

G-PHASE FROM METHYL ESTER PRODUCTION – SPLITTING AND REFINING

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Abstract:

The article describes the partial refinement of crude glycerol from KOH and NaOH alkali-catalysed transesterification of vegetable oils and/or animal fats. Heavier liquid phase from transesterification, where glycerol in concentration of 56 – 64 wt. % is present, especially together with alkali potassium soaps, is decomposed with mineral acids HCl, H₂SO₄, H₃PO₄ with concentrations 36 – 40 %, in case of H₃PO₄ 85 %. The lowest content of salts at the level of 0,95 wt. % in partially refined glycerol is achieved when H₂SO₄ is used, at the concentration of glycerol in the raffinate above 95 %. Low raffinate colour at the level of 3 is achieved by adsorption on activated clay or on a mixed adsorbent of clay and active coal. The article yields experimental data and information on the preparation of the crude glycerol from glycerol phase (K⁺) and glycerol phase (Na⁺), on their partial refinement, as well as on the possibility of its further commercial utilization.

Key words: glycerol, splitting by mineral acids, refining

1. Introduction

Methyl esters of higher fatty acids (ME) are used as alternative fuel, or its component for diesel engines from renewable sources. EU defined the program of replacement of 2 % of the consumption of liquid fuels by 2005 and 5.75 % by 2010 with biofuels, where ME should be the key component. They are usually prepared by alkali-catalyzed transesterification of vegetable oils and animal fats with methanol^[1]. By this reaction glycerol (G) is formed as a heavier separate liquid phase, so called glycerol phase (GP).

The portion of GP represents approximately 16 – 18 % of the weight of the input oil/fat and its composition is not stabilized. It is influenced by several factors, especially by the acidity number of the input oil. It contains 50 – 60 % of G, 12 – 16 % of alkalies especially in the form of alkali soaps and hydroxides, 15 - 18 % of ME, 8 – 12 % of methanol (MeOH), 2 –3 % of water and further components. The GP itself can be utilized in the production of ME in the treatment of oils and fats with increased acidity^[2].

The basic step during the GP treatment is its decomposition by a strong mineral acid. Applying the mineral acid the alkaline soaps decompose and transform to free fatty acids (FFA) that do not mix with the polar G and water and create a separate phase. By decomposition of the soaps the emulsifier is removed from the system so that the ME taken away from the ester phase to the GP during the transesterification de-emulgate and create together with FFA a separate so called organic layer (OL) with lower density. The semi-refined G (G-layer GL) creates another liquid layer with higher density. GL consists of 78 – 82 % of G, 10 – 12 % of water, 6 – 8 % of salts, 1 – 2 % of methanol, the rest are resins, dyes and other natural compounds. After resolving the partial problems connected mainly with the presence of the salts the semi-refined G can be refined on the film vacuum evaporator to purity of 99 %. Total refinement of G by vacuum distillation is both economically and technically demanding.

ME production expansion in Europe in the last years has considerably reduced the price of G. Tab. 1 summarizes the qualitative parameters and prices of commercially utilizable commodities in the area of semi-refined G^[3].

Tab. 1 Quality parameters and prices of semi-refined G (end 2004)
(NOR – non-volatile organic residue, MONG – matter organic non-glycerol)

Quality	G, min. % wt.	Ash, max. % wt.	MeOH, max. % wt.	NOR, max. % wt.	MONG, max. % wt.	Price, €/kg
A	80,0	8,0	0,5	3,0	2,0	0.171-0.185
B	70,0	9,8	0,5	3,0	3,0	0.118-0.131
C	90,0	2,0	0,5	1,0	1,0	0.421-0.474

ME production keeps progressively rising also elsewhere across the world, notably in South America, Australia and South-east Asia. ME's are produced mainly from cost-effective local sources of soybean and palm oils because of the high prices of diesel oil and crude oil. At present, G is considered as an inevitable by-product in the production of fatty acids and their derivatives from natural triacylglycerols (TAGs). As much as 97 % of G currently used in industry is a highly refined product containing 97%+ G. The refining costs are high (approx. US\$ 400 per tonne) and the prices of refined G vary from US\$ 1.3 to US\$ 2 per kilogram. As a result of the high G price, its market is small and fragmented.

If G is to be used in new technologies, a cheap method of G refining must be developed. There is a widely designed and heavily financed research of possible uses of G in the production of new inexpensive products but also of high-value chemical specialties. Owing to G's unique structure and properties, the research has a great potential to develop a range of new G-based processes and products. G is not toxic, and is edible and readily degradable. Many new products are based on chemically unmodified G (anti-icing spraying of airports) or on simple modifications of the G molecule. A reduction in G price may open important markets in the areas of polymers, ethers and other substances. The new applications will probably use mainly G selectively reduced to 1,3-propandiol for textile polymers (biochemical transformation), glycerol carbonate (reactions G + urea or G + ethyl carbonate) as a new type of high-boiling solvent, detergent, paint component, etc. or as polyglycerols and their esters. Another attractive application is in the field of car fuels due to the price of fossil fuels and the size of the market. For example, ketals, acetals, ethers of G with lower alcohols can easily fulfill the function of cetane improver^[4], lubrication enhancer^[4,5], low temperature properties additive, oxygenate additive with the influence on the composition of exhaust gases, or other parameters^[5]. However, it will be necessary to submit convincing evidence that G and its derivatives do not cause harm to the engine even in long use, that the price of modified G will be competitive with classical fuels, and that adequate finances are ensured to commercialize a new fuel or its component.

