

Technological separation procedure of tested substances from solid waste matter from production line of biodiesel on the principle of various dissolution in solvents

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Abstract

Biodiesel is a proven alternative to petroleum diesel fuel. The liquid and solid waste matters arise during production of mentioned ecological alternative fuels which could be further used to guarantee the ecological purity of production of these biofuels. Individual components from waste matter produced by biodiesel factory were separated: organic (soaps, polyphenolic compounds, tocopherols, total chlorophylls, and total carotenoids) and inorganic salts. On their separation the different solubility in five organic solvents (diethyl ether, toluene, acetic anhydride, ethanol and acetone) was used. The contents of two macroelements – potassium and sodium as well as the contents of two heavy metals – lead and cadmium in waste matter produced by production line were analyzed in our work. Also indicative concentration hydronium cations and hydroxide anions was determined. Optimal process of gravimetric method had been tested with mentioned organic solvents where the highest weight of non-soluble soaps was precipitated from waste matter. After soap separation by filtration and evaporation of organic solvents by further technological procedure also other organic compounds (polyphenolic compounds, tocopherols, total chlorophylls and total carotenoids) were separated from inorganic salts. According to results of our analyses the most suitable way of separations of individual components in waste product was evaluated the one with two organic solvents (acetone and diethyl ether) and distilled water. After termination of this working procedure both applied organic solvents were evaporated on rotary vacuum evaporator and in this way by recycle process could be reused in further separation of waste matter arising in biodiesel production. From waste produced by production line on biodiesel production the soaps or additives into sanitary cleaners could be added. Isolated natural organic compounds could be used further for example in pharmaceutical or food industry as healthy preparations or additives into foodstuffs. Isolated inorganic compounds could be used in agriculture as sodium-potassium fertilizers.

Keywords: biodiesel, waste, solvents, heavy metals

Introduction

With global warming and the price of fossil fuel rising, biodiesel is becoming favored as a kind of carbon neutral fuel (Topaiboul and Chollacoop 2010). The level of atmospheric CO₂ is rising because of increased anthropogenic emissions of CO₂. Given the elevated energy demand and limited accessibility to fossil fuels, there is an urgent need to explore renewable, ecofriendly, and cost-effective alternative fuel sources (Marella *et al* 2018).

During the biodiesel production process by transesterification, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acid, with glycerol as a primary byproduct (Xie *et al* 2012).

The purity level of biodiesel has a strong effect on fuel properties and on engine life. Therefore, a purification step is necessary. Generally, there are two accepted methods for purifying biodiesel: wet washing and dry washing (Abbaszadeh *et al* 2014). Crude ester must be purified to obtain high quality biodiesel which must meet international standard

specifications (EN14214, ASTM D6751 etc.) by removing excess contaminants (methanol, catalyst etc.) and impurities (soap, wax etc.) (Demir 2017).

Raw waste glycerol contains a variety of harmful compounds, such as 12-16% alkalis especially in the form of alkali soap and hydroxides, and 8-12% methanol, which may cause water pollution and environmental problems. Moreover, the cost for disposal of raw waste glycerol is quite expensive (Yazdani and Gonzalez 2007; Da Silva *et al* 2009).

Biodiesel is a proven alternative to petroleum diesel fuel. During production of biodiesel, the free fatty acids in the oil react with the sodium or potassium catalyst to form soaps. After the biodiesel and by-product glycerin are separated, trace amounts of glycerin remain in the biodiesel. These soap and glycerin impurities in the biodiesel can lead to engine operation and fuel storage problems. Traditionally, soap and glycerin are removed from the biodiesel by water washing. Water washing has several disadvantages, such as producing large amounts of waste water that requires treatment and causing plant operational problems such as emulsion formation. Recently, several alternative "waterless" purification procedures have been developed, such as ion exchange resins and solid adsorbents. Four different mechanisms were identified for soap and glycerin removal. These mechanisms are filtration, physical adsorption, ion exchange, and soap removal by glycerin affinity. It was found that ion exchange resins can reduce soap levels from 1200 ppm to below 50 ppm for about 550 bed volumes (BV) of processed biodiesel. Glycerin levels can be reduced from 0.08% to below 0.02% for about 200 BV of processed biodiesel. (Wall *et al* 2011).

