаимодействия низкокачественного рапсового масла с амином на $\approx 15\%$ меньше этих показателей для рафинированного рапсового масла. Снижение давления способствует ускорению получения алкилимидазолинов

Ключевые слова: амидирование, низкокачественные масла, алкилимидазолины, поверхностно-активные вещества, константа скорости

UDC 665.3:547

DOI: 10.15587/1729-4061.2016.74856

INFLUENCE OF VACUUM ON KINETIC OF LOW QUALITY RAPESEED OIL AMIDATION BY AMINOETHYL-ETHANOLAMINE

S. Kramarev

Candidate of Technical Sciences

Chemrise LLC.,

Arkhitekotorov str., 32, Kharkov, Ukraine, 61174

E-mail: kramarevsergey@yahoo.com

A. Khusanov

Candidate of Technical Sciences

Head of scientific laboratory "Water problems"

Auezov South Kazakhstan State University

Tauke-Khan str., 5, Shymkent, Kazakhstan, 160012

E-mail: husanov@inbox.ru

1. Introduction

One of the widespread methods for vegetable oils and fatty acids processing is obtaining of different surfactants on their base [1]. Alkylimidazolines (AI) are one of the most used nitrogen-containing surfactants. They are heterocyclic compounds and their five-membered ring contains two nitrogen atoms. By interacting with acids or by quaternization, AI transforms to respective salts or quaternized compounds that are cationic surfactants of asymmetric structure [2].

AI is used as corrosion inhibitors, dispergators, dewatering agents and emulsifiers in oil, metal-processing, textile industries as adhesion promoters for road building, in shampoos, shower gels and domestic cleaning products.

Kinetic researches of the process of refined vegetable oils amidation can be the basis for development of technology of alkylimidazolines obtaining [3, 4]. However, kinetic regularities of amidation of low-grade oils still aren't researched. In such case, free fatty acids can react with amine along with acylglycerols and can have great influence on processes that take place during amidation. Based on the current trend of complete processing of plant raw materials, researches directed to full cycle of plant raw materials processing into surfactants are actual.

2. Analysis of literature and statement of research problem

Obtaining of alkylimidazolines on the base of vegetable oils and fatty acids occurs in two stages: on the first stage amides of

fatty acids form, on the second stage due to cyclization process alkylimidazolines form from amides. However, the mechanism and reactions that take place during the amidation process are different for free fatty acids and for their esters.

Thus, during amidation of free fatty acids soaps of amine and fatty acids form on the first stage which transforms to amides with time. As a result of this reaction water forms, which can prevent further reactions of alkylimidazolines formation. Obtaining of amides of fatty acids usually takes place under temperatures more than $120\text{ }^{\circ}\text{C}$.

Formation of amides during amidation of triacylglycerols of vegetable oils occurs without water formation [5] and in milder conditions than formation of respective amides from free fatty acids.

A lot of factors have influence on the process of amidation. The main of them are temperature, presence of solvent, catalyst and pressure in the system. The most common way of alkylimidazolines obtaining is amidation of fatty acids or refined vegetable oils under temperatures of $170\text{--}240\text{ }^{\circ}\text{C}$ without solvent and with vacuum application [6]. Fatty amides are obtained under similar conditions but without vacuum application [7]. However, secondary amides of fatty acids can be obtained even under the temperature of $50\text{--}60\text{ }^{\circ}\text{C}$ as shown in [8]. For that purpose, high excess of amine is required, the molar ratio of tripalmitoyl glycerol:amine 1:10. In such case, amine acts as solvent for fatty components and, maybe, as alkali catalyst. Excess of amine does not allow for reaction masses to crystallize and because of that reaction is conducted for 12 hours in homogenous media.

Influence of solvent on the process of amidation of fatty acids has been described in [9]. The reaction took place under the temperature of 145 °C in xylene media. After 1 hour of interaction, water removing starts for 4 hours in order to obtain alkylimidazoline. The yield of alkylimidazolines is 20 % less for amidation of fatty acids in solvent media than for amidation without solvent and with vacuum.

Alkylimidazolines for industrial purpose are usually obtained by thermic methods with or without the use of catalyst [2, 10, 11]. The main application of alkylimidazolines of fatty acids is their utilization as a basis for corrosion inhibitors obtaining for the oil and gas extracting industry. There are a lot of researches dedicated to highly efficient corrosion inhibitors obtaining on the basis of alkylimidazolines [11–13]. At the same time, such utilization of alkylimidazolines doesn't require high purity. The main requirement for such products is their effectiveness in prevention of corrosion destruction. Based on this, alkylimidazolines for technical application can be obtained from blends of fat-containing products.

