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PROPOSALS FOR UTILIZING THE GLYCEROL BOTTOMS

Summary. Biodiesel production is accompanied by the formation of glycerol and after its separation yielding a number of so-called difficult recyclable glycerol bottoms. The paper analyzes in detail the commercial value of the components of glycerol bottoms and discusses possible methods of using this material as an antiseptic and protecting agent for wood and concrete, as building and road antifreeze, cheap coolants, moisturizing and anti-freezing agents for the dust-raising or hygroscopic materials, as a feed additive, or as a component of culture media for microorganisms, including used during the production of biogas, cheap additives to the media for emulsion polymerization, and the raw material to produce ethers of glycerol.

Key words: Glycerol, Glycerol bottoms, Recycling, Utilization, Antiseptic for wood and concrete, Moisturizer, Anti-freeze agent, Component of culture media for microorganisms, Raw materials for biogas production, Starting material to produce glycerol ethers, Biodiesel.

Introduction. Modern methods for obtaining of biodiesel fuel comprise transesterification of vegetable oils or animal fats, which are mainly triacylglycerols, with methanol or ethanol. Isolated methyl or ethyl esters of fatty acids substitute mineral petroleum-based diesel fuel. Prefix “bio” means that this diesel fuel can be produced from renewable agriculture sources. Compared to petroleum combustible matter, biodiesel fuel has many other complementary advantages such as low emission of carbon monoxide during combustion, a relatively high flash point (150 °C) due to less volatility, it is safer for transportation and handle [1]. Moreover, biodiesel fuel is biodegradable matter and can be produced in domestic aria, that can diminishes a import petroleum-based fuel into Ukraine.

Glycerol is a co-product from the production of biodiesel fuel. It was reported that for every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed [2] (Scheme 1).

In the glycerol refining process, once the purified glycerol has been removed, the remaining by-products are referred to as glycerin bottoms.

Glycerol bottoms usually contain several compounds (Table 1) and is appearing as material with the high potential of use [3].

Scheme 1. Transesterification of triglycerides with methanol to produce fatty acid methyl esters (biodiesel).

Table 1.

Composition of glycerol bottoms.

Constituent	%	CAS RN
1,2,3-Propanetriol (a.k.a. glycerin, glycerol)	30-40	56-81-5
Water	20-50	7732-18-5
Sodium Chloride	15-20	7647-14-5
Fatty acids, C8-18 and C18-unsatd., sodium salts	5-10	67701-10-4
Polyglycerols	2.5-5	

I. Utilization of Glycerin bottoms as a component of wood preservatives, including protection against fire, fungi and pest.

All components of glycerin bottoms can act in wood preservation compositions. Following is consecutive consideration what function of each component of Glycerin bottoms can be fulfilled.

Glycerol.

Glycerol [4] has three hydrophilic hydroxyl groups which are responsible for its solubility in water and its hygroscopic nature. Glycerol has low toxicity. Because of polar nature of glycerol this compound will be good absorbing by wood (i.e. cellulose). It can be predicted, that high concentration of glycerol in surface layer of wood could play protective function. This idea is coming from simple consideration that large amount of free glycerol is not usual in nature and glycerol high concentration will not create nutrient medium for living organisms. Moreover it was found that at a concentration of 5% and higher, glycerol greatly inhibited the growth, adhesion, and cellulolytic activity of two rumen cellulolytic bacterial species, and of an anaerobic fungal species [5].

From another hand because glycerol is less polar then water it will promote dissolving of common antiseptic or emulsification of wood preservatives, some of them like pentachlorophenol (PCP), or its sodium salt, lindane, which still can be restrictively used for wood protection in some countries, are poor soluble in water. Antiseptic agents often include salts of copper, usually copper naphtenate or sulfate, zinc chloride or naphtenate, potassium dichromate or their mixtures. Because glycerol can form soluble complexes with copper (II) and zinc (II) ions, it is possible use in wood preservative mixtures copper sulfate or zinc chloride instead more expensive naphtenates.

Sodium chloride (Table Salt).

This is known from ancient time using the table salt (NaCl, Sodium Chloride) solutions for protection of wood farm implement from over drying up [6]. Various parts of wooden tools were found in ancient mines of Armenia remained from primitive times. There were often found exhaustively do not rotted wood in the Dead Sea, salinity of which is well known. North America Pioneers found an intact boxes used by ancient aborigines at salt mining.

