UDC 364.3.032.1:665.3.002.8

CATALYSTS REACTIONS IN PROCESSES TO PRODUCE BIODIESEL FROM VEGETABLE OILS AND ANIMAL FATS

MM Mushtruk, applicant
JG Sukhenko, PhD
VU Sukhenko, Ph.D.

We characterize promising directions of catalysts in reactions of biodiesel production from vegetable oils and animal fats technical, given their classification and methods of use.

Catalyst, catalysis, selective action, acids, alkalis, oxides, enzymes, reaction.

Problem. Large-scale industrial production of biodiesel in Ukraine only begins. in the market from time to time there is a number of new catalysts for biodiesel production. Sometimes their effectiveness is questionable, and the resulting biofuel does not meet current domestic and foreign standards. theoretical and practical principles of classification and the conditions of use of catalysts in biodiesel production tested enough.

Analysis of recent research. The catalyst - a substance that increases the rate of chemical reactions (often reducing the activation energy of the reactants), and she, after the reaction remains chemically unchanged and in the same amount as the reaction. At the molecular level catalysts enter into a chemical reaction in some basic acts and restored in others. In the practical application of these substances are still undergoing changes due to various secondary processes.

Catalysts may be different substances and in any aggregate state (solid, liquid and gaseous). Their main characteristics are the catalytic activity and selectivity of action. Catalysts that speed up chemical reactions in the course of hundreds or even thousands of times called positive, while those that slow conversion of reactants is called negative (ACE) [1]. The phenomenon changes the speed of chemical reactions under the influence of catalyst called catalysis and reaction taking place under the influence of catalyst - catalytic.

© MM Mushtruk, JG Sukhenko, VY Sukhenko, 2013

The choice of catalyst quality is essential for sustainable process of passing pereesteryfikatsiyi vegetable and animal fats into diesel biofuel. Scientists studied very carefully alkaline, acidic, homogeneous, heterogeneous, enzymatic and other catalysts. alkaline catalysts such as sodium and potassium, most often used in the processes of biodiesel

production because they are effective at relatively low temperature reactions. acid catalysts are used less frequently because of some slowness of action.

ABOUTAIN advantages of using acids and heterogeneous (solid) catalysts is their relatively low cost, and in some cases, satisfactory performance, but they intensify pereesteryfikatsiyu fats in the presence of significant excess alcohol, which can lead to technical difficulties during its recovery and purification of fuel. The disadvantage of homogeneous catalysts is their high sensitivity to the presence of fat free fatty acids (FFA) and water, resulting in omylyuyutsya reagents. alkaline catalysts are better suited to pereesteryfikatsiyi triglycerides, and acid - for the esterification of fatty acids [2].

FROMGeneral notes advantage of heterogeneous catalysts have the opportunity to re-use and ease of separation from reaction products. In addition, they do not form soap, give great performance, and simplify purification of glycerol (99% pure glycerol to 75% in homogeneous catalysis). They are highly resistant to water and fatty acids, which are always present in the raw materials. However, the use of heterogeneous catalysts in biodiesel production requires more energy efficiency than using homogeneous catalysts, in particular, the high temperature and pressure for the reaction [2].

The promising technology is the production of biofuels, based on the use of enzyme catalysis in which implemented a moderate reaction conditions, lower alcohols used, provided easier recovery of reaction products and process compatibility with the environment, compared with chemical catalysts (homogeneous or heterogeneous). However, the cost of lipase, which is the most studied and promising catalyst in the reaction pereesteryfikatsiyi fat in order higher than alkaline catalysts. Therefore, using enzyme technology is still under investigation and process optimization.

The purpose of research. ABOUTbrʹruntuvannya conditions and methods of use of different types of catalysts and catalytic systems for esterification and pereesteryfikatsiyi vegetable and animal fats into diesel biofuel.

Results. Made us think study using a large number of references allowed to classify catalysts for biodiesel production and determine their conditions of use. We do not claim to be complete this classification, but believe that it is appropriate in terms of production and origin biodiesel market in Ukraine.

