The potential of biomass for obtaining of raw materials and chemical products

Iwona SZWACH, Renata KULESZA* – Institute Of Heavy Organic Synthesis „Blachownia", Kędzierzyn-Koźle, Poland

Please cite as: CHEMIK 2014, **68**, 10, 893–900

Introduction

Currently, the basic raw material in the chemical industry is petroleum. However, it is expected that the production of chemicals and materials with high added value from renewable resources will continue to play an increasingly greater role. Such a renewable resource is biomass coming from, among other sources, agriculture and food processing waste, recycled vegetable oils and waste animal fats. So far biomass is used mainly as a source of energy, but it can also be used for obtaining specialty chemicals such as plasticizers, lubricants and stabilizers. This however requires new approaches, conducting many research studies and developing new technologies. The article discusses the biomass market in Poland and the possibilities of the biomass processing.

1. Biomass and its potential in Poland

The definition of biomass: solid or liquid substances of plant or animal origin, which are biodegradable and are derived from wastes or residues from agriculture and forestry and related industries, as well as parts of other wastes that are biodegradable, and also grains that do not meet quality requirements for cereals in the intervention buying [1]. Natural sources of fats and oils include raw materials of plant origin (soil cultivation), marine and animal life. The concept of biomass also includes waste and residues of biological origin from the food industry, including waste fats (used vegetable oils, waste animal fats). Currently, environmental and economic reasons lead to the re-use of the used oils and fats after their suitable chemical modification [2].

1.1. Biomass for energy production and its potential in Poland

In Poland, the biomass is mainly used for energy purposes. Its reserves, as estimated in various strategic documents, are the highest among all other renewable resources. The biomass use in comparison to other renewable energy resources is predominating in all energy sectors: in power generating sector biomass stands for approximately 60% of all the energy produced from renewable sources, in heating and refrigeration industry it is approx. 95% in transport sector it is approx. 100% (these figure is for the first generation biofuels) [3]. Real economic potential of biomass in Poland is estimated at 600,168 TJ in 2020, the market potential at level of 533,118 TJ [4]. The current procurement of biomass for energy production [5] is:

- Biomass solid 292,562 TJ (88,84%)
- Liquid biofuels – bioethanol 5,124 TJ (1.56%)
- Liquid biofuels – biodiesel 23,247 TJ (7.06%)
- Biogas – landfill 2,249 TJ (0.68%)
- Biogas – sewage treatment plants 3,321 TJ (1.01%)
- Biogas – the remaining 1,463 TJ (0.44%)
- Municipal waste 1,360 TJ (0.41%).

The main technologies for biomass conversion into secondary energy carriers are shown in Figure 1.

Corresponding author:
Renata KULESZA – Ph.D., Eng., e-mail: kulesza.r@icso.com.pl

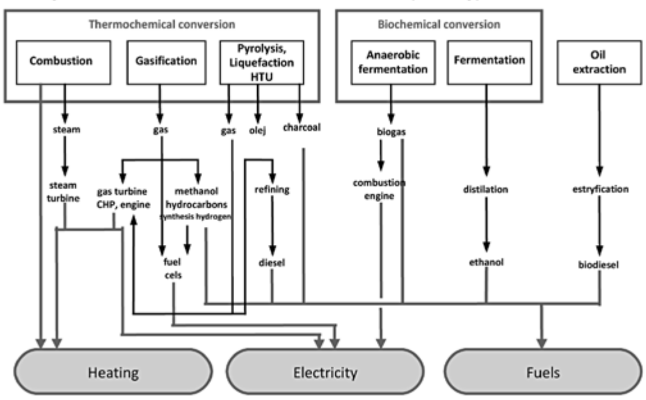

Fig. 1. Main technologies of conversion of biomass to secondary energy carriers [6]

1.2. Directions of chemical use of biomass

In the recent years there has been a rapid development of technology for the use of biomass for the production of various kinds of materials and chemical products. The market value of bioproducts, in the sector of non-food products derived from biomass can vary from a high value-added, these are the chemicals which are used for pharmaceuticals, cosmetics, food additives, etc., to a low value added as in case of mass products, such as bio-polymers, or chemical intermediates.