However, there is currently no standard indicator or criterion that is widely accepted to evaluate the effectiveness of the washing process. Subsequent to the washing process, different properties related to the impurities are often measured and the requirement for further reduction of the impurities is used as an assessment of the effectiveness of the washing process (Hingu *et al* 2010). For example, acidity index, alkalinity, glycerin, and turbidity of biodiesel were used as indicators of the efficiency of a purification process in the study of starch and cellulose as adsorbents (Gomes *et al* 2015). The impurities commonly found in the biodiesel can be grouped in nonelectrolytes (biodiesel, methanol, glycerol and water) and electrolytes (soaps and catalyst) (Di Felice *et al* 2008). One of the main undesired contaminants is the soap, which is formed through a saponification reaction (Free fatty acids + KOH → Water + Potassium soap) that occurs in the same reactor as the transesterification. Basically, soaps are metallic salts of aliphatic carboxylic acids with a long nonpolar hydrophobic tail and a charged hydrophilic head (Meyers 2002), and its content in biodiesel has been considered one of the main criteria to evaluate the wash process efficiency (Díaz-Ballote *et al* 2020).

Focusing on biodiesel purification, water washing is generally conducted although some "dry washing" methods have been proposed (Wang *et al* 2009; Vasudevan and Briggs 2008). Water washing is used mostly to remove impurities such as the remaining methanol and glycerol, as well as soaps and the remaining catalyst (Gomes *et al* 2010). After water washing, biodiesel is dehydrated, generally by using vacuum flash processes, anhydrous salts (such as Na₂SO₄) or other water absorbents. Water washing is the most used purification process due to the fact that the purified biodiesel usually satisfies the stringent quality standards imposed by EN 14214 or ASTM D6751. (Atadashi *et al* 2012). However, this

process leads to the production of high amounts of wastewater, which results in significant economic and environmental impacts (Ferrero *et al* 2014).

The main aim of our work was to find out the most effective way of separation of waste which was produced by biodiesel production line on individual fragments of substances on the basis of different solubility in solvents.

Material and methods

Waste of 4,000 g gained from producer of biodiesel was weighted into five 150 mL beakers and into each beaker 100 mL of solvents: 1) diethylether 2) toluene 3) acetic anhydride 4) ethanol 5) acetone were individually added. Solutions were blended for 5 minutes with glass rods, and left standing for 40 minutes. Mixtures were filtered through quantitative filtration paper Munktell (Germany) grade 390, 84 g.m⁻² (red), filtration residues in each beaker were after finished filtration twice decanted with 10 mL of the same solvent. Pre-weighted filtration papers (on analytical balances) with filtration residues were left for air-drying for 24 hours and afterwards they were weighted again on analytical balances. The filtration papers were placed into other five beakers with 100 mL hot re-distilled water (Milli-Q systém: EC=18.3 μS·cm⁻¹), where by dissolving the filtration residues were quantitatively transferred into this distilled water. After thorough dissolving of filtration residue from filtration paper this specific filtration paper was taken out from solution, then was washed down twice with 20 mL hot re-distilled water and these liquid fractions were mixed with solution where the filtration papers were immersed primarily. These liquid mixtures were quantitatively transferred into five 250 mL volumetric flasks where their volumes were after cooling of solutions filled up with distilled water to the mark. Solution from volumetric flask was filtered through filtration paper Munktell (Germany) grade 390, 84 g.m⁻² (green). Stock solutions were used for further analysis (determination of heavy metals contents: lead and cadmium, as well as contents of macroelements: sodium and potassium, and also for indicative determination of concentrations of H₃O⁺ and OH⁻ in individual samples).

Filtrates of solvents were concentrated in vacuum rotary evaporator (Heldolph, type: Basis Hei-Vap, Germany) till thick oil mass of constant weight by under pressure 75 torr and temperature 37 °C. Afterwards mentioned condensed mixtures were dissolved in flasks with 200 mL hot re-distilled water. They were quantitatively transferred (final washing down the flask by other volumes of re-distilled hot water 2 x 20mL) into five 250 mL volumetric flasks, after cooling they were filled up with re-distilled water to the mark. Solution from volumetric flask was filtered through filtration paper Munktell (Germany) grade 390, 84 g.m⁻² (green). Stock solutions were used for further analysis (determination of heavy metals contents: lead and cadmium, as well as contents of macroelements: sodium and potassium, also for gravimetric determination of phosphates, and also for indicative determination of concentrations of H₃O⁺ and OH⁻ in individual samples).