Homogeneous catalysts. Pereesteryfikatsiya triglycerides homogeneous catalysts is the most common process in the industrial production of biodiesel because of their low cost and high yield esters at moderate temperatures and relatively small terms of the reaction.

Hydroxides and oxides of metals alcohol - oxides and carbonates are widely used. Given the cost and availability, NaOH and KOH are used most frequently. Alco - oxides and hydroxides of the more expensive of them work harder because they are hygroscopic. general restriction in the use of alkaline catalysts to the quality of raw materials, in which the total content of fatty acids should not exceed 0.5% - 1% by weight, otherwise inevitable reaction saponification reagent complicates the production and purification of biodiesel.

Increasing the molar ratio of methanol / oil positively affects the reaction, braking saponification reagent mixture, but to a certain limit. Number soap decreases with increasing molar ratio of 3: 1 to 4.5: 1, but increased when the molar ratio increases from 4.5: 1 to 6: 1. catalyst concentration is practically no effect on the reaction rate.

The authors of [5] studied the effect of microwave heating on pereesteryfikatsiyu reacting a mixture of cotton oil using catalysts NaOH and KOH. The experimental results showed that microwave heating reduces the implementation of response from 30 minutes (for normal heating system) to 7 minutes.

Homogeneous acid catalysts. Such catalysts are more effective than alkaline, if esterification of fatty acids, but exhibit inertia in the reactions pereesteryfikatsiyi triglycerides. Acid-catalytic pereesteryfikatsiya is about 4000 times slower than a similar reaction using alkaline catalysts [6] and requires more stringent conditions of high - temperature and pressure. Benefits acid catalysts - low sensitivity to humidity and lack of raw materials saponification reacting mixture. Acid catalysts can be used in the reaction pereesteryfikatsiyi raw materials containing high content of fatty acids, such as waste oils and fats from restaurants institutions. They can also be used for biodiesel production in two stages: first - provide esterification of fatty acids, and the second - pereesteryfikatsiyu fats with lye.

Indicative study acid-catalytic esterification of fatty acids anhydrous and hydrated ethanol and methanol. When using methanol was found that sulfuric acid is a good catalyst and provides access ether greater than 90% at 1 h reaction period. at a temperature of 130 ° C. The reaction of esterification using anhydrous ethanol was with similar results. Even a small amount of sulfuric acid (0.01%) significantly promotes faster the reaction.

Geterohenni catalysts. High energy and slow interaction with the catalyst reaction mixture led researchers to study and application of heterogeneous catalysts. The use of such catalysts does not lead to the formation of soap in a reactor for the production of biofuels. In addition, the use of solid catalysts can improve process stability and esterification

pereesteryfikatsiyi fat, eliminate the problem of corrosion of equipment, ensure environmental safety of production. However, using heterogeneous catalysts is not as common as homogeneous, so that for reactions in the presence of elevated required temperature and pressure. Note that the diffusion processes may also limit the reaction surface of solid catalysts, which adversely affects the reaction rate. Thus, the use of all the fullness of the reaction area of the porous structure of the material determines the efficiency of catalysis. Promising for application include zeolites [7]. Among the large number of catalysts zeolites are the most studied inorganic solid catalysts for biodiesel production by pereesteryfikatsiyi fat. Oxides of zeolites provide ion reactions in pereesteryfikatsiyi triglycerides and may to some extent neutralize hydration moisture. problem in the use of heterogeneous catalysts is their gradual deactivation due to coking, sintering and leaching. It becomes particularly acute when the fuel production process takes place with the use of waste oils and fats. The most dangerous is the catalyst leaching, which not only increases the operational costs of production due to the need to replace the fuel catalyst, but also leads to contamination of the final product metal ions and increased cost of treatment. partial dissolution of the catalyst can provoke a backlash, which dramatically reduces the yield of fuel.

