PROBLEMS WITH UTYLISE OF GLICEROL FRACTION – WASTE PRODUCTS OF FAME PRODUCTION

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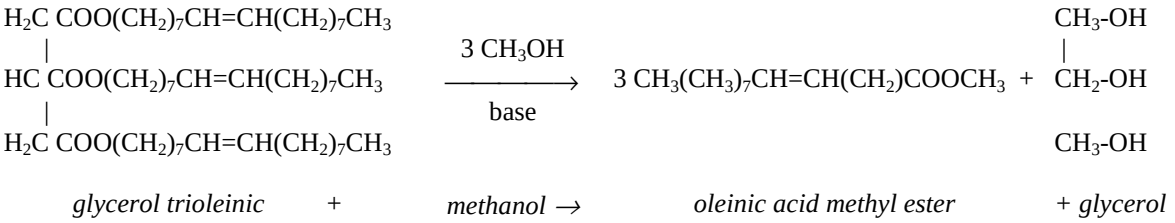
1. Introduction

One of the most popular biocomponents today for fossil fuels, except from bioethanol used widely for gasoline, is fatty acid methyl ester (FAME). It can be added to diesel fuel used in compression-ignition engines. Different blends are possible – from 5%(V/V), blends 10% up to 30%(V/V) and finally pure FAME used as fuel. FAME production is based on estrification of fats, i.e. rape seeds oil estrification with methanol (no free fatty acids). Equation 1 presents reaction of estrification (glycerol trioleinic as an example) [1].



(1)

This reaction by-product is glycerine fraction. In practice it is not a pure chemical compound, but widely and not correctly called glycerine, but fraction, that includes, depending on a type and efficiency od estrification equipment, from 40 to 90% of glycerine. Raw fraction is practically a waste, but after appropriate treatment may be widely used, i.e:

- in pharmaceutical and cosmetics industry;
- as a thickener in fodder for animals;
- as a component of fertilizers;
- as a component to be burned for heating purposes;
- as a component for greases and lubricants production.

2. Glycerine fraction characteristics

A few years ago, before installations for FAME production appeared in Poland, it was stated, that „glycerine" was to be sold, and income could improve economics, so production and use of so called „biodiesel" would be profitable. The reality proved something completely different. Glycerine fraction from estrification process includes many components, that as contaminants, make it completely usless for any purpose. It can not be used as fertilizer or fodder component (because of toxicity of methanol and metals), and it can not be burned (metallic compounds generated during burning process create hard ash compounds that can cause burners damages).

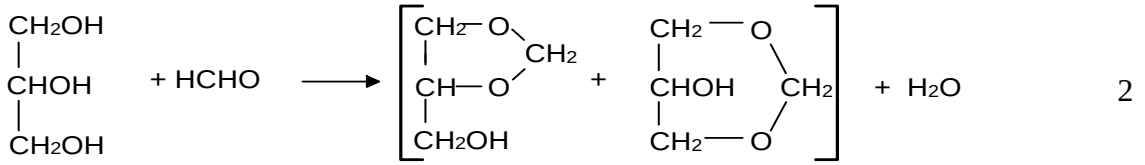
Depending on construction of installation for FAME production, its complexity and equipment used, technological process is different, so final product's and wastes' purity is also different. It is obvious, that ester's purity and its quality is the most important matter here, but glycerine fraction's purity and quality is also important for future use of it. Purification is a costs generating process. Building of processing module – treating glycerine fraction – is profitable for medium and big installations for FAME production. What are the most important differences between „wastes" from industrial and „home-grown" production? In the first option it is possible to receive product being recognized practically as technical glycerine. It is a clear, pale liquid highly processed. Its properties are stabilized, so for future use less complicated and less expensive treatment is required. In the second option mentioned above we receive brown, cloudy liquid, with high content of metal salts form catalyst and toxic methanol. Low level of processing and diversity (quality and composition strictly depending on raw material used for batch production). Those problems are more serious in case of use during estrification fats different than rape seeds oil, ie. vegetable oils, fried oils, animal fats. For appropriate preparation then high processing is required, that not always guaranties high quality of glycerine received finally. The only one advantage of such raw material is its proce – 35-40% lower, but finally it may not compensate for costs of processing ond purification. Additional cost generating agnt here are logistic problems connected with receiving small portions of fraction from different suppliers.
Below differences in glycerine fraction's parameters received in professional agrorefinery (with yearly FAME production over 60.000 tons) and „home-grown" installation (Table 1).