Analysis of soap amount in samples

Mentioned analyses were carried out for determination of maximal and minimal amounts of fragments to be found out which solvent has the highest and the lowest dissolving

ability. Nature of this process consisted in precipitation of these molecules by solution of lead nitrate with following gravimetric determination of their exact amount in tested solutions.

Volume of 50 mL stock solutions was pipetted into five 150 mL beakers, where the filtration residues dissolved were quantitatively transferred in five solvents into 250 mL volumetric flasks, as well as into other 150 mL flasks volume of 50 mL stock solutions was pipetted, where the oil residues were quantitatively transferred from rotary evaporated solvents in 250 mL volumetric flasks. Approximately 20 mL of solution lead nitrate ($c=0,1\text{mol.L}^{-1}$) was poured into 5 + 5 beakers and the solution was left to stand with mentioned precipitant by laboratory temperature for 1 hour. Then the mixtures were filtered through precisely pre-weighted filtration papers Munktell (Germany) grade 390, 84 g.m^{-2} (green) and weights of precipitates were gained by exact weighting on analytical balances.

Analysis of macroelements – sodium and potassium

From stock 250 mL solutions containing dissolved filtration residues, 0.5 mL of solution was pipetted into five 100 mL volumetric flasks and made up to the mark and into five other 100 mL volumetric flasks 0.5 mL from stock solutions was also pipetted, where quantitatively transferred concentrated mixtures from filtrates and volumes in flasks were made up with re-distilled water to the mark. Mentioned diluted solutions were used for determination of sodium contents. For potassium analysis the solutions were also diluted according to previous procedure into 100 mL volumetric flasks, but from original stock solutions 5 mL of solution was pipetted. Also the blanks were carried out in parallel with analyses of samples. Contents of sodium and potassium were determined by method AAS on an atomic absorption spectrometer (AAS Varian AA Spectr DUO 240FS/240Z/UltrAA, manufacturer Varian Australia Pty Ltd, A.C.N. 004 559 540, Mulgrave, Australia).

Parameters for analyses carried out for determinations of macroelements in samples:

K - detection limit - 0.001 mg.L^{-1} , sensitivity - 0.01 mg.L^{-1}

Na - detection limit - 0.04 mg.L^{-1} , sensitivity - 0.01 mg.L^{-1}

K - Wavelength 766.5 nm

Na - wavelength 589.0 nm

Analysis determination has not a deviation more than 3%, the gas flow: air- 13.5 L.min^{-1} , acetylene- 2.0 L.min^{-1} .

Analysis of heavy metals contents - lead and cadmium

The quantitative analysis of heavy metals contents - lead and cadmium was carried out from five stock mixtures (from solutions with dissolved filtration residues and with vacuum concentrated filtrates with final volume made up to 250 mL). Also the blanks were carried out in parallel with analyses of samples. The contents of these metals were determined by AAS method on an atomic absorption spectrometer (AAS Varian AA Spectr DUO 240FS/240Z/UltrAA, manufacturer Varian Australia Pty Ltd, A.C.N. 004 559 540, Mulgrave, Australia).

Parameters for analyses carried out for determinations of macroelements in samples:

Pb - detection limit - 0.02 mg.L^{-1} , sensitivity - 0.1 mg.L^{-1}

Cd - detection limit - 0.001 mg.L⁻¹, sensitivity - 0.01 mg.L⁻¹

Pb - wavelength 217.0 nm

Cd - wavelength 228.8 nm

Analysis determination has not a deviation more than 3%, the gas flow: air- 13.5 L.min⁻¹, acetylene- 2.0 L.min⁻¹.