It is known that AI can be obtained from blends of different oils [5] and in this case the technology for their obtaining is almost the same as for individual vegetable oils. Technologies for obtaining of alkylimidazolines from fat containing wastes is known as well [14]. For imidazolines obtaining, fats are preliminarily extracted from such wastes, converted into methyl or ethyl esters and only after that processed according to well-known technologies. Despite feedstock in such applications is low grade and cheap, obtaining of imidazolines occurs from chemically similar compounds, though with significant amounts of impurities.

Processing of fats with high free fatty acids content requires slightly another approaches. Ways of processing of low-grade and used cooking oils with high fatty acids content (up to 20 % wt. and more) have been described in [15–18]. It is noted that their processing occurs in a few stages: on one of which react preferably triacylglycerols, and on another – preferably free fatty acids. Proper conditions and catalysts used on different stages for reaching a high degree of feedstock transformation and duration of different stages may vary in several times [19].

Based on this, the process of AI obtaining is advisable to conduct in two stages, especially when free fatty acids is are used. That can be explained by the facts that if the reaction is conducted under vacuum, unreacted amine components will be removed from reaction masses and, as a result, amine will be lost.

Kinetics of the amidation process of low-grade vegetable oil when free fatty acids can react with amine components along with triacylglycerols requires further research in order to find rational amidation conditions. Besides, the influence of vacuum on the kinetics of amidation and formation of AI during joint interaction of acylglycerols and fatty acids with amine is still unknown.

3. Aim and tasks of research

The aim of the work is to research regularities of the amidation process of low-grade canola oil with aminoethylethanolamine and formation of alkylimidazolines of fatty acids under atmospheric pressure and vacuum.

The following research tasks are formulated for reaching of the stated aim:

- to determine the influence of pressure decreasing on the course of the reaction of triacylglycerols and free fatty acids of canola oil with aminoethylethanolamine;
- to estimate changes of alkylimidazolines concentration after decreasing of pressure in the system during the amidation process;
- to calculate reaction rate constants of interaction of acylglycerines and free fatty acids of rapeseed oil with aminoethylethanolamine.

4. Materials and methods of researches of low-grade canola oil amidation process

Amidation of low-grade canola oil that was obtained via processing of low-grade seeds with subsequent storage with the presence of oxygen has been researched.

Obtained low-grade canola oil has the following characteristics: Acid value – 19.9 mg KOH/g; peroxide number – 12 mmol O₂/kg, saponification number – 181.2 mg KOH/g, iodine value 102 mg J₂/g, unsaponified matter content – 3.23 % wt., water and volatile compounds – 0.36 % wt., phospholipids content – 2.2 % wt.

Fatty acid composition of low-grade canola oil is presented by the following fatty acids: palmitic acid – 15.2 %; stearic acid – 5.0 %; oleic acid – 62.4 %; linoleic acid – 7.9 %; linolenic acid – 5.4 %; arahidic acid – 3.7 %; C_{20:1} – 0.5 %.

Aminoethylethanolamine (AEEA) was produced by Merck (Germany) with active matter content not less than 99 %.

The research was conducted in a batch reactor that is equipped with heater, stirrer and system for removing vapors and water that is formed during the reaction. Vacuum in the system was created by a vacuum pump.

The research of imidazolines obtaining on the base of low-grade canola oil was conducted as follows. In a three-necked flask, 50 grams (0.054 mol) of low-grade canola oil was placed and the temperature was increased to the set value. After that, 16.8 grams (0.162 mol) of preliminarily heated aminoethylethanolamine was added in the flask. The time of aminoethylethanolamine addition is considered as the time of the beginning of the reaction.

The reaction was conducted in two stages. Atmospheric pressure was maintained on the first stage of the reaction and condensed vapors returned to reaction masses. After 1.5 hours of synthesis, pressure in the system has been decreased by vacuum pump up to 40–60 mm. Hg and the reaction took place for 1.5 hours more. Temperature of the reaction remained constant and was 160 °C. Samples out of the synthesis of reaction masses determine the conversion ratio of reagents and the formation ration of desirable components.

5. Results of studies of vacuum effect on the kinetics of amidation of low-grade canola oil

5.1. Vacuum effect on acylglycerol expenditure

Acylglycerols and free fatty acid react with aminoethylethanolamine in the amidation process of low-grade canola oil.