All of these undoubtedly prove that the salt excellently protect wood from rotting and spoilage. Brine is easy penetrating into wood and increase wood solidity. This function of salt was used for protecting of ship wood parts and railway ties. Peasants of Sardinia, Sicilia, Spain and south of France several centuries used salt for preserving their agricultural tools and wooden carriage parts. After salting the wooden workpieces became very durable that can be kept under direct sun without damage.

Fatty acids, C8-18 and C18-unsaturated, sodium salts.

Sodium salts of fatty acids (C8-18 and C18-unsaturated), commonly is known as a soap can play detergent and emulsification function. Technical grade of this material usually uses in industry or building for degreasing of various surfaces, including metal, wood or concrete. Application of technical soaps over treated surface creates intermediate layer or primer. Primer serves as binding layer between usually polar surface and less polar or even non-polar and waterproofing paint.

Sodium salts of fatty acids are responsible for formation of basic pH 10.0—11.5 of glycerin bottoms due to salt hydrolysis. This range of pH on its own account is positive factor preventing fungi and other organisms growing and feeding and hereby glycerin bottoms will be acting as antiseptic agent. Antiseptic action can be increased by adding phenol or polyphenols which are usually used as antiseptics. Basic pH will turn phenols to phenolates, thereby increase phenol solubility in water-glycerol solutions, decreasing phenol volatility and unwanted odor, thereby increase stability of antiseptic mixtures and their efficacy.

Sodium salts of fatty acids (C8-18 and C18-unsaturated) if they will be used in wood preservation mixtures, will enter into the exchange reaction with copper sulfate or zinc chloride or with oxides of these metals to form copper or zinc salts of fatty acids which can work as antiseptics, siccative or primer.

In Tables 2 and 3 theoretical wood protective compositions which comprise glycerol bottoms and known commonly used wood protectors are represented.

Table 2.

Wood preservation compositions with addition of glycerol bottoms.[a]

Components [Chemical formula, CAS number] (% approximately)									
№	*A*[b]	B	C	D	E	F	G	H	I
1.	55	15			15			15	
2.	45		25		15			15	
3.	25	20			20		15	20	
4.	20			30	25			25	
5.	20			30	13			17	
6.	17			32	32			17	
7.	20			60	10			10	
8.	40				30			30	
9.	30				30			30	10
10.	20				30			30	20
11.	15				30			30	25
12.	25			25			50		
13.	40		20	20			20		
14.	50		15	20			15		
15.	75			25					
16.	75	25							
17.	70		30						
18.	50						50		
19.	30		20	40	10				
20.	50		10	10	30				
21.	30					30	40		
22.	20					40	40		
23.	20		40			40			
24.	20	20		10	20	20			10
25.	40			30		30			
26.	50	10		10	30				
27.	75				25				
28.	70		20	10					
29.	80				20				

Notes: a) Proposed composition might be used for preliminary testing as 10, 15, 20, 30, and 50% solutions in water. *A*) Glycerol bottoms [See Table 1][b]; *B*) Ammonium bifluoride [NH_4HF_2,1341-49-7]; *C*) Ammonium fluoride [NH_4F, 12125-01-8]; *D*) Boric acid [H_3BO_3, 10043-35-3]; *E*) Copper sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$, 7758-99-8]; *F*) Diammonium phosphate [$(NH_4)_2HPO_4$, 7783-28-0]; *G*) Sodium fluoride [NaF, 7681-49-4]; *H*) Sodium dichromate dihydrate [$Na_2Cr_2O_7 \cdot 2H_2O$ 7789-12-0]; *I*) Zinc chloride [$ZnCl_2$ 7646-85-7].

b) Glycerol bottoms portion should be calculated without comprising water in it. Water content in glycerol bottoms may be easily determined by gravimetric analysis.

Procedure. About 0.5-1 g sample of glycerol bottoms should be weighted by high precision (0.1 mg or better) analytical balance in 2-3 Dram vial and placed in desiccator under high vacuum (1 Torr or better) for 24 hours or until weight will be constant. Water content %W is calculated by formula $\%W = (V_1\text{-}V_2) \cdot 100/V_1$; where V_1 is weight of sample before drying, V_2 is weight of sample after drying.