Approximate assessment of concentrations of H₃O⁺ and OH⁻ in stock solutions by titration method

In our experiments also indicative concentrations of H₃O⁺ a OH⁻ were carried out, but these analyses of pH are not the basic bearing part of this survey, with regard to better specification of medium of solvents containing analysed chemical components. From original solution in 250 mL volumetric flasks, were the whole filtration residue from filtration paper was quantitatively transferred and dissolved, 20 mL of solution was again pipetted into five titration flasks from each analysed mixtures and these were titrated by normal solution of oxalic acid (c=0.005M, Lachema Brno, Czech republic) in order to determine the concentration of hydroxide anions (c_{OH⁻}). Also concentrations of hydrogen protons (c_{H₃O⁺}) at residues obtained from waste matter which were quantitatively transferred into 250mL volumetric flasks were determined in our trials. These were also determined by titration method using 0.05M solution of NaOH (Merck Bratislava, Slovakia) with concentration accurately standardized by normal solution of oxalic acid (c=0.005M, Lachema Brno, Czech republic).

Results were evaluated by statistical program Statgraphics 4.0 (Statpoint Technologies, Inc., Czech Republic), the data were analyzed by means of oneway analysis of variance (ANOVA).

Results

Added solvents had various effects on dissolving of individual components of waste from producer of biodiesel. In tested solvents soluble and non-soluble part was separated from this mass - either in the form of dark-brown oil spot or white solid precipitate (except from acetic anhydride). After standing for 1 hour the large volume of white precipitate was precipitated when using ether, acetone, smaller share of this precipitate was precipitated when toluene as solvent was used. When stating about description of contact process of waste matter with solvents in the presence of acetone large particles of precipitates were formed and they rapidly settled, in the presence of ether and toluene the white macro particles were evenly distributed in medium of tested solvents. Practically homogenously coloured mixture (without any precipitated solid phase) was formed after standing in medium of acetic anhydride solvent for one hour. Furthermore, in ethanol, toluene and diethyl ether solvents a non-soluble brown bottom oil layer was formed after standing for one hour.

After following filtration the most transparent filtrate was gained only from acetone. Filtrate from ether was homogenously slightly cloudy. In ethanol filtrate in bottom layer a dark brown oil emulsion was observed. Filtrate from toluene and acetic anhydride was homogenously slightly turbid by brown emulsion. Weights of filtrate residues (Tab. 1) gained by process of filtration were after assessment of their number values in following order tested

solvents, from which were isolated: acetone > diethyl ether > toluene > ethanol > acetic anhydride - the same order of solvents was assessed also by ions OH⁻ determination by titration method in water solutions, in which dissolved filtration residues were isolated from mentioned solvents (Tab. 1). Approximate analogical order was estimated when the weights of precipitated organic fragments were compared (by the presence of dissolved lead salts) from water solutions, in which isolated filtrate residues were dissolved from these solvents: acetone > diethyl ether > toluene > acetic anhydride > ethanol.

Order of solvents (Tab. 1) from which after isolation of filtration residues and their subsequent transferring (and dissolving) into another 250 mL volumetric flasks, was according to contents of macroelements (sodium and potassium) as following:

- in the case of sodium was the order of solvents consistent to the order of solvents, from which the filtrate residues were precipitated and subsequently the lead precipitates were separated from water solutions.

- in the case of potassium was the following order: acetone > toluene > diethyl ether > acetic anhydride > ethanol

When the amounts of precipitated organic compounds were compared (with lead ions) from water solutions obtained from dissolving of vacuum concentrated filtrates from solvents and subsequent adding of saturated solution of Pb(NO₃)₂, we concluded that the contents of these precipitates have had in solvents the greatest presence at toluene and at diethylether – at remaining three solvents the presence of amounts of precipitated organic components was minimal. The order of amounts of testing macroelements in concentrated precipitates of these solvents was as following (Tab. 2):

- in the case of sodium: acetic anhydride > ethanol > toluene > acetone > diethyl ether.
- in the case of potassium: ethanol > acetic anhydride > diethyl ether > acetone > toluene

In our experiment also the analysis of contents of heavy metals (lead and cadmium) in solid matter of precipitated filtration residue was carried out, as well as in precipitates from solvents in which the fragments from waste when fatty acid methyl esters (FAME) producing were dissolved. Interesting findings indicated that higher accumulation of lead was in solid precipitated residues of tested samples (the order of solvents: diethyl ether > ethanol > toluene > acetic anhydride = acetone) (Tab. 1) and the second heavy metal - cadmium was more accumulated in soluble components of waste matter isolated from our solvents in following order: acetone > diethyl ether > toluene > ethanol > acetic anhydride (Tab. 2). Accumulation of cadmium into solid non-soluble residues was evaluated only at acetic anhydride and acetone solvents (Tab. 1). Also the presence of lead was evaluated in the same solvents but at soluble fragments of waste matter from biodiesel factory (Tab. 2), in other analyzed samples obtained from residual three solvents there were no detected contents.