Geteropolioksydy and heteropolyacid. In [8] investigated the use of a heterogeneous catalyst Cs2.5H0.5PW12O40 for the production of methyl esters of fatty acids of castor oil and technical animal fats. The use of this catalyst provides almost the same result in optimal reaction conditions as in the case of catalysis, sodium hydroxide or sulfuric acid, but with two advantages - removal capability of the catalyst, its regeneration and reuse. The advantages of this catalyst system also is possible that the reaction at room temperature, and its catalytic activity does not depend on the content of fatty acids or water in the stock, and the reaction time is reduced ..

It is also possible to use type heteropoly H3PW12O406N2O for catalysis reaction pereesteryfikatsiyi waste edible oils high in fatty acids and water [9]. This was a very promising catalyst in reactions pereesteryfikatsiyi waste vegetable oils and animal fats and provided out methyl ester at 87%, while the conversion of long chains of palmitic acid ester yield reached 97%. The catalyst and excess methanol can be easily removed from the final product simple distillation. The catalytic activity yho almost independent of the content of free fatty acids and water in waste vegetable oil and pereesteryfikatsiya occurs at relatively low temperatures (65 ° C) and moderate correlation methanol / oil (7: 1).

Sulfates zirconium oxides and metals. WITHulfaty zirconia with high activity in the process pereesteryfikatsiyi palm and coconut oils and

animal fats technical. When using 1% catalyst at a temperature of 200 ° C methyl ester yield exceeded 90% [10].

ABOUTksydy zirconium, aluminum and tin are also promising catalysts in the pereesteryfikatsiyi soybean oil. reaction was carried out at a temperature of 175 ° C. All three catalysts showed relatively high activity and (out of fuel close to ~ 100%) [10].

Ion exchange resins and immobilized sulfooksydy. Heterogeneous solid catalysts for the production of biodiesel from waste vegetable oils and animal fats engineering can be obtained by partial carbonization of carbohydrates: D-glucose, sucrose, cellulose, starch, etc. [11]. This catalyst is characterized by high efficiency, they can be made from recycled materials and the cost is close to the cost of acid catalysts. Catalysts of hydrocarbon transformed effective than sulfates zirconia, and provide a higher yield of methyl esters in the transformation of waste exhaust restaurant and technical animal fats containing 30% by weight of fatty acids in diesel biofuel. optimal reaction conditions the catalyst derived from starch retained the possibility of high yield ether (93%) even after 50 cycles of reuse.

The authors [12] studied the process of obtaining biodiesel from vegetable oils using commercially available polymeric sulfonic acid and ion exchange resins. Amberlyst-15 catalyst showed the best results among all the studied ion-exchange resins. These catalytic systems are more active than homogeneous catalysts.

Dvohmetalevi cyanide complexes. Fe-Zn cyanide complexes - a relatively cheap and effective catalysts. The hydrophobic nature of the catalyst and the presence of oxidized Zn resulted in high activity in pereesteryfikatsiyi triglycerides with simultaneous esterification of fatty acids .. These catalysts are easily obtained from aqueous ZnCl2 and K4Fe (CN) 6 [13].

Hidrotaltsydy. Hidrotaltsydy and hidrotaltsydo double hydroxides such compounds have the general molecular formula [(Mx2 +) - (Mx3 +) (OH) 2 (x + y)] Ay / nn - · mH2O. These systems have a high and strong basicity due to the presence of oxygen.

In [14] investigated a series hidrotaltsydiv type [(Mg (1 - x) 2+) Alx (OH) 2] x + (CO3) x / n 2 -]. Such materials are effective catalysts for liquid - phase pereesteryfikatsiyi and which increase the reaction rate change. Convert triglyceride methyl ester was immediately without the induction period and the accompanying formation of diglycerides.

Alkali metal oxides. In [15] investigated pereesteryfikatsiya rapeseed oil with methanol, which is conducted by highly reactive area (3.0 m2 / g) of magnesium oxide. This was particularly effective catalyst: molar ratio of methanol / oil / (fat) 6: 1. Fuel yield approaching 80%

through
1 hr. reaction.