Table 3.

Wood preservation compositions included glycerol bottoms.

Components [Chemical formula, CAS number] (% max approximately[a])									
A[b]	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
90	10								
90		10							
99			1						
99				1					
76.5						3.5	15	5	
55							30		15

Notes: a) Proposed composition might be used for preliminary testing as solutions diluted in 0, 2, 5, or 10 times in water. *A*) Glycerol bottoms [See Table 1]; *B*) Creosote; *C*) Pentachlorophenol, [C_6HCl_5O, 87-86-5]; *D*) Permethrin, [$C_{21}H_{20}Cl_2O_3$, 52645-53-1]; *E*) Cyproconazole, $C_{15}H_{18}ClN_3O$, 94361-06-5; *F*) Propiconazole; *G*) Bis-(N-cyclohexyldiazeniumdioxy)copper $C_{12}H_{22}N_4O_4Cu$, 312600-89-8; *H*) Copper sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$ 7758-99-8]; *I*) Boric acid [H_3BO_3, 10043-35-3]; *J*) Didecyldimethylammonium chloride (DDAC).

b) Glycerol bottoms portion should be calculated without comprising water in it. See Note b in Table 2.

Polyglycerols

The same considerations that for glycerol can be applied to anticipated properties of polyglycerols. These compounds have multiple industrial applications, from which mostly significant for this proposal are using polyglycerols as emulsifiers, stabilizers, dispersants, or humectants [7].

It is possible anticipate that using of glycerol bottoms in wood preservation mixtures can decrease utilization of currently in use and costly components without decreasing protective, and antiseptic quality and even will led to origination of adhesive and primer behavior.

In addition glycerol bottoms also can be directly or as water solutions used for the antisepsis of fresh cutaway of fruit and ornamental trees in the gardens or the forest.

II. Utilization of Glycerin bottoms as a component of concrete preservatives and antiseptics.

Glycerin bottoms as is or with addition of inorganic of organic antiseptics can be used for treatment of concrete surfaces against fungi, mold and pests in the same way as for a timber.

III. Utilization of Glycerin bottoms as concrete additives, i.e. anti-freeze agents, retarders and surface retarders, plasticisers, and superplasticisers (high range water reducers).

Glycerin bottoms is a mixture of electrolyte (NaCl) and surface-active compounds, namely glycerol (hydrophilic), polyglycerols (less hydrophilic) and sodium salts of fatty acids (hydrophobic). The structural and mechanical characteristics of concretes are improved by the introduction of electrolytes, which can regulate the rate of concrete hardening [8]. Surfactants like glycerol, polyglycerols and sodium salts of fatty acids make possible regulating the mobility of concrete mixtures, its air-content, fulfill bactericidal action, and hydrophobicity. These futures of concrete can be used for concrete work at low temperature, at concrete casting in dry and hot climate or for making porous concrete and molding products [9].

Utilization of glycerin bottoms as anti-freeze agents is following from well known futures of glycerol [3] and sodium chloride decrease water freezing temperature.

Sodium chloride is effective accelerator the rate of hydration in the cement additives and can be used in mass concrete, but because of its potential to promote corrosion in rebar it has been used with restriction, under supervision of specialist in concrete additives. However presence of other components of glycerol bottoms for example sodium salts of fatty acids and polyglycerols which will play hydrophobic role might diminish the drawbacks of salt.

This proposal is requiring some experiments, like mixing cement and solutions with various concentrations of glycerol bottoms in water. Glycerol bottoms portion should be calculated without comprising water in it. (See Note b in Table 2.) The measure of physical properties of obtained mortar and concrete, i.e. mobility of the mortar, time of hardening, strength of concrete block, etc. should be performed at special concrete laboratory.

IV. Glycerol bottoms solutions for removing the ice from roads or others ice over places and arias.

Anti-freeze properties of glycerol bottoms can be utilized for workup of iced roads in winter time or in similar cases. Moreover the combination in glycerol bottoms the anti-freeze futures of glycerol and salt with detergent futures of sodium salts of fatty acids will provide thawing of ice and washing the surface. It cannot be anticipate that the surface will be too slippery because formed glycerol bottoms solution in water will be drain out if amount of applied amount of glycerol bottoms will not be too large.

