

ASPECTS OF REFINING BIODIESEL BYPRODUCT GLYCERIN

András KOVÁCS

Kukk k+f, kft, Szigetvári u. 1., Budapest, 1083, Hungary

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ABSTRACT

The article addresses aspects of refining on the ground of colloid chemical principles. Chemical and physical operations have been employed with the aim of producing refined grade glycerine without the use of high vacuum distillation. In glycerine refining sequences neutralization, decanting, esterification, atmospheric distillation and adsorption have been employed. Acid-base titration and rheology tests formed the basis for colloid chemical characterization of glycerine byproduct and its intermediates in the refining procedures. It has been visualized in titration curve that in neutralization of the byproduct there are two levels of reactions: acid-base neutralization in the range of pH=9-11 and a hydrolysis in the range of pH=3-5. Rheology measurements indicated that glycerine byproduct and its intermediates are dispersions that resemble specifics of solid particle stabilized (Pickering) emulsions. A simple spectroscopic method is recommended for quick check of refining efficiency.

Keywords: Biodiesel; glycerine byproduct; refining; colloid chemistry.

1. Introduction

Biodiesel have matured to become a necessary component of automotive diesel fuels. Majority of production technologies convert oils and fats by trans-esterification. Oils and fats are mainly composed of tri-glycerides, molecules with fatty acids linked to glycerine frame via ester linkage. Trans-esterification substitutes glycerine with mono-alcohol to correct fuel properties to conditions of use. As a result of catalytic conversion the output of trans-esterification reaction is splitting into apolar fuel and polar glycerine phases. Glycerine with accumulated components, that are detrimental to engine operation form the glycerine-phase, known as G-phase. Existing, but limited mutual solubility characteristics of the phases contribute significantly to loss in yield of the main biodiesel product and reduces the market value of the glycerol [1].

The fast grow in biodiesel production associated high surplus of glycerine forced the synthetic glycerine producer to close it's flagship factory in Freeport, Texas in 2005. Customers demand may motivate Dow to consider to return it into operation. Capacity of the synthetic glycerine factory in Europe, Stade, Germany, is only half of that in Freeport. The raised demand is caused by largely unsuccessful efforts to convert biodiesel glycerine into high grade products [2]. This change in consumer demand can be associated with a tendency of biodiesel manufacturers to look to use low price feedstock. Since the glycerine streams (G-phase) are generally apprehended by technology developers and providers as collection bid for everything except of the pure biodiesel the task of refining the G-phase has become more and more challenging.

The amount of theoretically produced glycerine in biodiesel synthesis is close to 10% of the feedstock. The amount of G-phase produced in operational biodiesel processing is close to 16-18% [3]. Crude G-phase consists of 50-60% glycerine, 10-30% methanol, added in excess to biodiesel synthesis to shift the equilibrium of trans-esterification toward the desired direction of methanolysis, 8-20%, alkali catalyst that was consumed in saponification of free fatty acids, 5-15 soap formed from the catalyst and free fatty acid of the feedstock, up to 5%, water in saponification reaction and released from the feedstock and up to 1% different polar components splitted from the feedstock. The most worrisome component in the G phase is the relatively large concentration of partially and fully converted triglycerides beside not converted feedstock components. The amount of apolars and soaps can account 5-25% in industrial samples. To reduce this type of loss strict

observation of technology instructions and good manufacturing practice must be in place. For further reduction advanced biodiesel processing techniques must be employed [4].

Very limited knowledge is published about the technology of glycerine refining. Despite being an ancient technology and having been used for many centuries, high vacuum distillation is still the only accepted technique used in glycerine refining by the industry. In distillation for preventing polymerization and release of acrolein: high temperature, highly alkaline or acidic conditions must be prevented. Today, glycerine is distilled under extreme vacuum (below 10 mbar) which brings glycerine's boiling point down to as low as 160 °C. This requires expensive equipment and operational costs. Technology providers follow this route [5]. There are numerous laboratories engaged to research and develop alternative, low specific energy consumption technologies for the production of clean glycerine. Alas, none of these have really matured to operational industrial process. The industrial practice for obtaining high grade glycerine is still employing a challenging high vacuum distillation of pretreated G-phase. To reduce specific energy consumption trains of distillation units are employed, instead of operating a robust single column structure. Product structure of this final high vacuum distillation is given in figure 1. All fractions contain glycerine. The head product consists of a mixture of water and glycerine, the target side product is clean glycerine, while the bottom stream is a mixture of salts and glycerine.