Proved to be quite large and active calcium oxide in the reaction pereesteryfikatsiyi rapeseed oil with methanol. Pretreatment CaO methanol turned him into Ca (OCH3) 2, which was applied to intensify reactions. Then glycerine - calcium complex formed through reaction catalyst with glycerin, used as the main catalyst. Under optimal reaction conditions (0.1 g CaO, 3.9 g methanol, 15 g oil or animal fat, reaction time of 1.5 hours. at room temperature), it received 90% of the methyl ester.

Insoluble and immobilized metal salts and hydroxides. The authors [16] studied pereesteryfikatsiyu soybean oil using catalysts Na / NaOH-Al2O3. The results of this catalyst similar actions homogeneous catalyst NaOH. At a molar ratio of methanol / oil 9: 1 in the presence of a catalyst Na / NaOH-Al2O3 was obtained biodiesel yield greater than 90% after 2 h. reaction at 60 ° C.

It has been proved [16] that the process pereesteryfikatsiyi Triolein with methanol can be carried out at 60 ° C using aluminum, combined with alkali metal salts. This group of catalysts is not sensitive to the presence of water in the reacting mixture. Fuel yield approached 94%.

Solid organic bases. Salts of Ni, Cu, Cd, La, Fe, Zn salt and some amino acids, especially those containing quaternary ammonium groups or guanidine, showed good catalytic activity. For example, when palm oil methanolysis and technical animal fats and zinc as a catalyst, the yield of ester was 90% after 200 min. reaction at a temperature of 135 ° C and a pressure of 5 bar [17].

Alkaline oxides wide action. Alkaline catalysts in the form of mesoporous solids have been successfully used in the pereesteryfikatsiyi sunflower and castor oils with methanol and ethanol [18]. These catalysts were made from calcium oxide and porous silicon. Samples containing 14% CaO were most active during the experiments, the catalyst leaching problems almost did not exist, and the yield ethyl esters was at 96%.

Luzhno - land alkoxides. FROMand using alkaline - Land alkoxides can successfully catalyze the reaction pereesteryfikatsiyi. The authors [19] studied pereesteryfikatsiyu rapeseed oil using calcium methoxide, which has strong basic properties and good thermal stability. He showed excellent catalytic activity and stability of soybean oil and pereesteryfikatsiyi technical animal fat with methanol at a ratio of methanol / oil (fat) 1: 1 and Appendix 2% Ca (OCH3) 2, at 65 ° C. The reaction time was about 2 hours ., and the output of the fuel was at 97%. this catalyst retains its properties even after repeated use in 20 - cycles.

THtylat calcium also investigated as a catalyst for pereesteryfikatsiyi soybean oil or animal fat with methanol technical and ethanol. The results showed that the optimal conditions for success was the reaction molar ratio of methanol / oil 12: 1, the use of 3% catalyst Ca (OCH2CH3) 2, bringing the reaction temperature to 65 ° C, making it possible to receive 95% esters of fatty acids.

Enzymes. There are many problems associated with the use of homogeneous catalytic systems during pereesteryfikatsiyi fat: the difficulty of removing glycerol with the catalyst, the high cost of electricity, the need for pre-treatment of raw materials containing fatty acids and plenty of water. These problems may be withdrawn if the use of catalysts - enzymes. Such enzymatic catalysts such as lipase can effectively influence the pereesteryfikatsiyi triglycerides exhibit high resistance to fatty acids and water [20]. some samples were patented catalytic lipases to produce biodiesel from different raw materials, namely soybean, sunflower, palm, coconut and rice oils, mixtures of vegetable oils and fats technical animal fat.

Fermentatyvnyy catalysis has some drawbacks: the possibility of unexpected deactivation of enzymes, low reaction rate and low conversion catalyst. For example, the effect of immobilized enzymes in reactions disconnected in the absence of polar compounds such as water and methanol. Moreover, enzymes are significantly more expensive than conventional chemical catalysts.