The main components of oils are acylglycerols – esters of fatty acids and glycerol. Therefore, the vacuum effect on its reactivity has been primarily investigated. Fig. 1 shows the change in the concentration of ether groups of acylglycerols in the amidation process of low-grade canola oil under the

temperature of 160 °C. The pressure in the system decreased to the value of 40–60 mm Hg. after 90 min of reaction in the process of amidation.

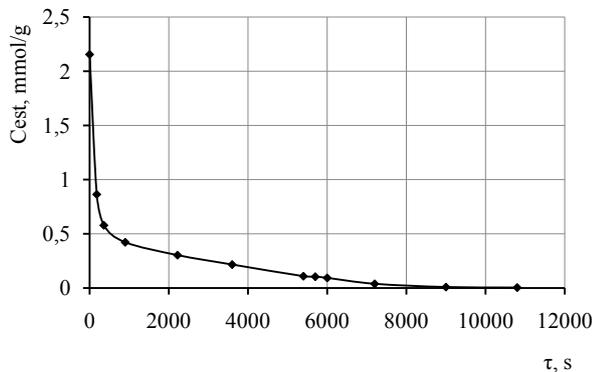


Fig. 1. The dependence of the concentration of ether groups of acylglycerols of canola oil (C_{est}) on the reaction time (τ), where vacuum is supplied after 1.5 hours of reaction

Reduction in concentration of ether groups goes rapidly in the first 900 seconds of reaction (Fig. 1) between acylglycerols of canola oil and aminoethylethanolamine that testifies about the intensity of the amidation process and formation of fatty acids amides at the initial moments of time. Thus, 80.4 % of ethers are converted to reaction products within the first 900 seconds.

At the formation stage of aminoamides and diamides of fatty acids, the supply of vacuum to the system will lead to removing and loss of the amine, so the pressure was reduced after 5400 seconds of the reaction in the study. It can be seen (Fig. 1) that when vacuum is supplied to the system, the tendency of concentration reduction of ether groups is not changed – the gradual minor drop continues until the end of the process. Fractional conversion of ether groups after the first stage of interaction is 94.5 %. At the second stage of interaction, fractional conversion is increased by 5.3 % and in the end of the reaction is 99.8 %. In this connection, the conclusion can be made that pressure suppression in the system has no significant influence on the interaction between acylglycerols of canola oil and aminoethylethanolamine with amine formation. On this basis, its use for fatty acids amides obtaining from triacylglycerols of vegetable oils is inadvisable.

Evaluation of the kinetic patterns of reactions between acylglycerols and aminoethylethanolamine is carried out based on the fact that the reaction of ethers of fatty acids and glycerol with amines conforms to the law of the second-order reactions [20–22]. For evaluation of effective reaction rate constant of interaction between acylglycerols of canola oil and aminoethylethanolamine, dependencies in $1/C=f(\tau)$ coordinates, which are of the second order, have been composed. Dependencies in such coordinates take linear shape with a slope numerically equal to effective reaction rate constant. These dependencies are shown in Fig. 2.

On these dependencies of the concentration of ether groups on the reaction time in coordinates of the second order (Fig. 2), two linear sections can be distinguished, which coincide in time with the reaction periods under atmospheric pressure and under vacuum. It can be seen, that at the second stage of the reaction, dependencies have a greater angle of inclination that testifies about the increase of the

rate constant of ether groups interaction. Thus, after result processing according to [23], effective reaction rate constant of ether groups expenditure under atmospheric pressure is $0.5445 \text{ g}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, whereas under the low pressure rate constant is three times increased and is $1.6725 \text{ g}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Rate constant increase after decreasing of pressure in the system can be related to partial removal of glycerol from the reaction zone, which is the final conversion product of triacylglycerols in reactions of amidation. Its removal shifts the position of equilibrium towards products formation thereby increase the rate of ether groups' expenditure. At the same time, it's worth noting again, that the use of vacuum at initial stages of amidation is inexpedient, since it can lead to removal of unreacted amine from the reaction mass and consequently to decrease of final product yield.

It should be noted, that evaluated rate constant of low-grade oil amidation, which is $\approx 0.651 \text{ g}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, is somewhat lower than rate constants for refined canola oil under the same temperature [24]. Such differences may be caused by the presence of significant amounts of various impurities in low-grade oils, which affect the reaction rate.

Decrease of the reaction rate constant expressed in percentage is $\approx 15\%$. It testifies about inefficiency in the use of completely similar conditions applicable for refined oil amidation, in the process of low-grade oil amidation.