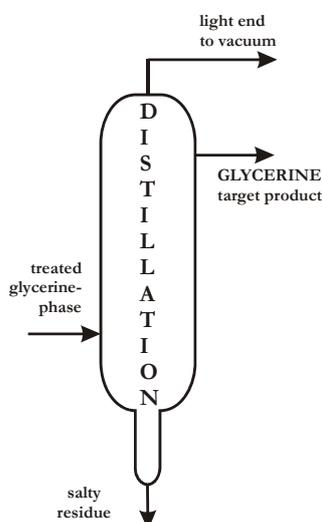


Figure 1. Standard industrial practice for producing glycerine by high vacuum distillation

Our objective was to produce animal food grade forage component technical glycerine. This target product can substitute energy components in food mixtures. Our operational goal was to produce this grade without employing high energy consuming vacuum distillation. The present article reports results and conclusions of mainly colloid chemical and refining tests.

2. Experimental

2.1. Materials and analytics

Industrial G-phase samples have been collected from a number of operational units. The unit from which the feedstock was selected operates with mixture of refined rapeseed oil and used cooking oil in different rates. The catalyst employed in transesterification is CH_3OK . Composition of the selected G-phase, together with the employed test method designations and apparatuses are compiled in table 1. Characteristics of representative target and intermediary products, refined in laboratory experiments have also been included in this table. It is to note that glycerine products have also been tested for environmental health and animal feed tests. These proved that the "refined" grade glycerine has no adverse effect to human and environmental health if it is mixed into animal feed. For further reference [6].

Commercial, reagent grade chemicals (phosphoric acid 86%, sulfuric acid, 98%) were used in neutralization. Recycled and technical grade methanol were used in experiments. Commercial grade fuller earth, carbon active and Lanxess 303, 404 and 505 ion exchange resins were used in adsorption experiments. Treatment rates of adsorbents and ion exchange resins were between 0.5 and 2.5%.

2.2. Treatment procedures

a) (*industrial practice*:) straightforward neutralization followed by downstream treatment: crude glycerine was neutralized with concentrated acids by the use of a magnetic stirrer and an attached pH apparatus with combined Pt electrode. Neutralization was stopped at pH~5-7. This pH range could have been clearly visualized without the addition of any indicator because the color of the mixture turned from dark to light brown with appearance of salt crystals at pH~8. White potassium salt crystals (K_2SO_4 , $K_{(1-3)}H_{(0-2)}PO_4$) caused this change in color. The neutralized stream was either left in still for overnight and the supernatant layers decanted or separated in a laboratory centrifuge. The separated solid phase was washed with 2*10% methanol. The filtrate of the washing operation was united with the glycerine phase. Both the glycerine and oil phases were submitted to distillation for methanol recycle, although the oil layer dissolved methanol in traces.

b) (*advanced treatment*) neutralization and esterification: The G-phase was neutralized to acidic conditions (pH=2-4) and the sour mixture was submitted to esterification under reflux for a given period of time (0-6 hours). In esterification the system was mixed with an overhead stirrer and heated in electric mantel. Final refining steps were similar to straightforward neutralization procedures: decanting, separation and washing the potassium salt crystals, phase separation of oil and glycerine, methanol distillation followed by adsorption treatment.

c) Adsorption treatment of distilled glycerine samples were carried out in stirred and temperature controlled beakers, followed by filtration. Beside those tests listed in table 1. hue index of green and blue color absorption of visible spectra (Shimadzu UV-160, cell: 10 mm) was also recorded.