Table 4.

Temperature of freezing of Glycerol, Sodium Chloride (experimental) and Glycerol bottoms (estimated) water solutions.

Concentration of Glycerol in solution, % w	Temperature of freezing, °C	Concentration of NaCl in solution, % w	Temperature of freezing, °C	Concentration of Glycerol bottoms in solution, % w[a]	Temperature of freezing, [b] °C, estimated
10	-1.6	5	-2.8	20 (1:4)	-2
20	-4.8	10	-6.4	33 (1:2)	-4
30	-9.5	15	-11.1	50 (1:1)	-8
40	-15.4	20	-16.8	66 (2:1)	-11
50	-23	23	-21.1		
60	-34.7	25	-8.8		
70	-38.9				

Note: a) Glycerol bottoms portion should be calculated without comprising water in it. b) Temperatures of freezing were estimated following additive scheme of calculation: Temperatures of freezing of solution with Glycerol bottoms = Temperature of freezing appropriate Glycerol solution + Temperature of freezing appropriate NaCl solution. These temperatures will be easy measured precisely.

V. Glycerol bottoms as wetting and anti-freezing agents.

In addition to anti-freezing properties glycerol bottoms has high wetting potential. Mostly common wetting remedy is water. Unfortunately, water provides only a short-term remedy that is labor-intensive and requires costly multiple applications. Various dust suppressant compositions and methods are known in the art for spraying in air to reduce air-borne dust or for spraying on substances which develop dust. (See for example [10, 11] and references therein.)

Because of hydrophilic properties of components glycerol bottoms can absorb water from atmosphere and work as long-term wetting agent, also having anti-freezing feature, keeping dust or protected dusty material in friable state. Glycerol bottoms contains only several elements i.e. carbon, hydrogen, oxygen, sodium and chlorine which cannot pollute protective material. Glycerol bottoms can be combined and used together with building material, easy washed if necessary, or glycerol bottoms can be burned, if protective material is for example batch or ore.

VI. Glycerol bottoms as a coolant or heat-transfer agents.

From anti-freezing futures of Glycerol bottoms is following idea to use solutions of Glycerol bottoms in water as is or as a mixture with another antifreeze in purposes to decrease cost as cheap coolant, refrigerant or heat-transfer agent just as brine is used in industrial refrigeration as a secondary refrigerant [13-15]. However addition of corrosion and scale formation inhibitors might be required. Factors, which should be considered when brine was selecting, were discussed [16, 17].

VII. Glycerol bottoms as feed additive for animal feeding.

Because all components of glycerol bottoms are non-toxic in small concentration, and analytical data are showing very low contents heavy metals and toxic elements it is possible use glycerol bottoms as sweet salty feed additive for animal feeding. It was found that glycerol at low concentrations (0.1–1%) had no effect on the growth, adhesion, and cellulolytic activity of the two rumen cellulolytic bacterial species. The conclusion was made that glycerol can be added to animal feed at low concentrations [5]. Because salt is usually used as feed additive than glycerol bottoms also can be used. Presence in glycerol bottoms fatty acid sodium salts and basic character of pH of glycerol bottoms especially can be utilized as addition to silo, because silo has acidic nature and the acids from silage like nitric acid will be partially neutralized by fatty acid sodium salts from glycerol bottoms to form consumable fatty acids [18–20].

VIII. Glycerol bottoms as a carbon and energy source for yeast growing.

Usual the carbon and energy source for yeast growth are sugar containing raw vegetable materials like beet and cane molasses [21]. The sugars present in molasses, a mixture of sucrose, fructose and glucose are readily fermentable. Glycerol also can be fermentable by yeast and can be carbon source for yeast growing. It is discovered also that glycerol can penetrate through cell membranes [22] and transformed by glycerol kinase to glycerol-6-phosphate, common metabolite of glycerol utilization in living cells. In addition for excellent growing yeast require certain minerals, vitamins and salts, particularly sodium chloride [23]. Because required nitrogen is supplied in the form of ammonia and phosphate is supplied in the form of phosphoric acid and the basic sodium salts of fatty acids in glycerol bottoms will be neutralized and pH of the mash can be easy controlled and regulated during the yeast growing process. Thereby all constituents of glycerol bottoms can be utilized in production of baker yeast for human or animal nutrition [24].