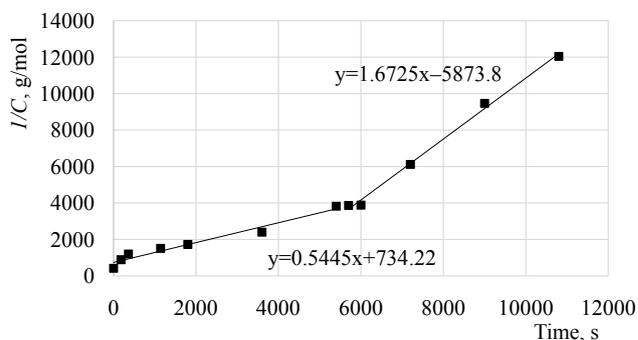


Fig. 2. The dependence of the concentration of ether groups on the reaction time in $1/C=f(\tau)$ coordinates, where vacuum is supplied to mixture after 5400 seconds of reaction

5. 2. Vacuum effect on fatty acids consumption

Fatty acids in conjunction with acylglycerols react with amine in amidation of low-grade canola oil. At the same time, the reactivity of the fatty acids is lower than of acylglycerols in the reactions with amine [25]. Also, when amine interacts with free fatty acids (1) with subsequent amides (2) formation, the water of reaction is released, removing of which from the reaction zone may facilitate acceleration of the fatty acids amidation process.



Removal of water of reaction can be implemented by pressure decreasing in the system, thereby shifting the position of equilibrium towards reaction products formation. For investigation of vacuum influence on the reactivity of free fatty acids contained in low-grade canola oil, changes of concentration in reactive masses in the amidation process have been determined (Fig. 3).

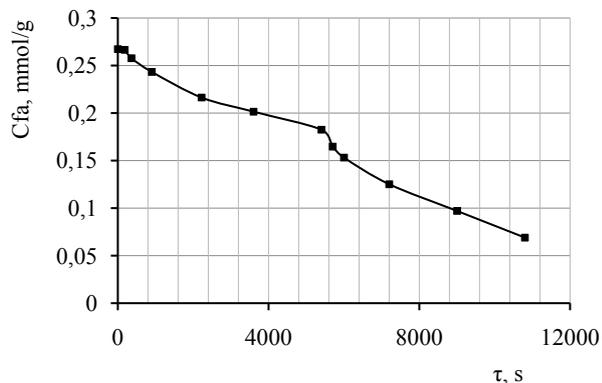


Fig. 3. The dependence of free fatty acids concentration (Cfa) in the reaction mass on the reaction time (τ), where vacuum is supplied to mixture after 5400 seconds of reaction

It can be seen, from these dependencies of change in fatty acids concentration (Fig. 3) that the rate of fatty acids expenditure is increased after decreasing of pressure. Thus, 31.7 % of fatty acids reacted with aminoethylethanolamine within the first 5400 seconds without vacuum, and 62.2 % of fatty acids – within the next 5400 seconds under vacuum. The ultimate conversion degree of fatty acids is 74.15 % after two stages of the reaction.

For assessment of vacuum effect on the acceleration of fatty acids conversion, effective reaction rate constants for its expenditure without vacuum and with taking into account of vacuum influence are evaluated (Fig. 4).

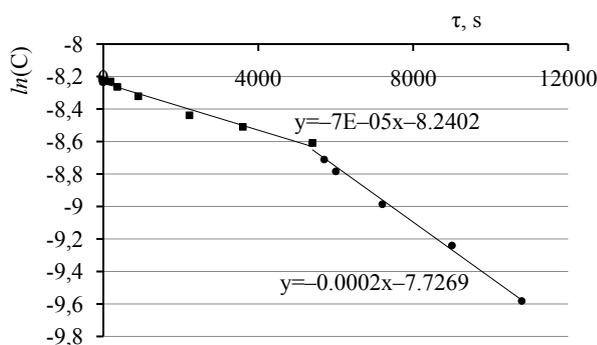


Fig. 4. The dependence of free fatty acids concentration on time (τ) in logarithmic coordinates ($\ln(C)=f(\tau)$), where 0–5400 seconds – reaction under atmospheric pressure, 5400–10800 seconds – reaction under vacuum

Since the reaction of fatty acids expenditure conforms to dependencies for the first-order reaction [20], the logarithm of fatty acids concentration is linearly dependent on time. And the rate constant is determined by the equation (3) [26]:

$$k = -tg\alpha, \quad (3)$$

where α – inclination of line to the time axis in the coordinates of the first order.