Naturally, certain adjustment and partial refinement of GP is necessary, at least to an extent, which meets the requirements for some of the commodity classes. The effort is concentrated on such partial refinement of G, which allows the utilization of refined G in selected technologies.

Except of the total refinement by vacuum distillation on vacuum evaporators with wiped film^[6] there exist a whole range of processes, which are from the point of view of energy consumption and machinery less demanding, but also less effective. Raw G is successfully refined with the use of ion exchangers^[7,8,9] G is a non-iogenic substance and the inorganic salts, FFA, soaps and coloring agents are removed by ion exchangers upon the passage of diluted G through a system of katex and anex stations. Clear and clean water solution of G is obtained, which is then thickened by vacuum distillation. Bleaching is not required. The membrane processes as electrodialysis^[10,11] and reverse osmosis^[9,12] are also applied, electrolysis is also reported^[10].

The aim of the presented article is primarily to select such refinement processes with minimum content of salts in partially refined G, but secondarily also to find such refining possibilities even with higher content of salts, but potentially usable for selected application. Study is oriented to the splitting of GP with suitable mineral acid with minimum economical and ecological problems with the salt disposal. It is necessary to treat raw G in the way, which facilitates its refinement in vacuum evaporators, or its use in selected applications without further treatment.

2. Experimental

Materials. For the study of partial refinement of G from glycerol layer (GL) the GP from alkali-catalyzed transesterification of rapeseed oil with KOH/MeOH and NaOH/MeOH were used^[1]. For the measurements 300 g of GP was used. Three types of mineral acids, HCl 36 % wt., H₂SO₄ 40 % wt., H₃PO₄ 85 % wt. were used for decomposition. The used acids were of pure grade.

Methodology of evaluation. The acid number (AN) was determined according to the STN EN 65 6070, sulphate ash according to the STN EN 65 6063. The colour of G was determined according to the colour scale STN 58 0101 on selected specimens only. The content of MONG was not followed in this set of measurements.

Working procedure. Decomposition of GP was carried out in a glass vessel at intensive stirring and gradual input of the acid at the temperature of 60 °C. The process of decomposition is monitored by the pH measurement with a pH probe (OMEGA Newport Electronics, Inc., Santa Ana, USA). Four pH values (4.5, 4.0, 3.5, 2.5) were selected by the GP decomposition. After the selected pH value was achieved, the stirring was stopped and the bottom GL was separated. Filtration at elevated temperature is a helpful factor for decomposition, as it removes the formed interlayer. The AN of OL was determined after the separation, and the balance between OL and GL was carried out. Subsequently, the pH of GL was adjusted to 6 using the 15 % water solution of KOH. After the removal of water and MeOH from GL on a film rotor evaporator at the temperature of 120 – 130 °C and at the pressure of 2 kPa, the GL was cooled a precipitated salts were removed by filtration.

3. Results and discussion

Table 2 summarizes the results of measurement of the content of salts in semi-refined G obtained from decomposition of G-phase (catalyst K⁺).

Tab. 2 Content of salts in semi-refined G from G-phase (K⁺)

G-phase (K ⁺)	pH	Acid, mol	GL:OL wt. : wt.	AN of OL, mg KOH/g	Ash, %
HCl (36%)	4,5	0,269	77,1:22,9	187,9	6,62
	2,5	0,298	77,5:22,5	176,9	6,62
H ₃ PO ₄ (85%)	4,5	0,297	76,6:23,4	187,2	4,27
	2,5	0,378	82,7:17,3	194,2	3,82
H ₂ SO ₄ (40%)	4,5	0,128	80,2:19,8	184,5	1,46
	2,5	0,134	77,8:22,2	190,8	1,74

In Tab. 3 are the results of measurement of the content of salts in semi-refined G obtained from decomposition of G-phase (catalyst Na⁺).