IX. Glycerol bottoms as a component of emulsion polymerization media.

Emulsion polymerization is the method of polymerization of monomers in disperse media (usually in water) that leads to formation of polymeric suspension with average size of particles 50-150 nm [25].

Generally emulsion polymerization occurs according to radical mechanism. Polymerization is initiating by water or oil soluble initiators, for example $K_2S_2O_8$, H_2O_2, or organic peroxides and also redox systems. For stabilization of monomer emulsion various emulgators are applied: anionic sodium alkylsulfonate, or sodium salts of fatty acids, and also nonionic surfactants like esters of polyethylene glycol and acids, polypropylene glycols etc.

Glycerol and sodium chloride were used as osmotic agents during preparation of silicone microspheres by emulsion polymerization [26].

It was investigated that emulsion polymerization in a glycerol suspension medium yielded three different latex morphologies depending upon the polymerization temperature and the type of emulsifier, monomer, initiator, or hydrocarbon applied. The latex morphologies obtained range from large porous latex (1-10 μm in size) to medium-sized porous latex (0.1-1 μm in size) to small latex (up to 0.1 μm in size) [27].

In the several works it was shown use glycerol-functionalized silica during emulsion polymerization with formation of nanoparticles [28-30.]

Analysis of various reports indicate that glycerol bottoms might be used as a media for emulsion polymerization, but the process conditions, yield and structure of obtained polymer should be investigated.

X. Glycerol bottoms as the raw material for producing of biogas.

Biogas is a biofuel obtained by anaerobic fermentation of biomass of various sources like sewage, municipal, farm and bioindustrial wastes [31-33]. Certain amount of glycerol bottoms can be added to biodegradable materials. Considerations should be made on influence of amount of added salt and sodium salts of fatty acids on biogas production process and this is require not sophisticated research. In addition, the glycerol bottoms as biodegradable material can be added in limited quantities to compost and other organic fertilizers.

XI. Glycerol bottoms as the reactant for polyesterification reaction.

Pachauri and He presented report [3] concerning utilization of crude glycerol from biodiesel production. This report generally deals with research related to pure or crude glycerol, not with glycerol bottoms, but several reported laboratory processes can be applied also to glycerol bottoms as a starting material in purposes to transform it into valuable product.

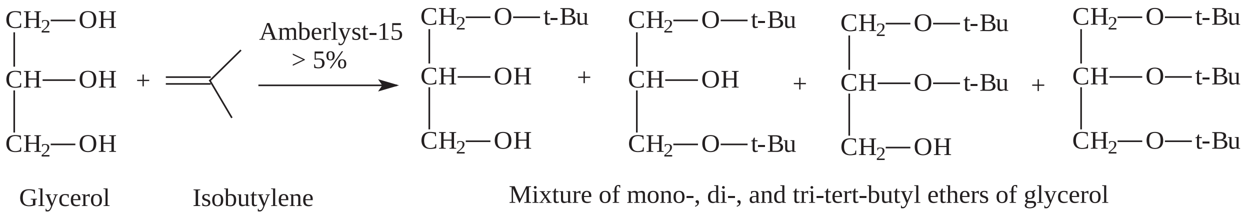
Microbiological transformations probably will be difficult to tune because of salt and soap are present in glycerol bottoms, but chemical reactions will be less sensitive to other components and final product will be easy separated.

One from chemical processes might be polyesterification of remained in bottoms glycerol with cheapest diacid like adipic or phthalic acids or their derivatives. These processes are well developed and will require minimal preliminary adaptive experiments and will yield glycerol adipate or phthalate which can find numerous applications in polyester or paint industry.

XII. Glycerol bottoms as the starting material for synthesis mono-, di-, and tri-tert-butyl ethers of glycerol.

Mono-, di-, and tri-tert-butyl ethers of glycerol are the main products of glycerol etherification reaction and are excellent oxygen additives for diesel fuel.