The dependencies of experimentally determined fatty acids concentrations (Fig. 2) on reaction time in coordinates of the first order represent two straight lines (Fig. 3). Linear dependence (0–5400 s.) is characteristic for the first stage of the reaction, which takes place under atmospheric pressure. The second linear dependence (5400–10800 s.) describes the amidation process under low pressure. After

processing of experimental results in accordance with [23], the following rate constants of fatty acids expenditure have been determined: without vacuum – $0.7 \cdot 10^{-4} \text{ s}^{-1}$, with vacuum – $2 \cdot 10^{-4} \text{ s}^{-1}$. The difference in rate constant values indicates that the rate of fatty acids expenditure grows under decreasing of pressure. This can be explained by acceleration of water of reaction removing from the reaction zone and shift of the position of equilibrium (2) towards formation of fatty acid amides.

5. 3. Vacuum effect on alkylimidazoline formation

Conversion of aminoethylethanolamine in reactions with acylglycerols and fatty acids goes in two stages. At the first stage, aminoamides are formed, and at the second – cyclization of aminoamides takes place with hydroxyethylimidazoline and water formation.

It is known that alkylimidazolines of fatty acids are quite easily hydrolyzed at C=N bond in the presence of water or watered alcohols [27]. Researchers [28] found out that tertiary amine content reduced on 5–8 % wt. in 18 months when stored in a closed container. Addition of water in quantity of 2 % by weight to the reaction product, which contains 38 % by weight of alkylimidazoline, causes decrease of its content up to 6 % by weight in 72 hours.

Therefore, continuous removal of water of reaction is essential for the flow of cyclization reaction and provision of a good yield of alkylimidazolines. For this, carrying out of the process under vacuum is expedient.

In this paper, for studying of alkylimidazolines formation from low-grade oil and assessment of vacuum influence on the process of cyclization, change in the concentration of tertiary amine groups [29], which are present in imidazoline ring depending on the reaction time has been determined (Fig. 5).

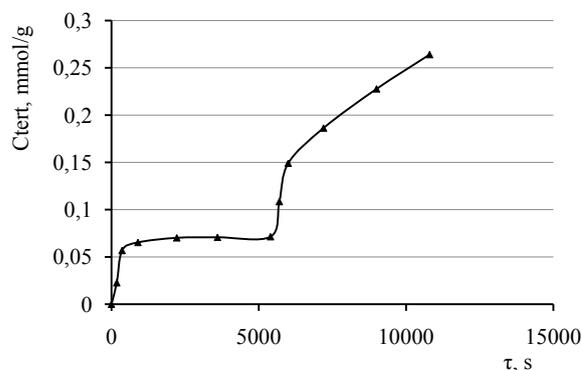


Fig. 5. The dependence of tertiary amine groups concentration (Ctert) on time (τ)

Formation of insignificant amounts of alkylimidazolines at the initial stage of reaction goes without vacuum application. Thus, the concentration of tertiary amine groups (Fig. 5) during the first 900 s reaches 0.065 mmol/g and from that moment on its accumulation almost ceased. During the next 4500 s increasing of concentration is observed only at 0.006 mmol/g and is 0.071 mmol/g. Which seems to indicate the establishment of an equilibrium in the formation reaction and hydrolysis of alkylimidazoline. Subsequent decreasing of pressure noticeably shifts the position of equilibrium towards alkylimidazoline formation. Its concentration starts to increase rapidly in the reaction mass reaching the value of 0.264 mmol/g on 10800 s of reaction. Consequently, decreasing of pressure has a signif-

ificant influence on the cyclization process and alkylimidazoline formation.

Since alkylimidazolines are the final product of sequential conversion of aminoethylethanamine, to evaluate kinetics patterns of its formation is possible only after additional researches of aminoamides concentrations – intermediate products of reaction and diamides – final product of reaction, which can be formed along with alkylimidazolines and aminoamides.

To confirm the accumulation of alkylimidazolines in reaction masses when vacuum supplied, research of obtained IR spectra of the reaction mass has been carried out (Fig. 6).