Analyzed previous studies and concluded by making low efficiency methanolysis using lipases and their inability to reuse, the authors [21] have developed a phased system methanolysis fat immobilized lipases Candida. They suggested that the problem is related to irreversible inactivation of lipase in contact with concentrated methanol, which is present in the reaction mixture. To avoid deactivation first step methanolysis was carried out at 30 ° C in mixtures of oil. In molar equivalent is required 1/3 of methanol and 4% immobolizovanoyi lipase mass in the reaction mixture. The transformation in oil esters was close to 33.1% in 7 hours. In the second stage, the reaction mixture was added 33% MeOH. after 10 h. ether reaction yield was 66.4%. The third stage was added again 33% MeOH in the reactor. after content control reagents in the mixture for 24 h., the reaction time was extended for another 24 hours. After 48 hr., The reaction yield methyl ester was 97.3%.

Doslidzhennya influence the pH of the reaction mixture at appropriate molar ratio of reactants and reaction temperature pereesteryfikatsiyi rapeseed oil (containing 0.3% fatty acids and acid number of 0.6 mhKOH / g) of immobilized lipase catalysis showed that methyl ester yield increased with increasing molar ratio oil / methanol ox

1: 1 to 1: 6. was received out of fuel close to 85.8%. Further increase of the molar ratio resulted in significant performance degradation process. It was also found that the temperature of 40 ° C is optimum for the reaction because the enzyme activity decreases rapidly at temperatures higher 50 ° C.

Pereesteryfikatsiya in alternative solvents. Most catalytic systems pereesteryfikatsiyi (homogeneous, heterogeneous, enzymatic) processes based on mass transfer through the liquid reagents. Related mass transfer limitations normally reduce speed and efficiency of responses. There are several ways to intensify reactions that enhance or simplify the distribution of mass transfer of reactants and catalysts - a mole or phase catalysis using alternative solvents (ionic liquids, supercritical fluids, etc.).

ANDlternatyvni solvents, combined with the technology of supercritical methanolysis (350 ° C and 30-40 MPa), widely used for methanolysis fat [22]. One of the advantages of supercritical fluids is their high diffusion constant, and their density approaches the density of the liquid. In response pereesteryfikatsiyi is no phase separation if it is carried out in supercritical methanol, making this system ideal to overcome mass transfer limitations. In the process of supercritical methanol pereesteryfikatsiyi diesel biofuel can be obtained even in the absence of a catalyst. Our efficient and easy-to-use method lets the air out greater than 98% in just a few minutes without the use of catalytic reactions. Other advantages of this system is the behavior of methanol, which does not respond to the presence of water and FFA.

Conclusions

1. Technology biodiesel production using alkaline catalysts in practical implementation of simple, cost-effective, requiring a relatively short period for the reaction pereesteryfikatsiyi yield and high yield.

2. The effectiveness of alkaline homogeneous catalysts is limited to the characteristics of raw materials, which should not contain water and FFA.

3. Use a combination of acid catalysts esterification with alkaline catalysts pereesteryfikatsiyi fats can solve the problem of processing raw materials with a high content of fatty acids.

4. Homogeneous catalysts may be replaced by heterogeneous process to run pereesteryfikatsiyi and prevent saponification reaction mixture.

5. Promising new songs catalysts - zeolites hidrotaltsydiv, mezostrukturovanyh oxides with different acid - base balance and improved porous structure with increased reactive area that stabilize conditions transformation reactions of various fatty materials in diesel biofuel.

References

1.

.

AS .

/ - -

/Singh, A. P. B. B. He, J. H. Van Gerpen, - M .: 2006. - № 22 -597.

5. Azcan N.Fuel 2008 [Text] / N. Azcan, A. Danisman //,-S.:2007, - p. 1781.

6. Aranda D. A., Catalis chemistry / DA Aranda, RT Santos, NC Tapanes, - Lett. 2008, - № 122 - 20 p.

7. N. Ostrovsky Kinetics heterohennыh katalyzatorov [Text] / NM Ostrovsky - M .: Nauka, 2001. - 167 pp

8.*Bio*echnolgy[F. Cao, Y. Chen, F. Zhai et al.] - Bioeng .: 2008-93 p.

9. Carnahan B. Applied Numerical Methods [Text] / B. Carnahan, HA Luthersy, O. JAMES; -NY .: Editorial John Wiley & Sons, 1999.