Table 1. Characteristics of the G-phase

Characteristics	Feedstock	Partially refined	Refined	Test method	Apparatus
Appearance	Black, viscous	Light brown	Light yellow	visual	
pH	13.7	5.5	5.5	"Adjusted"	Boece BT – 600
Density, 20°C, g/cm ³	1.239	1.288	1.254	ASTM D 70	Gay-Lussac Pycnometer
Glycerine, %	57	88	92	HPLC	PerkinElmer Series 200
Ash content, %	4.7	1.3	0.5	ISO 3987	
Water, %	0.9	3.2	3.4	ISO 12937	KEM MKC 501
Methanol, %	17	0.35	0.28	EN14110	ACME 6100
Oil, %	15.2	2.4	0.4	Hexane elution	Adsorption chromatography
Viscosity, 20°C, mPas	figure 3.	figure 4.	figure 5.	ASTM D2196	Brookfield*

*spindles were selected to match reasonable measuring range

3. Results and discussion

Sulfuric and phosphoric acids were similarly proper for neutralization and salt removal. Deeper deashing could have been achieved with sulfuric acid. This is because the phosphoric acid was weaker and contained more water. This dissolved part of the salts formed in neutralization and by such produced slightly higher ash levels. Hydrochloric acid was tried and rejected on this ground. The more water added with this to the system dissolved all salt constituents. It is to support those who use this technique in industrial practice. The added water and dissolved salt was beneficial on the other hand in splitting the glycerine and oil layer in settling (desalting action).

Titration curve of crude glycerine is presented in figure 2. Characteristics of dispersions can easily detected in titration curve pattern. There are two inflection points. The "high pH" inflection point is an output for acid-base titration. The other the "low pH" inflection point output can – and must probably does - represent both the process of breaking the disperse system and hydrolysis of soap molecules.

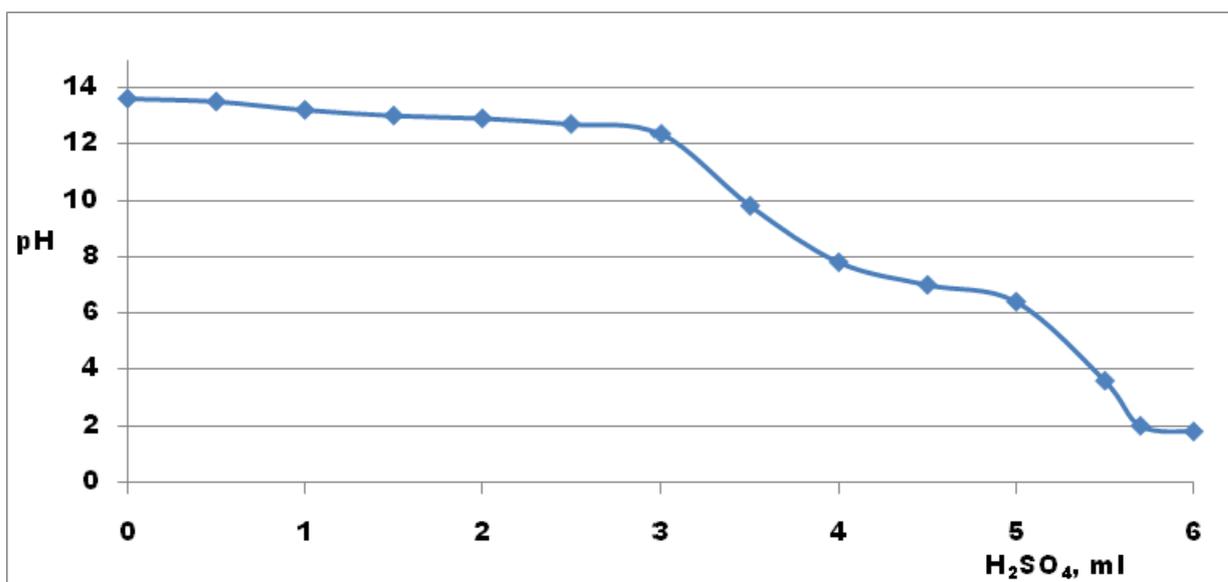


Figure 2. Titration curve of crude G-phase with concentrated sulfuric acid

It is to note that along titration there occurs a split of apolar and polar phases. The upper apolar (oil) phase is carrying over the dark color, while the lower "glycerine" phase is turning lighter into ocher with a slight tint of brown. This is a sign for dispersion of salt particles in the polar phase. This dispersion can be broken if the pH of the system is acidified below the level of pH~3.6.