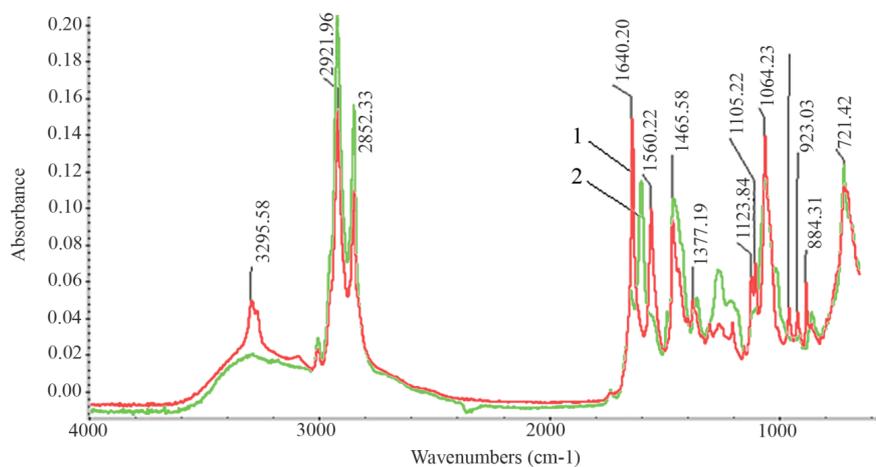


Fig. 6. IR spectra of reaction masses, obtained in the amidation of low-grade canola oil by aminoethylethanamine, where: 1 – without vacuum, 2 – under vacuum of 40–60 mm Hg. Art.

Absorption band (Fig. 6) at 3295 cm^{-1} corresponds to stretching vibration of $-\text{O}-\text{H}$ groups presented in acylglycerols and amines. This band is overlapped with absorption band $-\text{N}-\text{H}$ bonds of primary and secondary amino groups contained in nitrogen-containing derivatives of fatty acids and free amine. A significant width of this band signifies about the presence of hydrogen bonds. Tall narrow band at 2922 cm^{-1} and 2852 cm^{-1} corresponds to bond vibration in fragments of $-\text{CH}_2-$ and $-\text{CH}_3$ respectively. The absence of band at 1730 cm^{-1} , which belongs to stretching vibrations of $\text{C}=\text{O}$ in ethers, confirms the results of definition of high (99.8 %) conversion degree of acylglycerols. The presence of primary and secondary amide groups is confirmed by the presence of typical peaks in the spectra at 1640 cm^{-1} and 1560 cm^{-1} , respectively. Band at 1602 cm^{-1} is related to vibrations of $\text{C}=\text{N}$ band in imidazoline ring [30, 31].

In addition, at the spectra of the reaction mass (1), obtained without vacuum application, clearly pronounced peaks of amido groups (1640 cm^{-1} and 1560 cm^{-1}) and

the peak of $-\text{C}=\text{N}$ bond of imidazoline ring (1602 cm^{-1}) is absent. At IR spectra of the reaction mass obtained with vacuum application (2), amide peaks become much less pronounced and clearly pronounced peak appears at 1602 cm^{-1} , that proves formation of alkylimidazolines in amidation of low-grade canola oil under vacuum applied. Also there are visible differences in peaks at 3295 cm^{-1} , characterizes vibration of $-\text{O}-\text{H}$ and $-\text{N}-\text{H}$ bonds. A smaller peak height in reaction masses obtained under decreased pressure can be explained by the fact that, first of all, distillation of accumulated water of reaction begins, and second when alkylimidazolines are formed in primary and secondary amino groups, $-\text{N}-\text{H}$ bond cleavage occurs in the process of cyclization. Significant width of this band is explained by the hydrogen bonds presence.

6. Conclusions

1. It is determined that pressure decreasing in the system causes different influence on transformation of low-grade canola oil components. It has been found that 94.5 % of initial esters and 31.6 % of initial fatty acids have been transformed after the first stage of the reaction. On the second stage of reaction, additional 5.3 % of esters and 42.55 % of fatty acids have been transformed with vacuum applying that can be evidence of higher vacuum influence on reactions with fatty acids rather than reactions with esters.

2. Accumulation of alkylimidazolines and amides of fatty acids in reaction masses is confirmed by IR-spectrometry. It is confirmed that alkylimidazolines of fatty acids forms in small quantities even during the reaction under atmospheric pressure. During the first 900 seconds of the reaction, their concentration reaches an almost constant value and subsequently doesn't change. Pressure decreasing leads to rapid increasing in alkylimidazolines content and subsequent accumulation in reaction masses.

3. Effective rate constants of acylglycerols and free fatty acids amidation have been calculated. It is established that pressure decreasing has influence on the speed of transformation of acylglycerols and increases effective rate constants of their consumption by ≈ 3.1 times. Pressure decreasing leads to increasing of the speed of amidation of free fatty acids as well and increases rate constants of their consumption by ≈ 2.85 times. It is established that effective rate constant of low-grade canola oil amidation less by $\approx 15\%$ than rate constant of amidation of refined canola oil.