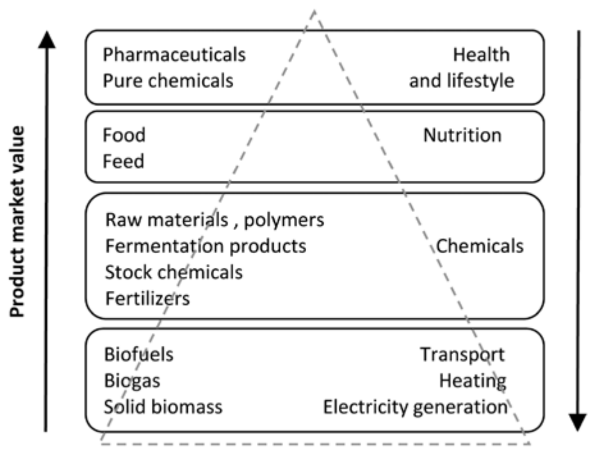

Fig. 2. Market potential of bioproducts [7]

The main directions of development of biomass utilization technologies materialize to biorefining processes, as a result of which new products can be obtained. In that a wide variety of chemical and biochemical processes are used: chemical and/or enzymatic hydrolysis, dehydration, microbial fermentation, pyrolysis, thermal deoxygenation and hydrogenation etc. Below (Fig. 3) is a diagram of a biorefinery. The most important chemical products and materials received in biorefineries are chemicals (specialty chemicals, raw materials bases, mass products), organic acids (succinic acid, lactic acid, itaconic acid and other sugar derivatives), polymers and resins (plastics based on starch, phenolic resins, furan resins), biomaterials (panels from wood, pulp, paper, cellulose), food, feed, fertilizers [8–11].

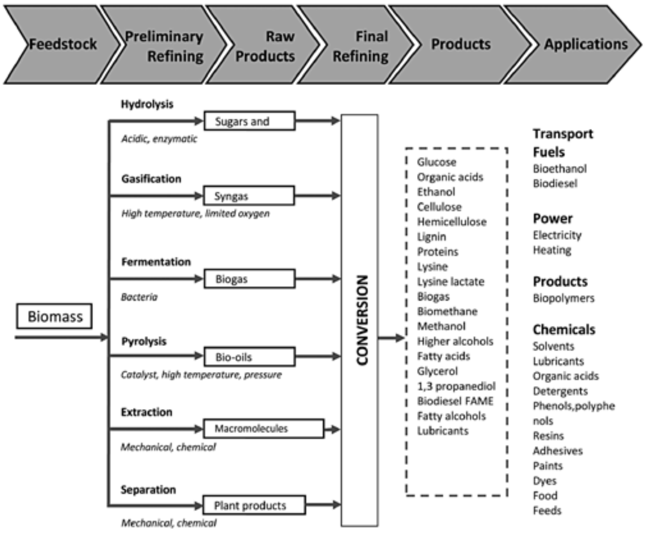

Fig.3. Biorefinery chart [9–12]

In order to maximize the use of biomass in biorefineries an integrated technology solutions should be used, which would allow for both the energy generation and the production of a wide range of bio-products, as well as for utilization of several types of the biomass. It is possible to put forward many solutions, which will depend on the available sources of biomass, technological processes and a demand for energy, fuel and bioproducts made. A classification of biorefineries based on four basic features (in order of importance): platforms, products, feedstock and processes [8,11,13] has been established. There are several technological platforms, i.e. biogas platform, syngas platform, hydrogen platform, platform of C6/C5 sugars, pyrolysis platform (bio-oil), oil platform, organic juice platform, the platform of combined electricity and heat [8 – 13]. In the context of lubricants the most interesting is the oil platform (Fig. 4).