These observations in titration have been proven in rheology test of crude and refined glycerine samples.

The dark, viscous crude glycerine was freed from methanol to a content below 0.5%. Brookfield (dynamic) viscosity figures of this are reproduced in figure 3. Viscosity curves of "partially" refined glycerine are given in figure 4, while viscosity curves of refined grade glycerine in figure 5. Characteristics of the partially and fully refined glycerine samples are given in table 1.

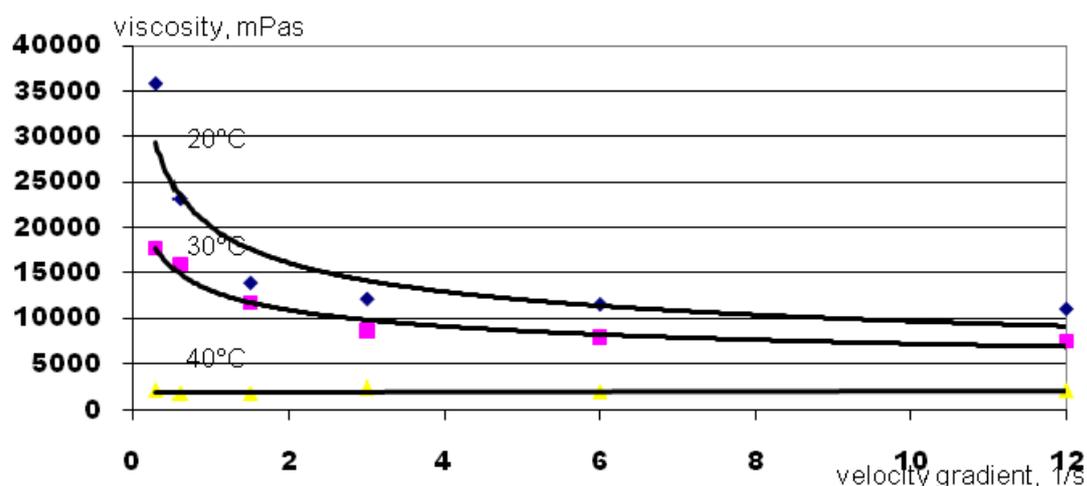


Figure 3. Viscosity of industrial G-phase (freed of methanol)(for the sake of comparison: viscosity of neat glycerine: 1410 mPaS at 20°C, 612 mPaS at 30°C and 284 mPa at 40°C) (<http://www.dow.com/glycerine/resources/table18.htm>)

It is striking that shapes and levels of curves changed significantly as a result of refining treatment.

Pattern of curves of crude glycerine in figure 3. indicates the existence of a colloid structure that is typical to dispersions with internal friction resistance. By employing high velocity gradient the applied shearing forces rearrange the globules of the disperse phase in favor to flow with less resistance. Even at such rearranged dispersion structure under high velocity gradient and relatively high temperature the ratio of shear stress to shear rate (viscosity) is more than 15 times higher than viscosity of clean glycerine.