Tab. 1 Contents of monitored elements, concentration of hydroxide anions, weight of total precipitate and precipitated soaps from solid phases isolated from five solvents

| <i>Solvent</i> | K (mg.kg ⁻¹) | Na (mg.kg ⁻¹) | Pb (mg.kg ⁻¹) | Cd (mg.kg ⁻¹) | Precipitated lead salt (g) | cOH- (mol.L ⁻¹) | Precipitate (g) |
|------------------|-----------------------------|------------------------------|------------------------------|------------------------------|----------------------------|--------------------------------|---------------------|
| ether | 73.10 ^c | 386.8 ^b | 1.20 ^c | 0.00 ^a | 0.4771 ^c | 2.035.10 ^{-2b} | 2.4324 ^c |
| toluene | 77.00 ^d | 351.6 ^b | 1.00 ^b | 0.00 ^a | 0.3836 ^b | 1.472.10 ^{-2a} | 2.0137 ^b |
| acetic anhydride | 17.00 ^b | 29.2 ^a | 0.60 ^a | 0.03 ^b | 0.0529 ^a | 2.595.10 ^{-4c} | 0.1027 ^a |
| ethanol | 10.50 ^a | 19.2 ^a | 1.10 ^b | 0.00 ^a | 0.0488 ^a | 5.191.10 ^{-4d} | 0.1553 ^a |
| acetone | 98.00 ^c | 680.0 ^c | 0.60 ^a | 0.03 ^b | 0.6056 ^d | 2.616.10 ^{-2c} | 2.4796 ^c |

NOTE: Letters in table stand for statistical significance in columns (p<0.05). Their conformity means that the values are statistically non-significant and different letters characterize statistically significance

Tab. 2 Contents of monitored elements of, concentrations of oxonium ions and hydroxide ions and weight of precipitated soaps in residues gained from five solvents

| <i>Solvent</i> | K (mg.kg ⁻¹) | Na (mg.kg ⁻¹) | Pb (mg.kg ⁻¹) | Cd (mg.kg ⁻¹) | Precipitated lead salt (g) | cH ₃ O+ (mol.L ⁻¹) | cOH- (mol.L ⁻¹) |
|------------------|-----------------------------|------------------------------|------------------------------|------------------------------|----------------------------|--|--------------------------------|
| ether | 33.30 ^c | 55.8 ^a | 0.00 ^a | 0.13 ^c | 0.1292 ^c | 2.680.10 ^{-6a} | |
| toluene | 16.00 ^a | 269.9 ^b | 0.00 ^a | 0.10 ^b | 0.1507 ^d | | 5.410.10 ^{-5ab} |
| acetic anhydride | 54.80 ^d | 608.3 ^c | 0.70 ^b | 0.08 ^a | 0.0817 ^a | 2.232.10 ^{-2a} | |
| ethanol | 61.20 ^e | 294.2 ^b | 0.00 ^a | 0.09 ^{ab} | 0.0965 ^b | 9.140.10 ^{-6ab} | |
| acetone | 23.80 ^b | 73.4 ^a | 1.90 ^c | 0.68 ^d | 0.0718 ^a | 6.778.10 ^{-6b} | |

NOTE: Letters in table stand for statistical significance in columns (p<0.05). Their conformity means that the values are statistically non-significant and different letters characterize statistically significance.