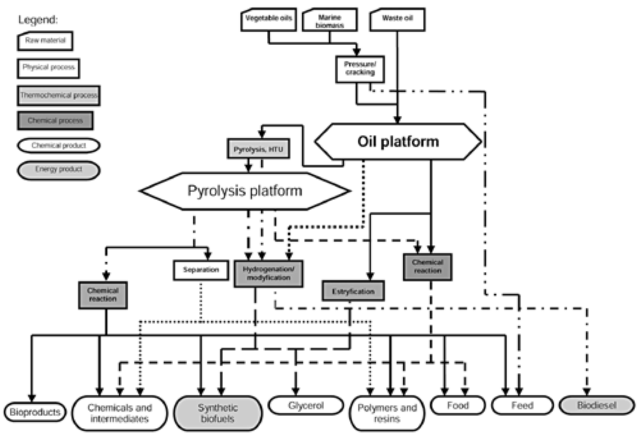

Fig. 4. Use of oil biomass in biorefineries [13]

1.3. Bio-oleochemistry

Utilization of natural sources of fats and oils by the humans dates back to antiquity. Their chemical composition and specific properties allowed them to be used as food, fuels and lubricants. A pressure on the use of renewable raw materials caused an interest in the use of oils and fats for purposes other than food. Technology of processing fats and fat wastes, both of vegetable and animal origins into useful products is a separate branch of organic technology – oleochemistry. For many years, vegetable oils and animal fats were used on industrial scale for production of biofuels, as well as lubricants because of their non-toxicity and biodegradability. Oleochemicals can also be used as monomers, plasticizers, lubricants, antiadhesive agents, antistatic agents, stabilizers and the likes. When speaking of bio-petrochemistry, we talk about the utilization of biomass.

Among raw materials of plant origin the most important is rapeseed oil. The oil (approx. 70% in the EU and about. 50% in Poland) is processed into biodiesel. Used vegetable oils and animal fats in the European Union make only approx. 7% of the feedstock. The analysis of production trends to indicate that the total production of vegetable oil in the world, now approx. 150 Mt, will show an average annual growth of approx. 4%. The largest increase in supply is expected for palm oil (5%), with an accompanying decrease in the supply of rapeseed oil by 1.4% [15]. It is estimated that by 2020 the number of animal fat made in meat processing will reach 791.7 thousand tons and the potential for production of biofuels from wastes from the meat industry is estimated at 699.2 thousand tons – assuming that biodiesel is produced from the waste, or at 347.9 thousand tons – assuming that biogas is produced from the waste [16]. However, the production of biodiesel requires a supply of relatively pure fatty raw materials, containing neither water, nor proteins, nor free fatty acids. As a result of the use of oils and fats for food preparation, as well as for technical applications, a degradation of their chemical composition often takes place.

1.4. Lubricants market

The total market for lubricating oils in 2012 was approximately 222 thousand tons of sold ready oils for the automotive industry and oils classified as "others". This means that after two years of an increase the market declined year to year by approx. 7.61%, reaching the level from around 2006. The automotive segment declined by 5.2% compared to the levels of the last year, reaching 118 thousand tons, while oil industry segment declined in 2012 by 8% reaching the level of 97 thousand tons [16].

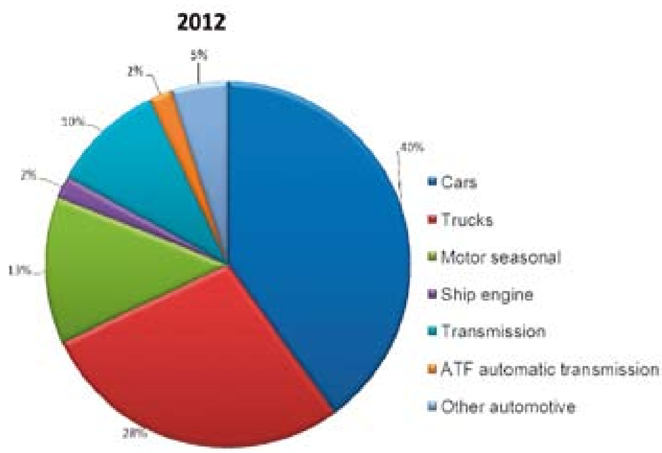

Fig. 5. Structure of sales of lubricating oils for automotive segment [16]