Noureddini, Dailey, and Hunt reported experimental procedure for transforming crude glycerol to tert-butyl ethers of glycerol [34]. The procedure is based on reaction crude glycerol with isobutylene pressurized to 250 psig to maintain isobutylene in the liquid state. The reaction requires acid catalyst sulphonic ion exchange resin Amberlyst-15. This procedure can be adapted to conversion of glycerol from glycerol bottoms to tert-butyl ethers of glycerol (Scheme 2).



Scheme 2. Synthesis of mixture of mono-, di-, and tri-tertiary butyl ethers of glycerol.

In starting mixture the glycerol as the part of glycerol bottoms will react with isobutylene to form tert-butyl ethers of glycerol. The polyglycerols from glycerol bottoms also will yield tert-butyl ethers of polyglycerols, which also can be used in additives for diesel fuel or after separation of tert-butyl ethers of glycerol can find another practice.

Under action of acid catalyst sodium salts of fatty acid will be transformed to free acids then will react with isobutylene yielded tert-butyl esters of fatty acids which also can serve as oxygen additives for diesel fuel. Partially neutralized catalyst can be recycled after completion of reaction by facile procedure.

Sodium chloride from glycerol bottoms will have not noticeable influence on the process.

Water which is presents in glycerol bottoms can be removed by distillation in vacuo, and remaining traces will react with isobutylene to form tert-butanol, which in its turn can be utilized by various ways. Obtained products may be refined by distillation similar to published methods [35].

Conclusion.

Due to glycerol bottoms contents only one unwanted substance i.e. water, which even in some cases has not influence, but water concentration should be taken into account, this material has the high potential of utilization.

According to our opinion and literature data glycerol bottoms can be used as wood and concrete preservative and antiseptic, concrete additive, ice removing agent, wetting and anti-freezing agent, component of coolant or heat-transfer agents, animal feed additive, component of emulsion polymerization media, source for yeast growing, for producing of biogas, starting material for synthesis of triglycerides, and tert-butyl ethers of glycerol.

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Бачеріков В. А. Пропозиції щодо використання гліцеролових кубових залишків.

Анотація. Виробництво біодизельного палива супроводжується утворенням гліцерину і після його відділення деякої кількості важко утилізованих т.зв. гліцеринових кубових залишків. У статті детально аналізується промислова цінність компонентів гліцеринових кубових залишків та розглядаються можливі методи застосування цього матеріалу як антисептичного і захисного засобу для деревини і бетону, в якості будівельних і дорожніх антифризів, дешевих теплоносіїв, зволожуючих і проти промерзаючих засобів для пилоутворюючих або гігроскопічних матеріалів, в якості кормової добавки, або компонента поживних середовищ для мікроорганізмів, у тому числі для виробництва біогазу, дешевих адитивів до середовищ які застосовуються у процесі емульсійної полімеризації, та вихідної сировини для одержання етерів гліцерину.

Ключові слова: Гліцерол, Кубові залишки, Утилізація, Антисептичний засіб для деревини і бетону, Зволожуючий засіб, Протипромерзаючий засіб, Компонент поживних середовищ для мікроорганізмів, Сировина для виробництва біогазу, Сировина для отримання простих ефірів гліцеролу, Біодизельне паливо.

Бачериков В. А. Предложения для использования глицероловых кубовых остатков.

Аннотация. Производство биодизельного топлива сопровождается образованием глицерина и после его отделения некоторого количества трудно утилизируемых т.н. глицериновых кубовых остатков. В статье подробно анализируется промышленная ценность компонентов глицериновых кубовых остатков и рассматриваются возможные методы применения этого материала как антисептического и защитного средства для древесины и бетона, в качестве строительных и дорожных антифризов, дешевых теплоносителей, увлажняющих и анти-промерзающих средств для пылеобразующих или гигроскопичных материалов, в качестве кормовой добавки, или компонента питательных сред для микроорганизмов, в том числе для производства биогаза, дешевых аддитивов к средам для эмульсионной полимеризации, и исходного сырья для получения эфиров глицерина.

Ключевые слова: Глицерол, Кубовые остатки, Утилизация, Антисептическое средство для древесины и бетона, Увлажняющее средство, Антипромерзающее средство, Компонент питательных сред для микроорганизмов, Сырьё для производства биогаза, Сырьё для получения простых эфиров глицерола, Биодизельное топливо.