Discussion

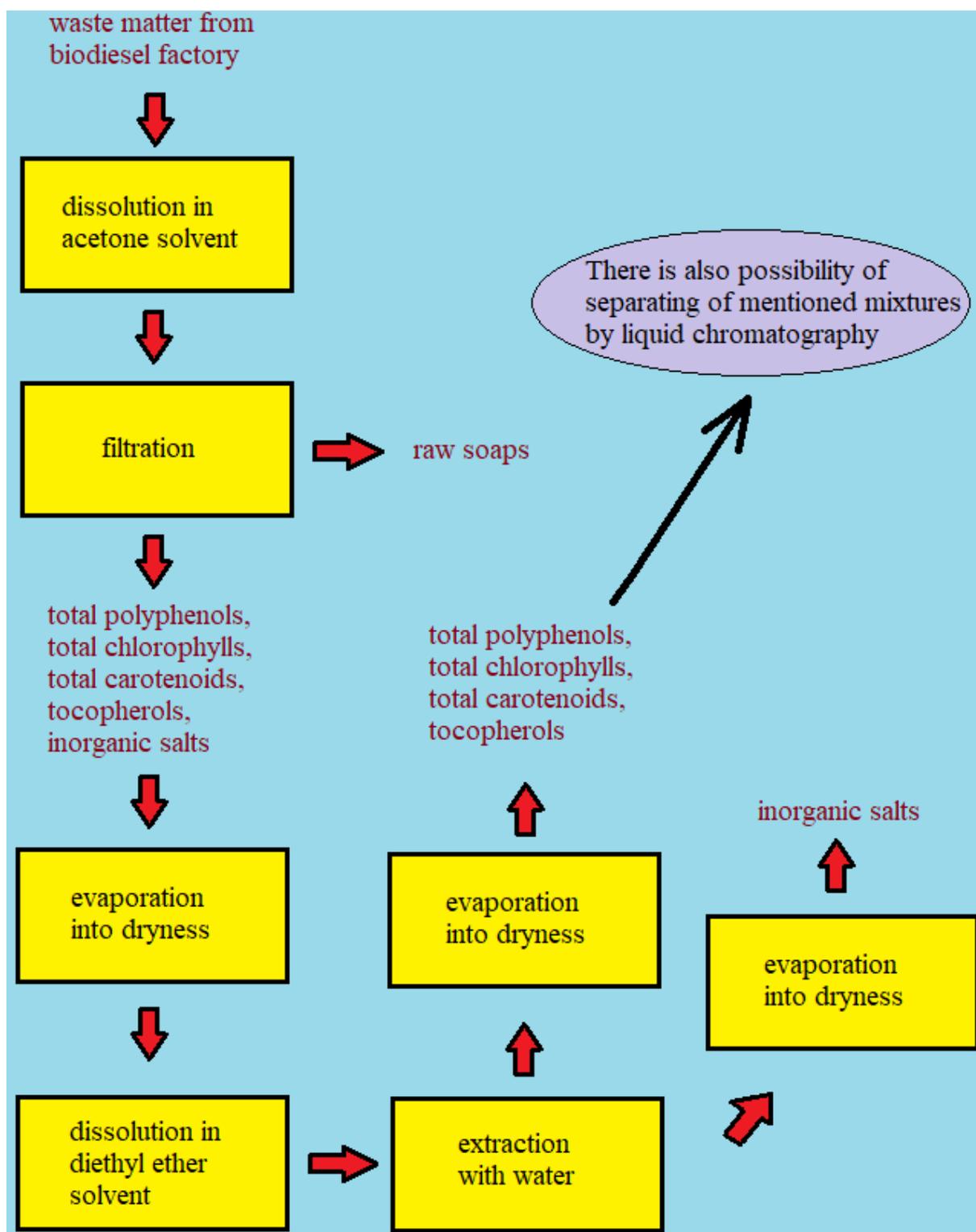
While the norm by biodiesel defines the limit for glycerol maximum 0,02 %, produced biodiesel is washed by water in order to reduce the content of glycerol in biodiesel. Due to bases soaps have been formed in raw product by washing of biodiesel which form one of components of waste matter arising during the production of biodiesel. Mentioned matter (after separating of soap residues) contains also many other organic compounds (polyphenolic compounds, tocoferols, total chlorophylls and total carotenoids), which could be used in food and pharmaceutical industry as well as compost. These substances after cleaning could be used also in other branches of production and thus form economic benefits for device on biodiesel production.