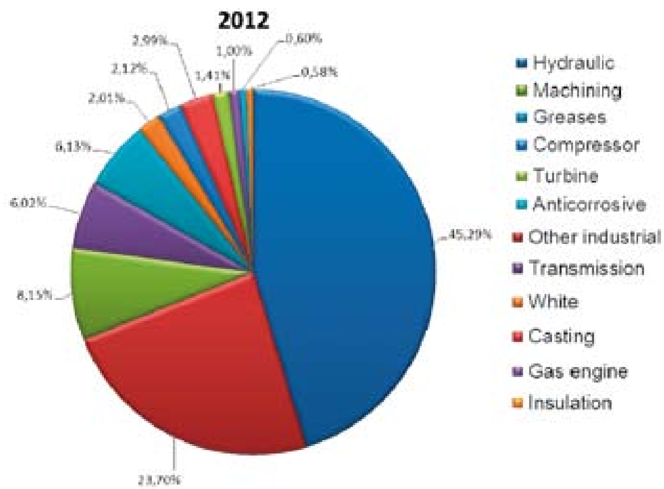

Fig. 6. Structure of sales of lubricants for industry segment [16]

In the recent years, in the segment of industrial lubricants the hydraulic oils are dominating by approx. 45%. Nearly 70% of the industrial oils are mineral oils, and the rest are non-mineral oils [16]. Approximately 90% of lubricants currently used can be replaced by materials of plant origin.

1.5. Lubricants based on biomass

The term bio-lubricants refers to all lubricants that are both well-biodegradable and non-toxic to humans and aquatic environments. A bio-lubricant may be oil-based (e.g. rapeseed oil), or based on synthetic esters produced from renewable sources or from modified mineral oils [2].

In practice, for many years, vegetable oils and animal fats were used for industrial purposes. Today, in favor for the use of fats and their wastes, after a suitable chemical modification, as a base lubricants speaks ecological and economic considerations. A practical way of composing lubricants is in the diagram below (Fig. 7).

Therefore the properties of the oil base are important. Direct use of fats as lubricants is not recommended for several reasons. Fats are characterized by a limited thermal and oxidation stability and a low hydrolysis resistance, which is due to the presence of unsaturated C=C bonds, β-CH parts and acyl groups. In the following diagram (Fig. 8) the properties of bio-oil base, mineral oils and synthetic esters are compared. The reduction or removal of deficiencies is possible by a chemical modification of the fatty materials [18].

A method for obtaining a bio-base with the desired properties is to reduce the number of double bonds by epoxidation of vegetable fats or by their selective hydrogenation. Epoxidized vegetable oils are not compatible with mineral oils because of poor solubility. This feature can be improved by transesterification of the epoxidized products by fatty alcohols [19, 20].

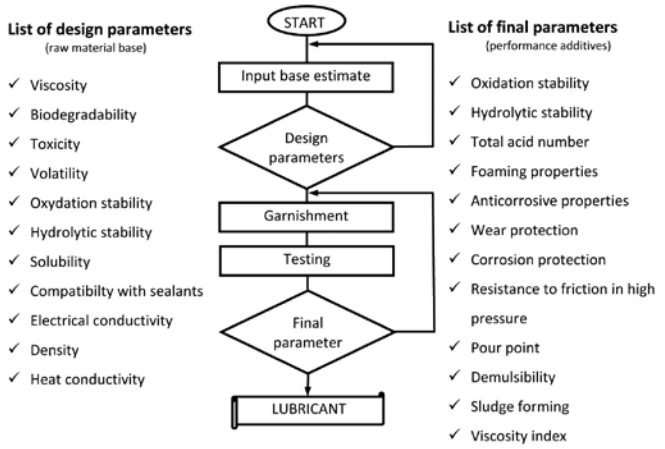

Fig. 7. Diagram of designing of lubricants [17]