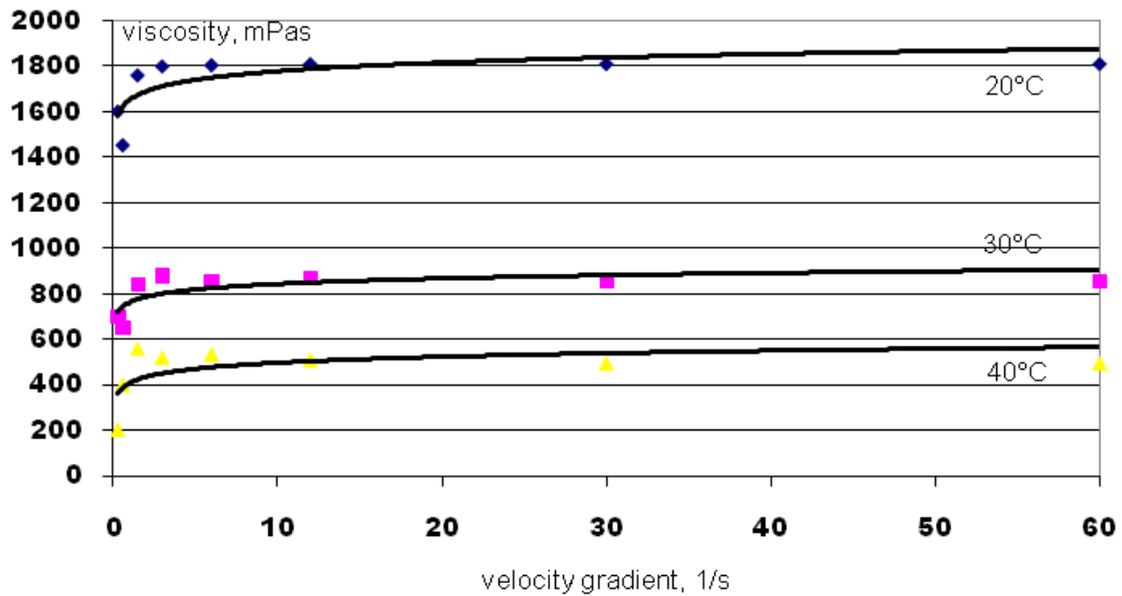


Figure 4. Viscosity of partially refined glycerine

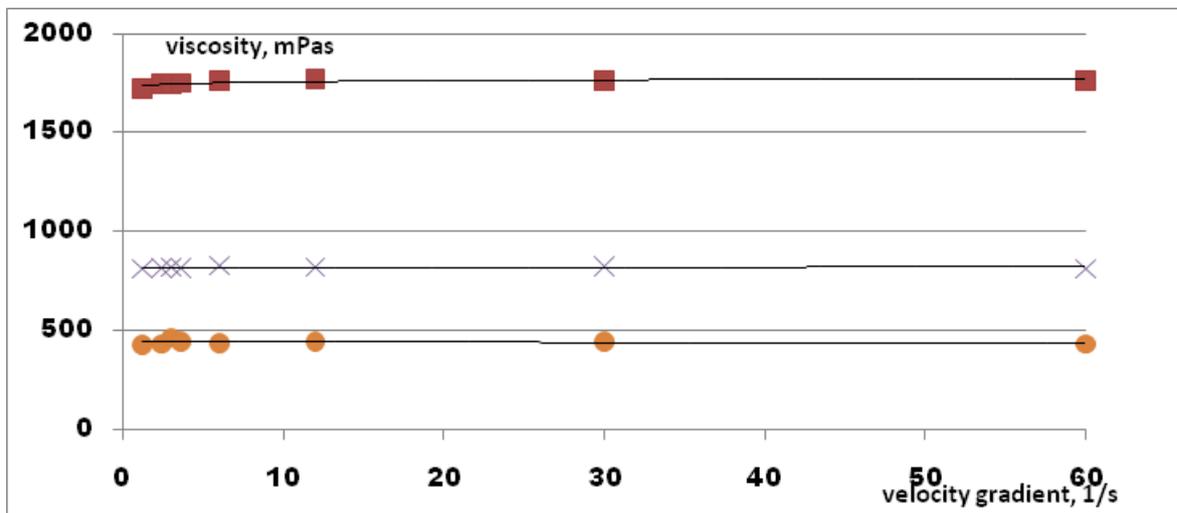


Figure 5. Viscosity of refined glycerine

By treating the G-phase to remove majority of ash forming components and some of the oil, viscosity curves of the selected sample changed in shape and level. It is to note that severity of this treatment represents the accepted industrial practice. Straightforward neutralization, removal of methanol by distillation and decanting in a centrifuge to produce technical grade glycerine, that can be for further refined by distillation and adsorption. Viscosity of partially refined glycerine products (figure 4). obtained by this refining severity is lower by two orders of magnitude than viscosity of the crude grade products. Note that velocity gradients scales are different in figures 3 and 4. At high velocity grades neat glycerine flows more freely by only 15-20% than the partially refined glycerine. The specific feature of viscosity curve pattern of partially refined glycerine is specific to dispersion systems with structural dilatation. By increased velocity gradient dragging forces in the dispersed system can be only slightly released.

The refined glycerine produced viscosity curves very close to Newtonian fluids (figure 5.). Indifferent of the velocity gradient the rate of shear stress to shear rate is close to constant. The remaining sign of slight structural dilatation is considered to be a function of residual ash content components (mainly). This is supported by viscosity values at higher shear stress ranges. Viscosity values of refined glycerine are close to theoretical viscosity values of neat glycerine.

A proposed structure of the crude glycerol was drawn on the basis of these results and is presented in figure 6. We concluded that the dispersion structure resembles features of a Pickering emulsion. In constructing the model we had to take into account the initial