During the separation analysis it was found out that the highest amounts of solid non-soluble matter of soaps occurred in acetone, diethyl ether and toluene solvent and from thus reason had the highest amounts of cations of sodium and potassium (one of these macroelements in mentioned solvents always showed statistically non-significant dependence). It is presumed that alkali metals present in biodiesel are bound to soap (Bart *et al* 2010). Soaps of alkali metals always have in water medium alkaline pH (Mak-Mensah and Firempong 2011), what is also referred in Tab. 1 with evaluated approximate correlation of concentrations of OH⁻ ions in water solution dissolved in filtrate residues mainly from contents of sodium cations contained in these non-soluble residues isolated from tested solvents (statistically significant in toluene, anhydride and ethanol solvent), as well as complete statistically significant correlation conformity of concentrations of OH⁻ ions from amounts of precipitated organic components by Pb²⁺ ions.

According to increasing polarity the solvents were lined up as following: toluene < diethyl ether < acetic anhydride < acetone < ethanol (Reichardt and Welton 2011).

The most part of soaps were isolated in acetone that have high polarity, as well as in other two solvents (diethyl ether and toluene) with the lowest polarity. Molecules of soaps contain in their branched chain long chain with polar and non-polar part (Fiandaca and Bankiewicz 2013) and thus they do not have good solubility in tested solvents with various polarities (Malik *et al* 1971). Other components present in waste matter – total polyphenols, tocopherols, total chlorophylls and total carotenoids form soluble aliquot part in tested solvents. It is obvious that these organic compounds are very good soluble in organic solvents. Due to hydroxyl groups (mainly by total polyphenols (Manach *et al* 2004)) there is predominance of acidic pH by these compounds (Tab. 2). In water medium dissolved precipitates had the value of pH < 7, except from precipitate gained from toluene. This only system had alkaline pH value (Tab. 2) – it is caused by the non-ability of toluene solvent to separate soaps from other organic substances. While the alkali salts of carboxylic acids from the chemical point of view in water medium hydrolyse always alkaline (Atiku *et al* 2014), it could be presumed that these soaps are present not only in solid non-soluble phase which was separated by precipitation, but also in aqueous medium of soluble precipitate gained from mentioned toluene solvent. Therefore the pH value was in the case of both analyzed samples gained from toluene always alkaline (Tab. 2). Presence of soaps in oil precipitate from toluene could be proved by the presence of saturated solution Pb(NO₃)₂, where in aqueous medium of mentioned dissolved precipitate with Pb²⁺ ions lead soaps were precipitated. In

principle smaller amount of soaps was precipitated by lead ions also in aqueous solution of isolated precipitate from diethyl ether.



Scheme no. 1 Schedule of partial steps of separations of individual parts of compounds from waste mixture produced by biodiesel factory

Isolation of organic compounds from waste produced by producer operation methyl-ester of plant oil should be conducted in suggested steps (Scheme 1): dissolution of this waste matter in acetone solvent (recommended dose is $50\text{g}\cdot\text{L}^{-1}$ of solvent). In this initial phase the sodium-potassium soaps from other organic compounds (organic secondary metabolites occurring at oilseed seeds) will be separated. These will be in another step separated by filtration with following decantation of this non-soluble matter by pure acetone – recommended amounts of this solvent is twice 8 % from original volume of pure solvent. These raw soaps after washing will be dried in drying machine by $70\text{ }^{\circ}\text{C}$ and afterwards they could be used by other technological process for producing of hygienic soaps, or additives into detergents commonly used in households. Weight percentage of such obtained soaps is approx. 62 %. Acetone filtrate will be vacuum concentrated by $60\text{ }^{\circ}\text{C}$ till constant weight of oil consistency (acetone solvent trapped in reservoir in cooling part will be repeatedly used by subsequent processing of waste produced during manufacturing of biodiesel fuel). Organic layer gained by this procedure containing total polyphenols, tocopherols, total chlorophylls and total carotenoids and small amount of inorganic salts could be dissolved in diethylether solvent. Mentioned compounds have been dissolved in exact solvent and the last step can be carried out - two-step extraction of this diethylether solvent with water – for the purpose of isolation of organic compounds from inorganic fragments. Isolated health beneficial natural compounds (after complete evaporation of solvents) could be further used for example in pharmaceutical or food industry as health preparations, or additives into foodstuffs (Martillanes *et al* 2017; Silva and Lidon 2016; Butu *et al* 2010; Bogacz-Radomska and Harasym 2018). It is possible to carry out also other more demanding step of separation of these organic metabolites of plants by chromatographic method. Diethylether solvent is retained in container of cooling part of evaporator and after its recycling could be used in further waste processing. Isolated inorganic compounds could be used in agriculture as potassium sodium fertilizers (mainly for plant nutrition of sugar beet).