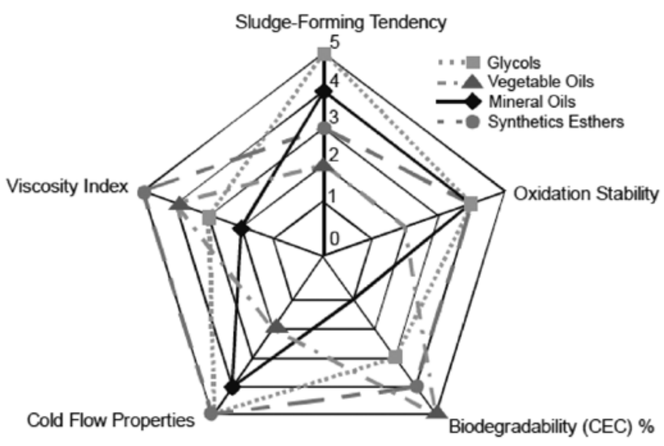

Fig. 8. Comparison of some properties of base bio-oil, mineral oil and synthetic ester [17]

An important direction of modification of the raw materials is a process of esterification of fatty acids, transesterification of oils or the methyl esters by other alcohols. Esters from animal fats, which contain lower numbers of unsaturated bonds in the carbon chain are characterized by a higher freezing point. Transesterification products of fatty acid methyl esters with alcohols containing quaternary carbons do not contain a β-CH moiety in an alcoholic fragment, so they are characterized by a high thermal stability. Esters of higher molecular weight are characterized by an increased oxidative and hydrolytic stability, so they are suitable for the use as lubricant oil bases [18].

An important group in terms of applications as lubricants are oligomers and estolides of fatty acids and their esters. These compounds have high molecular weights, high viscosity and at the same time have a low pour point as a consequence of their branched structure. Modification of fatty acids by dimerization (and oligomerization) proceeds according to Diels-Alder reaction scheme [21]. The estolidation of fatty acids is a process of addition of an acid carboxyl group of one molecule to a double bond in the carbon chain of the second molecule. For estolides their secondary ester bonds are less susceptible to hydrolysis than ester bonds in vegetable oils [22].

Currently, many studies focus on the development and optimization of processes of conversion of the biomass obtained from the base in order to change its properties into the desired ones. Here are included both chemical modifications and biotechnological processes (using bacteria or enzymes) and even modifications of oilseed crops [2, 22÷39].

2. Summary

In Poland, the biomass is mainly used for energy purposes. Steadily going for more than ten years development of the biomass technology now gives the ability to produce materials and chemicals with a high added value. Biorefineries on the oil platform (fat) allow, for the acquisition of feedstock, for a broad range of oleochemistry processing. Production of lubricants made from the biomass is one of the directions of their use. Direct use of fats as lubricants is not recommended due to their limited thermal and oxidation stability, and their low resistance to hydrolysis. Obtaining a bio-base with the desired properties will allow for formulation of bio–lubricants with desired parameters appropriate for a given application. Currently, many studies focus on the development and optimization of modification processes of the extracted bio-base; these are mainly chemical and biochemical conversions. Lubricants from renewable raw material base are available on the market. Expansion of this offer will require further research in order to develop and optimize fairly complex technologies for modifications of a biodegradable fat base into a base having desired properties.

Literature

1. Rozporządzenie Ministra Gospodarki z dn. 14 sierpnia 2008 r. (Dz. U. z dn. 28 sierpnia 2008 r. Nr 156, poz. 969 ze zm.).
2. Salimon J., Salih N., Yousi E.: *Biolubricants: Raw materials, chemical modifications and environmental benefits*, Eur. J. Lipid Sci. Technol. 2010, **112**, 519–530.
3. http://www.pigeo.org.pl, 5.04.2014 r., Polska Izba Gospodarcza Energii Odnawialnej.
4. *Możliwości wykorzystania OZE w Polsce do roku 2020, http://www.ieo.pl, 28*.03.2014 r., Instytut Energetyki Odnawialnej.
5. *Energia ze źródeł odnawialnych w 2012 r.*, GUS 2013.
6. *Bioenergetyka*, http://www.environet.eu/bioenergetyka, 28.03.2014 r.
7. Kwant K.W.: *Przejście do biogospodarki z fermentacją beztlenową w Niderlandach", http://www.minrol.gov.pl,* 3.04.2014 r.