viscosity responses at low velocity gradients as added information to observations made in neutralization. We explained the experienced behavior as a response of a disperse system. The viscosity drag was a response reaction of an intermediary oil layer, that can only exert this effect at low velocity gradients and giving up the resistance in the rearranged colloid structure. Accordingly the salt particles self arrange between the oil and glycerine layers. It is another probable scheme in which the solid particle constitutes the core for self assembling without entrapping oil phase into the core. The disperse system have a form of a multiple emulsion of the order of polar/apolar/polar, namely: (oil/solid/ amphiphilic +oil/ glycerine +methanol. This explains how and why the G-phase includes relatively high amounts of components that can be extracted with hexane. In either case (central or interfacial) the salt exerts the function of stabilizer and renders a charge to the dispersed globules. Polar functional groups of mono- and diglycerides organize a self assembled layer around the core. A second layer of self assembled intermediates (un biodiesel transesterification) form a polar shield for becoming soluble in the G-phase. This layer of mono and diglycerides, that wraps the intermediate structure must be broken to get rid of ash forming components of the glycerine.

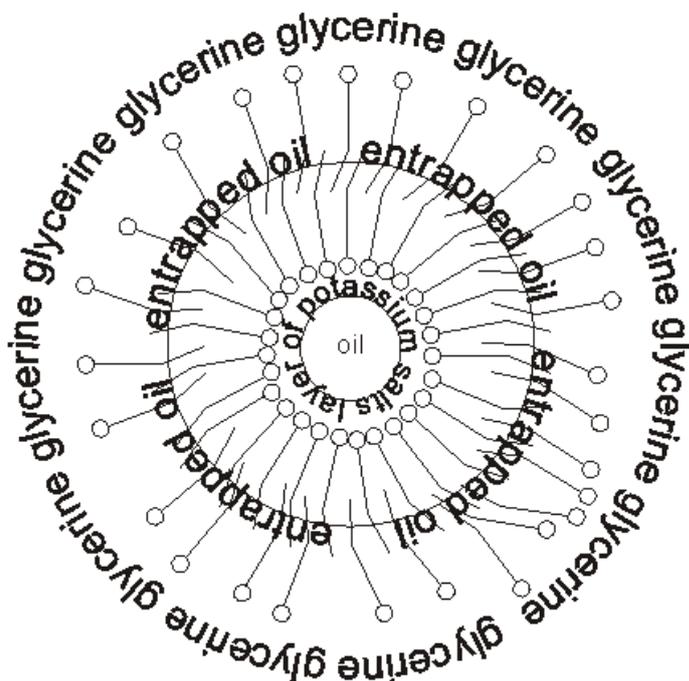


Figure 6 Proposed Pickering emulsion structure of G-phase

By employing the scenario of treatment of neutralization, esterification, distillation and decanting the relative rate of amphiphilic molecules can be reduced to (partially) protect the system from self assembled interfacial layers. In esterification treatment the amount of mono- and di-glycerides have been converted to lower polarity fatty acid methyl esters. By such the amount of surface active components were reduced and the resistance exerted by the intermediary layer was reduced. This made that the ash content of the decanted glycerine could have been dropped.