References

1. Surfactants: chemistry, interfacial properties, applications [Text] / V. B. Fainerman, D. Mobius, R. Miller (Eds.). – Elsevier, 2001. – 661 p.
2. Tyagi, R. Imidazoline and its derivatives: an overview [Text] / R Tyagi, V Tyagi, S Pandey // Journal of oleo science. – 2007. – Vol. 56, Issue 5. – P. 211–222. doi: 10.5650/jos.56.211
3. Kramarev, S. Issledovanie polucheniya azotoproizvodnih zhirnich kislot [Text] / S. Kramarev, A. Melnik, T. Matveeva et. al. // Sovremenniy Nauchny Vestnik. – 2013. – Vol. 31, Issue 170. – P. 79–83.
4. Malik, S. Doslidzhennya oderzhannya kysen' i azotovmisnuh pohidnyh zhirnuh kislot amiduvannyam llyanoyi oliyi [Text] / S. Malik, A. Melnik // Vestnik NTU "KhPI". – 2013. – Vol. 38. – P. 157–160.

5. Patent 0315142 USA. Process to obtain imidazoline mixtures from vegetable oils [Text] / Gomez L. M., De La Escalera L. M., Gutierrez J. A. et al. – declared: 01.07.2014; published: 05.11.2015.
6. Bajpai, D. Fatty imidazolines: chemistry, synthesis, properties and their industrial applications [Text] / D. Bajpai, V. K. Tyagi // Journal of oleo science. – 2006. – Vol. 55, Issue 7. – P. 319–329. doi: 10.5650/jos.55.319
7. McKenna, A. L. Fatty amides, synthesis, properties, reactions and applications [Text] / A. L. McKenna. – Memphis, Tenn.: Witco Chemical Corporation, 1982. – 225 p.
8. Bilyk, A. A novel technique for the preparation of secondary fatty amides [Text] / A. Bilyk, R. G. Bistline, G. J. Piazza, S. H. Fearheller, M. J. Haas // Journal of the American Oil Chemists' Society. – 1992. – Vol. 69, Issue 5. – P. 488–491. doi: 10.1007/bf02540956
9. Wu, Y. Thermal reactions of fatty acids with diethylene triamine [Text] / Y. Wu, P. R. Herrington // Journal of the American Oil Chemists' Society. – 1997. – Vol. 74, Issue 1. – P. 61–64. doi: 10.1007/s11746-997-0120-2
10. Bajpai, D. Microwave synthesis of cationic fatty imidazolines and their characterization [Text] / D. Bajpai, V. K. Tyagi // Journal of surfactants and detergents. – 2008. – Vol. 11, Issue 1. – P. 79–87. doi: 10.1007/s11743-007-1057-z
11. Yoo, S.-H. Synthesis and corrosion inhibition behavior of imidazoline derivatives based on vegetable oil [Text] / S.-H. Yoo, Y.-W. Kim, K. Chung, S.-Y. Baik, J.-S. Kim // Corrosion science. – 2012. – Vol. 59. – P. 42–54. doi: 10.1016/j.corsci.2012.02.011
12. Liu, H. Synthesis and corrosion inhibition behavior of imidazoline derivatives based on vegetable oil [Text] / H. Liu, J. Hu, X. Zhou, D. Liu, B. Xu, Y. Zhou // Journal of surfactants and detergents. – 2015. – Vol. 18. – P. 1025–1031. doi: 10.1007/s11743-015-1725-3
13. Finsgar, M. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review [Text] / M. Finsgar, J. Jackson // Corrosion science. – 2014. – Vol. 86. – P. 17–41. doi: 10.1016/j.corsci.2014.04.044
14. Patent 0225351 USA. Process to obtain mixtures of imidazolines and corrosion inhibitors from coffee waste [Text] / Contreras J. I. R., Negrete P. S. D., Gutierrez A. et al. – declared: 20.03.2014; published: 13.08.2015.
15. Frohlich, A. The Conversion of Low Grade Tallow into Biodiesel-Grade Methyl Ester [Text] / A. Frohlich, B. Rice, G. Vicente // Journal of the American Oil Chemists' Society. – 2010. – Vol. 87, Issue 7. – P. 825–833. doi: 10.1007/s11746-010-1561-6