Table 1. Comparison of properties for farmaceutical glicerne and glycerine fractions

Properties	Farmaceutical glycerine	Glycerine fraction (big installation)	Glycerine fraction („home-grown" installation)
Glycerine content	99,7 %(m/m)	80 – 90 %(m/m)	35 – 40 %(m/m)
Colour	Clear, colourless	Yellow to light brown, clear	Opaque, cloudy
Sulfate ash content	max 0,01 %(m/m)	1,5 – 5 %(m/m)	
Water content	max 0,3 %(m/m)	a few %	to several a dozen or so %
Methanol content	not include	max a few %	even to 20 %
Metals content (total)	several dozen ppm	to a few % (as salts and soaps)	
Esters and its derivatives content	not include	to about 5 %	to several a dozen or so %
Others content	not include	to a few %	to several a dozen or so %

3. Glycerol formal

One of available processes for glycerine fraction treatment is its processing for substances, that can be added to engine fuels as additives improving selected parameters. It is possible after glycerine processing to glicerol formal. Below two typical chemical reactions are presented, that describe the process of glycerol formal obtaining [2]:



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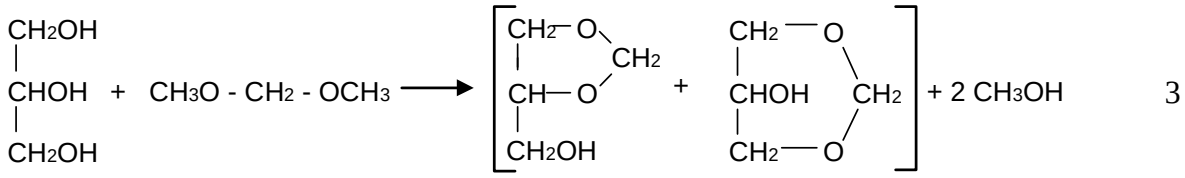

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It was assumed, that chemical compound obtained in this way can be used as a compound for diesel fuels used in compression-ignition engines (regardless of their application: cars, machines, agregates, marine).Such product was obtained in Institute of Heavy Organic synthesis "Blachownia" in Kędzierzyn-Koźle, and testing of product was carried out in the Air Force Institute of Technology as a part of european research project Eureka [3].
Initial assumption was, that for base fuel (diesel fuel), 5%(V/V) of methylal will be added. During blending first problems appeared with its homogenosity. After intensive gomogenisation the blend was stable for a short time. But basic testing was done, according to methodology typical for diese fuels.
Testing results are presented in Table 2.

Table 2. Results of basic physical properties testing for diesel fuel blend with 5% of glycerol forma

No.	Physical property	Diesel fuel	Diesel fuel + 5% glycerol formal
1	Density, 15C	0,8242	0,8277
2	Kinematic viscosity, 40C	2,120	2,112
3	Distillation To 250C is distilled To 350C is distilled 95% (V/V) distilled to	 59,8 98,7 300,7	 60,5 98,7 299,8
4	Lubricity, HFRR	401	171
5	Flash point, C	85,0	81,0
6	Cetane index, calculated	52,0	29,9
7	Insolubles content	4,62	fuel disolve filter
8	Oxidation resistance	5,99	fuel disolve filter
9	Carbon residue, %(m/m)	0,02	0,02
10	Ash content, %(m/m)	0,001	0,001
11	Corrosive reaction on Cu	st. 1	st. 1

During testing it was observed, that glycerol formal concentration is to high. The result of it was cetane index value decrease. It is supposed, that fuel's self-ignition properties were worsened. This thesis requires engine testing, but these were skipped because of other factors. 5%(V/V) blend could not be filtered through paper filters, that suggests, that during normal application of that fuel in engines paper filters could be damaged. Flash point temperature was decreased, but in

acceptable limits. Positive aspects of glycerol formal must be also underlined. Its lubricity improving properties are very good. Scar diameters during HFRR (High Frequency Reciprotating Rig) test was three times smaller than required by appropriate standard. This is a very interesting result, but not equivalent to all disadvantages mentioned above.
Because of results described above methylals application, that should improve fuel's thermal stability, low temperature properties, lubricity and viscosity, was not abandoned. The aim of testing but modified. Glycerol formal application as an additive for diesel fuels will be evaluated. Such testing was stared in December 2006, so the results could not be presented here.

4. Conclusions

- With development of industry dealing with fuels from estrification of vegetable and animals fats essential problem of glycerine fraction application appeared.
- It seems, that glycerine derivatives should be used as fuels additive (because of positive effect in fossil and vegetable fuels).
- Glycerine derivatives application in petroleum industry could improve economical and technological effect.
- First stage of research project was not successful, but testing results show the need for continuation of research – after program modifications.

Literature

[1] Rosiak, D., Kolczyński, J., Dzięgielewski, W., Walisiewicz–Niedbalska, W., Struś, M., *Problemy technologiczne produkcji estrów metylowych oleju rzepakowego – Odnawialne źródła energii u progu XXI wieku*, Warszawa 2001.
[2] Trybuła, S., Terelak, S., *Formal gliceryny jako komponent paliwowy*, ICSO 2006.
[3] Gołębiowski, T., Dzięgielewski, W., *Zastosowanie formalu gliceryny jako komponentu do paliw samochodowych*, ISCO 2006.