8. Cherubini F.: *The biorefinery concept: Using biomass instead of oil for producing energy and chemicals*, Energ. Convers. Manage. 2010, **51** (7), 1412-1421.
9. *The future of industrial biorefineries*, World Economic Forum, 2010. Report., http://www3.weforum.org, 5.04.2014 r.
10. *Bio-based chemicals: Value added products from biorefineries*, IEA Bioenergy 2012, Report., http://www.ieabioenergy.com, 28.03.2014r.
11. *Biorefineries Roadmap as part of the German Federal Government action plans for the material and energetic utilisation of renewable raw materials*, Federal Ministry of Food, Agriculture and Consumer Protection, 2012, http://www.bmelv.de, 28.03.2014r.
12. Górecki R.: *Energia odnawialna szansą rozwojową przemysłu chemicznego?, http://www.senat.gov.pl, 3*.04.2014r.
13. Cherubini F. et al.: *Toward a common classification approach for biorefinery systems*, Biofuels, Bioprod., Bioref. 2009, **3**(5), 534-546.
14. *Rynek rzepaku – stan i perspektywy. Analizy rynkowe,* Instytut Ekonomiki Rolnictwa i Gospodarki Żywnościowej PIB, 2011, 40, ISSN 1231-269X, 6.
15. *Biopaliwa. Produkcja biopaliw z tłuszczów zwierzęcych*, 2012, http://www.zyjmyeko.pl/, 28.03.2014r.
16. *Rynek olejów smarowych*, *Raport roczny 2012*, Polska Organizacja Przemysłu i Handlu Naftowego, 2013, http://www.popihn.pl/, 28.03.2014r.
17. Pulcu G.: *Bio-based lubricants*, Opet Petrolcülük A.S., 2008, http://www.fp7.org.tr, 9.04.2014r.
18. Mosio-Mosiewski, J., Muszyński, M., Nosal H., Warzała M.: *Nowe możliwości wytwarzania biopaliw oraz biodegradowalnych środków smarowych w oparciu o surowce oleochemiczne*, Środowisko i Rozwój 2008, **18**/2.
19. Fox, N. J., Stachowiak G.W.: *Vegetable oil-based lubricants-A review of oxidation*, Tribol. Int. 2007, **40**, 1035-1046.
20. Fischer S., Szałajko U., Szeja W., Niemiec P.: *Epoksydowane oleje roślinne jako środki smarowe*, Przem.Chem. 2003, **82**/8-9, 1016-1017.
21. Walisiewicz-Niedbalska W., Chmielarz B., Kosmacińska B., Dyczewski M.: *Synteza dimerów i estolidów nienasyconych kwasów tłuszczowych oraz ich adduktów z bezwodnikiem maleinowym*, Przem. Chem. 2001, **80**/2, 52-55.
22. Fischer S., Niemiec P., Szeja W.: *Estolidy-oligomerowe pochodne kwasów tłuszczowych jako środki smarowe*, Przem. Chem. 2005, **84**/7, 512-515.
23. Quinchia L.A. et al.: *Viscosity modification of different vegetable oils with EVA copolymer for lubricant applications*, Ind. Crop. Prod. 2010, **32**/3, 607-612.
24. Silva, J. A. C.: *Biodegradable lubricants and their production via chemical catalysis*, Tribology - Lubricants and Lubrication, C. Kuo, 2011, ISBN 978-953-307-371-2.
25. Abdullah, B.M., Salimon J.: *Optimization of Process Parameters for Diesters Biolubricant using D-optimal Design*, World Acad. Sci., Eng. Technol. 2011, **56**, 773-781.
26. Åkerman, C.O. et. al.: *Clean synthesis of biolubricants for low temperature applications using heterogeneous catalysts*, J. Mol. Catal. B-Enzym., 2011, **72**, 3-4, 263-269.
27. Åkerman, C.O. et. al.: *Biolubricant synthesis using immobilised lipase: Process optimisation of trimethylolpropane oleate production*, Process Biochem. 2011, **46**, 12, 2225-2231.
28. Quinchia, L.A., et al.: *Low-temperature flow behaviour of vegetable oil-based lubricants*, Ind. Crop. Produ. 2012, **37**, 1, 383-388.
29. Bart, J. C. J., Cavallaro, S., Gucciardi, E.: *Biolubricants: Science and Technology*, Elsevier 2012.
30. Salimon, J., Salih, N., Yousif, E.: *Biolubricant basestocks from chemically modified ricinooleic acid*, J. King. Saud. Univ. Sci. 2012, **24**, 11-17.
31. Hamid, H.A.: *Synthesis of palm oil-based trimethylolpropane ester as potential biolubricant: Chemical kinetics modeling*, Chem. Engin. Jour. 2012, **200-202**, 532-540.
32. Salimon, J., Salih N., Yousif E.: *Triester derivatives of oleic acid: The effect of chemical structure on low temperature, thermo-oxidation and tribological properties*, Ind. Crop. Prod. 2012, **38**, 107-114.
33. Zulkifli, N.W.M et al., *Wear prevention characteristics of a palm oil-based TMP (trimethylolpropane) ester as an engine lubricant*, Energy 2013, **54**, 167-173.
34. Bilal S. et al.: *Production of biolubricant from Jatropha curcas seed oil*, J. Chem. Eng. Mater. Sci. 2013, **4**(6), 72-79.
35. Avisha, C., Debarati, M., Dipa B.: *Biolubricant synthesis from waste cooking oil via enzymatic hydrolysis followed by chemical esterification*, J. Chem. Technol. Biot. 2013, **88**, 139-144.
35. Cermak, S.C. et al.: *Synthesis and physical properties of new estolide esters*, Ind. Crop. Prod. 2013, **46**, 386-391.
36. Lawal, S. A., Choudhury, I. A., Nukman, Y.: *A critical assessment of lubrication techniques in machining processes: a case for minimum quantity lubrication using vegetable oil-based lubricant*, J. Clean. Prod. 2013, **41**, 210-221.
37. Biswas, A., Cheng, H. N., Kim, S., Liu, Z.: *Modified triglyceride oil through reactions with phenyltriazolinedione*, J. Am. Oil Chem. Soc. 2014, **91**, 1, 125 - 131.
38. US Patent WO20140024869 A1 *Production of lubricant base oils from biomas.*
39. US Patent WO 2013123393 A1 *Biobased semi-solid lubricant and method of preparation.*