Pollution from biodiesel has not been given much attention because it has not (as yet) reached the level of recognition (and application) as petro-diesel. It is common knowledge that the presence of trace metals in biofuels can be detrimental to the environment and long-term sustainable development (Elkadi *et al* 2014). It is well known that abnormal metal content of biofuel is deleterious to the environment (Ozsezen and Canakci 2011; Buyukkaya 2010) as well as engines (Lin *et al* 2009). However, toxic metals from biodiesel can find its way into the environment by various means. According to researchers Elkadi *et al.* (2014) lower levels of some toxic elements (Be, Se, Tl, Pb, Bi) were produced by treatment with NaOH. On the other hand, lower measured concentrations of other toxic elements (Sb, Th) were recorded with KOH treatment. These deleterious elements can be released into the atmosphere as exhaust fumes from biodiesel combustion and could also migrate into the soil and water table, especially if poor quality biofuel is dumped. Sustainable development is the key factor in producing biofuel and it is necessary to guard against the threat of contamination.

These pollutants may be found also in waste matters from production process of biodiesel and thus cause considerable problems for environment. Organic solvents, which were applied in separating process of separating waste product, also contain heavy metals. In

our experiments lead content was found out in interval $0-1.9 \text{ mg.kg}^{-1}$ and cadmium in interval $0-0.68 \text{ mg.kg}^{-1}$. An interesting fact is that the atoms of lead have the tendency to accumulate in filtration residues (statistically significant only in ethanol and acetone solvent), while the atoms of cadmium on the contrary - they accumulated in isolated precipitates of filtrates. The tested solvents from our experiment contained minimally one atom of oxygen in their molecules (except for toluene solvent). The highest accumulation of both heavy metals was evaluated in acetone solvent (except for lead ions extracted from filtration residues). Carbonyl group present in acetone solvent is strongly polar - its polarity becomes greater by positive inductive effect both bounded methyl groups to atom of carbon of this carbonyl group. As is well known, the methyl group ($-\text{CH}_3$) usually plays a key role in the C1 chemistry, because it is the main precursor of HCHO, HCOOH, and other organic micro-molecules. (Zhu *et al* 2017; Hou *et al* 2018). Oxygen atom with partial negative charge has higher affinity to both heavy metals. Similarly as carbonyl groups in acetic anhydride solvent by means of polarized atoms of oxygens and carbons, mutually bounded by multiple bonds, show higher ability to attract these analysed heavy metals (only acetic anhydride and acetone formed positive medium for accumulation of cadmium atoms into filtrates residues and atoms of lead into filtrates).

Conclusion

Processing of wastes belongs among the most important human activities. There is in fact no production operations which does not produce any final unnecessary product because each industrial and consumer operations are related always with production of these wastes. In our work technologically the most suitable alternative of recovery of the waste from biodiesel factory have been found where the most appropriate material evaluation of mentioned solid matter and exactly with waste adjustment as secondary raw-material on production of usable products (such as soaps or biological nutritive substances for humans or plants) has been studied. In this case the waste do not form major component of inorganic toxic compounds or heavy metals because by actual production only natural organic compounds (plant oils or natural lipids as well as biological degradable low-molecular weight alcohol) are used. Also inorganic KOH, or NaOH used during this production have highly degradable properties and thus do not pollute the environment.

Processing procedure of waste matter mainly comprises separations of soaps and inorganic salts from other natural substances on the basis of different solubility in solvents. Algorithms of the most suitable separations of mentioned substances contained in waste matter from biodiesel factory could have more possibilities. In two step graduated procedure two organic solvents (acetone and diethyl ether) and also water were used. With acetone solvent the raw soaps will be separated, further after evaporation of this solvent with subsequent residue dissolution in diethyl ether and extracted into water inorganic salts from organic compounds: polyphenols, tocopherols, total chlorophylls and total carotenoids that were obtained finally by evaporating into dryness from both liquid proportions.

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