By further treating the refined glycerine with different adsorbents the light brownish ocher colour of the glycerine could have been turned into slightly ocher- white. The best in inventory was the series of ion exchange resins Lanxess, series 6,7,8 in figure 7. This is another supportive findings to the conclusion of a solid particles stabilized dispersion system. Fuller earth (series 5) was close in color removal to activated carbon (series 9). Spectroscopic analysis of undiluted sample showed that the adsorption treatment removes those components that absorb mainly in red, the component of blue color remains at fairly constant level. The selected Hue index (relative change of adsorption in red with reference to absorption in blue) can be used for a tool of quick qualitative check for evaluating efficiency of adsorption treatment of glycerine produced for technical use.

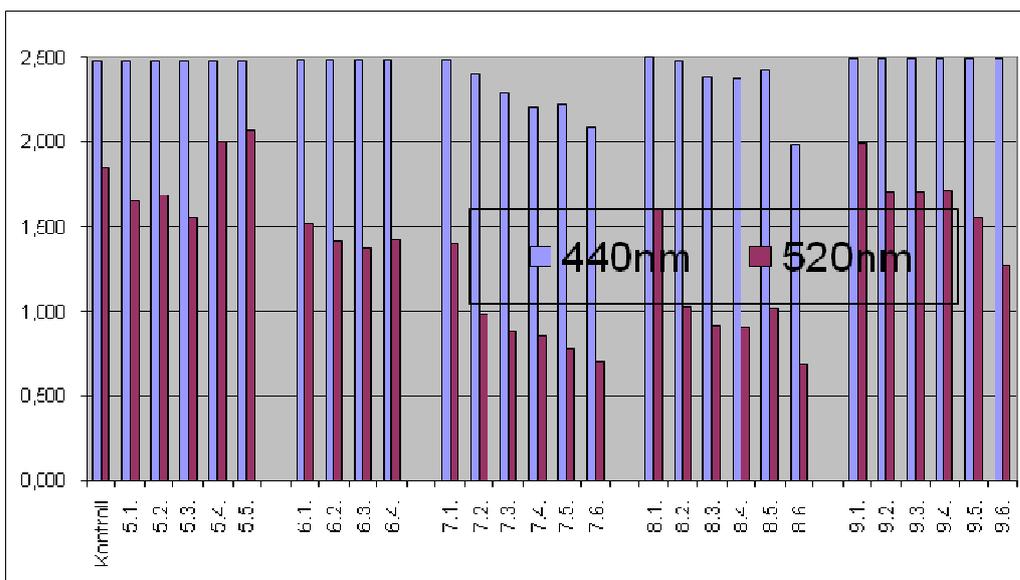


Figure 6. Adsorption treatment of refined ("kontroll") glycerine (series 5: fuller earth, series 6, 7, 8: ion exchange resins, Lanxess, 9: activated carbon)

4. Conclusions

Refining crude glycerol byproduct of biodiesel production needs to be supported by understanding of colloid chemical characteristics. For efficient refining not only the excess alkali catalyst must be neutralized, but the entrapped oil and soap molecules, as well as partially converted glycerides must be released from the colloid network. In deciding to apply a refining treatment it is to bear in mind that the colloid structure can change, by accommodating to prevalent circumstances.

From colloid chemical points of view the quality and quantity of the upper oil layer separated in refining the crude glycerine might present little interest. But these exert dominant influence on the whole of feasibility of biodiesel production. Analysis and treatment technology of the oil layer must be part of any development plans before turning a conventional biodiesel plant to operate, even partially, on used oil basis.

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