Tab. 3 Content of salts in semi-refined G from G-phase (Na⁺)

G-phase (Na ⁺)	pH	Acid, mol	GL:OL wt. : wt.	AN of OL, mg KOH/g	Ash, %
HCl (36%)	4,5	0,242	75,4:24,6	181,1	7,78
	2,5	0,264	76,2:23,8	195,5	8,00
H ₃ PO ₄ (85%)	4,5	0,271	75,7:24,3	191,6	9,32
	2,5	0,421	76,8:23,2	195,4	12,42
H ₂ SO ₄ (40%)	4,5	0,124	75,9:24,1	188,8	1,99
	2,5	0,129	79,0:21,0	192,0	1,10

The results show several interesting points:

1. Once the pH value 4.5 – 4.0 is achieved the weight ratio GL:OL remains practically constant. This pH value is characteristic for total decomposition of GP. Further increase of acidity to pH value around 6 leads at final treatment of semi-refined G to formation of additional salts.
2. Surprisingly high acidity numbers AN were in this study determined for OL during the decomposition of GP(K⁺) and GP(Na⁺). Although the value of 80 – 120 mg KOH/g was expected, the values as high as 180 – 195 mg KOH/g have been determined. This high value is not related to the residua of mineral acid from decomposition of OL (verified by several attempts to remove the mineral acidity by water extraction). As shown by subsequent measurements with high quality oils/fats used for transesterification (low acidity, minimum water content), the fraction of ME carried to GP is small, and the AN of OL is then high. This result is of great significance from the point of view of the yield of ME during transesterification.
3. The lowest content of salts, at the level of 0.95 wt. % in semi-refined G after removal of water and salt, has been achieved when GP(Na⁺) was decomposed by diluted H₂SO₄. Although it is generally known that the solubility of Na salts in glycerol is usually higher than the solubility of K salts, the lowest ash contents in case of sulfates were detected in case of the Na salt.
4. The results of splitting of GP(K⁺) and GP(Na⁺) with H₂SO₄ are from the point of view of the ash

content comparable; however a precipitate with paste consistence is formed when $\text{GP}(\text{Na}^+)$ is decomposed. Processing of these occluded salts is then markedly more difficult than in case of $\text{GP}(\text{K}^+)$. The reason may be also different consistence of both source phases. Residual SO_4 ions present in semi-refined GP then do not have to prevent necessarily the use of such semi-refined G in specific reactions catalyzed by H_2SO_4 .

5. Despite of low ash content, decomposition of GP with diluted H_2SO_4 is from the environmental point of view not welcome. Decomposition of e.g. 1 kg of GP yields around 80 g of K_2SO_4 , or 60 g of Na_2SO_4 . Production of phosphates is from this point of view more acceptable, as the inorganic by-products can be used as fertilizers. This applies especially in case of $\text{GP}(\text{K}^+)$, where the content of salts in GL is 3 – 4 %. This value is 8- 12 % in case of $\text{GL}(\text{Na}^+)$, which is not acceptable. Moreover, similarly to Na sulphates, occlusion of the salt crystals with liquid, and thus higher fraction of solid is observed in case of Na phosphates.
6. Decomposition of GP with HCl in case of $\text{GP}(\text{K}^+)$ leads to the highest salt contents in semi-refined G: however, in case of $\text{GP}(\text{Na}^+)$ the content of the salt is comparable with sodium phosphates. Despite of negative features (high ash content, ecology), decomposition of GP with HCl prevails in praxis. The most important factors are not only low price of HCl, but also simpler processing of GP after decomposition, which is related to rate and sharpness of separation.
7. The content of salts in semi-refined G, which is characteristic for the HCl process will not cause any significant problems during total refinement of G in vacuum evaporators.
8. By far the lowest contents of ash for both types of GP were achieved when GP were cleaved with diluted H_2SO_4 . The ash contents are slightly higher when $\text{GP}(\text{K}^+)$ is decomposed with concentrated H_3PO_4 ; production of K phosphates is acceptable from the ecological point of view.
9. For decomposition of GP a concentrated or diluted mineral acid can be used. Concentrated, 36 % HCl is considered to be sufficiently diluted, concentrated H_2SO_4 is not suitable due to its oxidation-dehydration effect. H_3PO_4 can be with advantage used as diluted, in the ratio of 1:1 (ca 40 %). In this case the decomposition is simpler, viscosity of the system is lower, sharpness and rate of phase separation are good. On the other hand, increased content of water increases the solubility of salt, and lowers yield of the salt after the first step. After thickening (evaporation of water) dissolved salts precipitate, and are then removed. The effect is identical both in case of concentrated and diluted H_3PO_4 . Energy demands are higher in case of diluted H_3PO_4 . Decomposition with diluted H_3PO_4 is more advantageous in case of $\text{GP}(\text{Na}^+)$. During decomposition H_3PO_4 behaves as a dibasic acid.
10. Treatment of GL by adsorption, after filtration of the salt, and before the water is removed, yields solutions with minimum colour. Active coal is a suitable adsorbent, in the amount of 1 – 1.5 wt. %, and at ambient temperature. The colour of treated specimens then corresponds to the value 3 of the colour scale according to the STN 58101.

4. Conclusion

The results of study of partial refinement of G coupled with bleaching showed that simple processes are available, which lead to acquiring of G concentrates with low content of residual salts with high yield of G, which have a good chance to become starting materials for further synthesis without further difficult refinement steps, e.g. vacuum distillation in evaporators with wiped film.

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