16. Jamal, Y. Determination of methanolysis rate constants for low and high fatty acid oils using heterogeneous surface reaction kinetic models [Text] / Y. Jamal, A. Rabie, B. O. Boulanger // Reaction Kinetics, Mechanisms and Catalysis. – 2015. – Vol. 114, Issue 1. – P. 63–74. doi: 10.1007/s11144-014-0780-5
17. Rattanaphra, D. Simultaneous Conversion of Triglyceride/Free Fatty Acid Mixtures into Biodiesel Using Sulfated Zirconia [Text] / D. Rattanaphra, A. Harvey, P. Srinophakun // Topics in Catalysis. – 2010. – Vol. 53, Issue 11-12. – P. 773–782. doi: 10.1007/s11244-010-9463-2
18. Hayyana, A. Treatment of industrial low-grade palm oil via esterification reaction using sonoreactor [Text] / A. Hayyana, M.-A. Hashima, E. S. Mohamed, K. Mirghani, M. Hayyan, I. M. AlNashef // Journal of Industrial and Engineering Chemistry. – 2014. – Vol. 20, Issue 4. – P. 2066–2070. doi: 10.1016/j.jiec.2013.09.033
19. Shawkat, S. M. Ispolzovaniye zhirnih kislot soapstoka dlya polucheniya butilovih efirov zhirnih kislot [Text] / S. M. Shawkat, I. Demidov // Vestnik NTU "KhPI". – 2013. – Vol. 4. – P. 130–134.
20. Saiks, P. Mechanizmy reaksii v organicheskoi himii [Text] / P. Saiks. – Moscow: Chem, 1971. – P. 196–197.
21. Melnik, A. Polucheniye mono-, diacylglicerinov i etanolamidov zhirnih kislot amidirovaniem podsolnechnogo masla [Text] / A. Melnik, T. Matveeva, V. Papchenko. – Lambert academic publishing, 2013. – 264 p.
22. Malik, S. G. Kinyetika amiduvannia soievoi olii monoetanolinom [Text] / S. G. Malik, A. P. Melnyk, T. I. Martseniuk // Vestnik NTU "KhPI". – 2011. – P. 16–19.
23. Knorre, D. G. Fizicheskaia himiia [Text] / D. G. Knorre, L. F. Krilova, V. S. Muzykantov. – Moscow: High sch., 1990. – 416 p.
24. Kramarev, S. Kinetic Regularities of Canola Oil Amidation by Aminoethylethanolamine [Text] / S. Kramarev, S. Malik // Studies in Chemical Process Technology (SCPT). – 2014. – Vol. 2. – P. 17–20.
25. Khusanov, A. Perspectives of low-grade vegetable oils utilization in surfactants production [Text] / A. Khusanov, B. Kaldybayeva, S. Kramarev, A. Melnik, A. Abilmagzhanov // Industrial technology and engineering. – 2015. – Vol. 2, Issue 15. – P. 35–41
26. Shmid, R. Informal kinetics. In the quest for chemical reactions [Text] / R. Shmid, V. N. Sapunov. – Moscow: Mir, 1985. – 264 p.
27. Lisitskii, V. V. Hydrolysis of 2-Substituted and 1,2-Disubstituted Imidazolines [Text] / V. V. Lisitskii, Z. A. Akhmetchenko, I. E. Alekhina, Yu. I. Murinov // Russian Journal of Applied Chemistry. – 2007. – Vol. 80, Issue 5. – P. 761–766. doi: 10.1134/s107042720705014x
28. Bistline, R. G. Synthesis and properties of fatty imidazolines and their N-(2-aminoethyl) derivatives [Text] / R. G. Bistline, J. W. Hampson, W. M. Linfield // Journal of the American Oil Chemists' Society. – 1983. – Vol. 60, Issue 4. – P. 823–828. doi: 10.1007/bf02787436
29. ASTM Standard D 2074–92 (Reapproved 1998) [Text]. – Standard test method for total, primary secondary and tertiary amine values of fatty amines by alternative indicator method.
30. Tarasevich, B. N. IK spektru osnovnykh klassov organicheskikh soedinenii [Text]: sprav. materialy / B. N. Tarasevich. – Moscow, 2012. – 54 p.
31. Kushwaha, N. Synthesis of some amide derivatives and their biological activity [Text] / N. Kushwaha, R. K. Saini, S. K. S. Kushwaha // International Journal of Chem Tech Research CODEN (USA). – 2011. – Vol. 3, Issue 1. – P. 203–209.