10. S. Furuta, H. Matsuhashi, K. Arata, C*atalysts*. [Text] / S. Furuta, H. Matsuhashi, K. Arata, - Commun. 2004, - № 5, -721 p.

11. Green Chemistry [M. H. Zong, ZQ Duan, WY Lou et al.] - Bioeng .: 2010,- 193 - 194 p.

12. Applied Oil Chemistry [S. C. Dos Reis, ER Lachter, RS Nascimento, J. Rodrigues et al.] - Soc .: 2005, -661 p.

13. Srivastava R., Catalyst and catalysis [Text] / R. Srivastava, D. Srinivas, P. Ratnasamy, - Min .: 2006. -34 p.

14. Xie W. Mol. catalyst and catalysis catalyst and catalysis [Text] /W. Xie, H. Peng, L. Chen, - A. Chem .: 2006., -24 p.

15. Leclercq E. Applied Oil Chemistry [Text] / E. Leclercq, A. Finiels, C. Moreau - Soc .: 2001, - № 78,-1161 p.

16. Satalyst and catalysis [L. Bournay, D. Casanave, B. Delfort et al.] Today 2005, - № 106 -190 p.

17. Omota F., Chemistry English [Text] / F. Omota, AC Dimian, A. Bliek, - Sci .: 2003 -375 p.

18. *Noureddine* H. Kinetics of Transesterification animal fat of oil [Text] / H. Noureddine, DY Zhu // JAOCS - 1997. - № 11, - p. 1457-1461.

19. Lipid science technology [S. KF Peter, R. Ganswindt, HP Neuner et al.] - R .: 2002.,-324.

20. Liu X., Energy Fuels [text] / X. Liu, X. Piao, Y Wang, S. Zhu - B .: 2008., - № 22-1313 p.

21. Saka S. Energy Fuels[Text] / S. Saka, D. Kusdiana //, - M .: 2001, - № 80, -225 p.

22. Pat. US 6509487, MPK7 C 11 C 3/00. Process for produsing lower alkyl fatty esters / Tatsumi Nobuhiro, Katayama Takanobu, Tabata Osamu, Mimura Taku, Fukuoka Noriaki, Yamamoto Katsutoshi; Kao Corp. - № 09/989409; Appl. 21.11.2001; Publish. 21.01.2003.

Oharakteryzovanы perspektyvnыe direction of application katalyzatorov reactions in the production of diesel byotoplyva IZ rastytelnыh oils and animal fats tehnycheskyh, given s classification and Methods of application.

Katalyzator, catalysis, yzbyratelnost action, acid, alkali, oksydы, fermentы, reaction.

We characterize the promising areas of the catalysts in the reactions of biodiesel production from vegetable oils and animal fats technology, given their classification and methods of application.

The catalyst, catalysis, selectivity, acids, alkalis, oxides, enzymes, reactions.

UDC 631,363,004

Approach to assessing the reliability index of complex technical systems "man-machine"

AV Novitsky, Z. Ruzhylo candidates tehnichnh Sciences

The paper analyzed the research to ensure the reliability of machines, systems as "man-machine". Formed main areas of software reliability.

Machine, system reliability, operator.

Problem. Analysis of the main trends of the modern complex technical systems "man-machine" (CCC "PM"), which include farming shows that these systems have a number of features, including the following: the presence of elements, subsystems and relations between them; hierarchy and the possibility of structural mapping; versatility and technical state of uncertainty during all life cycles; Multivariate implementation of management functions at each of its levels; dependence CTC reliability of component reliability "Machine" and "human operator."

Analysis of recent research.One of the main features of modern STS "PM" is that their structure and parameters
may change under the influence of objective and subjective factors, indicating the need to ensure their reliability required and is one of the important ways to increase their effectiveness. Machinery and equipment for agricultural production, particularly high-tech and durable, require the services of technical service, that complex maintenance and repair of machines.

One of the promising areas of software reliability CCC is the development of engineering services farms and enterprises of technical service, attracting manufacturers of machines

AV Novitsky, Z. Ruzhylo, 2013