*Renata KULESZA – Ph.D., Eng., graduated from the Faculty of Chemical Engineering and Technology, Cracow University of Technology (1992). Ph.D. at Cracow University of Technology, Faculty of Environmental Engineering (2003). She currently works at The Analytical Department of Institute of Heavy Organic Synthesis “Blachownia” in Kedzierzyn-Koźle. Research interests: analytical chemistry, engineering, and environmental protection, chemical technology, product safety, management of innovation projects. She is the author of 6 chapters in monographs, 11 articles in the scientific and technical journals and 42 papers and posters at national and international conferences. She co-authored 3 patent applications.

e-mail: kulesza.r@icso.com.pl, phone: +48 77 487 3568

Iwona SZWACH – Ph.D., is a graduate of the Faculty of Biology and Environmental Protection, University of Silesia in Katowice (1987). Ph.D. at Czestochowa University of Technology, Faculty of Engineering and the Environment (2000). She currently serves as deputy director for Research and Development at the Institute of Heavy Organic Synthesis “Blachownia” in Kedzierzyn-Koźle. Research interests: engineering sciences, chemical organic technology, properties of surfactants, surfactant biodegradability testing and analysis related to environmental protection. Innovative project management, product safety. She is the author of 14 articles in the scientific and technical journals and 41 papers and posters at national and international conferences.

e-mail: szwach.i@icso.com.pl, phone: +48 77 487 34 70