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VIABILITY OF NEWLY DEVELOPED PROCESS FOR CATALYTIC CONVERSION OF BIO-GLICERIN INTO VARIOUS “GREEN CHEMICAL” AND DEVELOPMENT OPPORTUNITIES FOR SERBIA

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Crude bio-glycerin is a by-product in the production of biodiesel. An economically efficient valorization of crude bio-glycerin usually significantly defines the profitability of the biodiesel plant. A strong technological development in recent years has provided an additional option for economically viable use of glycerin through conversion of a crude bio-glycerin, in first step into a technical glycerin, and then further by use of new catalytic processes into various „green chemicals“, such as epichlorohydrin, propylene-glycol, bio-methanol, acrolein, acrylic acid, etc. Many of those newly-developed technologies are already in use on an industrial scale.This trend had caused a growth in demand of bio-glycerin, which gradually has led to a rise of bio-glycerin's market value and contributed to an overall growth in profitability of biodiesel industry. This paper has the aim to assess: global availability of the emerging technologies intended for valorization of bio-glycerin via production of commercially attractive „green chemicals“, local and regional availability of bio-glycerin for an economically justifiable production of „green chemicals“, and local and regional potential for marketing of the most viable „green chemicals“. All market assessments and expected challenges that are stated in this paper took into account a reality that development of the biodiesel industry is still largely influenced by government subsidies and mandates, and also by a price of crude oil.

Key words: Biodiesel Industry, Crude Bio-Glycerin Market, Bio-Glycerin to „Green Chemicals“, Serbia's Development Opportunities

INTRODUCTION

Conventional biodiesel (Methyl Esters of Fatty Acids or abbreviated FAME) is manufactured by trans-esterification of vegetable oils and/or animal fats by methanol in presence of catalyst.

By-product (or co-product) of transesterification process is crude bio-glycerin. For every 1,000 kg of FAME manufactured by transesterification, approximately 100 kg of crude bio-glycerin is also produced. An economically efficient valorization of crude bio-glycerin lowers the cost of FAME production and usually significantly defines the profitability of FAME manufacturing. European biodiesel industry has already gone through a period of crisis from 2008 to 2010, when extremely rapid growth in FAME production caused enormous oversupply of bio-glycerin, so that glycerin had got minor or no economic value.

Almost an immediate response to this situation had been a strong technological development, and through which the invention of a whole range of new catalyzed thermochemical processes for converting crude bio-glycerin into profitable chemical intermediates. Many of those processes have already been translated to the level of commercial exploitation on an industrial scale (epichlorohydrin, propylene-glycol, bio-methanol, acrolein, acrylic acid, ...) [18]. This trend had caused a growth in demand of bio-glycerin, which gradually has led to a rise of bio-glycerin's mar-

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ket value and contributed to an overall growth in profitability of biodiesel industry.

The volume of biodiesel production in Serbia is currently at a very low level. However, there are at least a doezen factories that currently produce biodiesel on an industrial scale in the neighboring countries (Hungary, Romania, Bulgaria and Croatia) [06].

In this sense, this paper has the aim to assess:

1) global availability of the emerging technologies intended for valorization of bio-glycerin via production of commercially attractive chemical derivatives,
2) local and regional availability of bio-glycerin for an economically justifiable production of chemical derivatives that are identified under item (1), and
3) local and regional potential for marketing of products that are identified under item (1).

All market assessments and expected challenges that are stated in this paper took into account a reality that development of the biodiesel industry is still largely influenced by government subsidies and mandates, and also by a price of crude oil [16].

GLYCERIN MARKET WORLDWIDE

Glycerin (glycerol or 1,2,3-propanetriol) is the oldest organic molecule isolated by human beings in a such a way that fats were heated in the presence of ash in order to produce soap, and that was happened around 2800 BC. In the modern era, the first industrial application of glycerin was by the military industry in the production of nitroglycerin as a strategically important raw material for the production of explosives and gunpowder (1840's). The next industrial applications were use of technical glycerin as raw material in the manufacture of alkyd resins for coatings industry and various direct uses of high-quality glycerin in the formulations of personal care products and pharmaceuticals (1920's).

Due to the rapid growth in demand of glycerin and its limited supply from production of soaps and oleochemicals, as of mid-1930s began production of petrochemical (synthetic) glycerin. From this moment, glycerin had been an extremely profitable chemical product, and high-purity grades of glycerin were sold even at prices ranging from 2,500 to 3,500 USD per t [02].

Since 2003, however, the boom in FAME production and rapidly increasing glycerin oversupply caused a dramatic fall in the price of both refined and crude glycerin. Very soon after that, the production of synthetic glycerin worldwide was almost completely abandoned. Prices had continued to drop and in 2009-2010 the European price of highly-purified glycerin was less than 320 EUR per t, while the prices of crude bio-glycerin ranged from 80-100 EUR per t (for GMO-free origin) to zero (for GMO origin). Crude bio-glycerin of lower quality had become a waste material of no economic value, except the incinerated as a low-calorific fuel [11]. Changes in average structure of the origin of glycerin at global level are shown in Figure 1. As can be seen, an increased contribution of biodiesel is obvious, from 9% in 2000 to 64% in 2013. Changes in Europe were even more radical, because in 2014 the share of FAME in structure of glycerin produced reached over 85% [04]. Global biodiesel production has grown from about 200,000 t in 2003 to about 29 million t produced in 2014. Practically, this means that in just 11 years global supply of glycerin from biodiesel production (i.e. bio-glycerin) increased about 150 times. The worldwide leader in consumption and production of glycerin is Europe. With current consumption of around 1 million t per year (toy) its share in global demand is 28-30%, while the share in global production is even higher, approximately 33%. The major end-uses of glycerin in Europe are production of toiletries & cosmetics, food & beverages industry, production of polyether polyols and pharmaceutical industry. Besides Europe very large users of glycerin are China (27%) and the United States (21%). Cumulative share of all other countries in global consumption of glycerin is less than 25%.

Today, glycerin is among the most important industrial oleochemicals, along with fatty acids, fatty alcohols and FAME, and it has many end-uses since a variety of these applications is growing continuously.

Among these new applications are the newly-developed catalytic processes for conversion of refined glycerin into chemical intermediates.

Other new uses of glycerin with high market potential include replacement of more expensive sorbitol and propylene-glycol as sweeteners and humectant, as well as substitution of mono-ethylene-glycol with technical grade glycerin in formulations of windshield wash fluids and coolants and antifreeze products. The latest application of this kind is liquid for e-cigarettes which contain glycerin of Kosher quality (100% GMO-free) in a function of the artificial sweetener. Thanks to the combination of new applications and market expansion in traditional markets, the price of glycerol partly recovered since the 2009-2010 historic lows (see Figure 2).

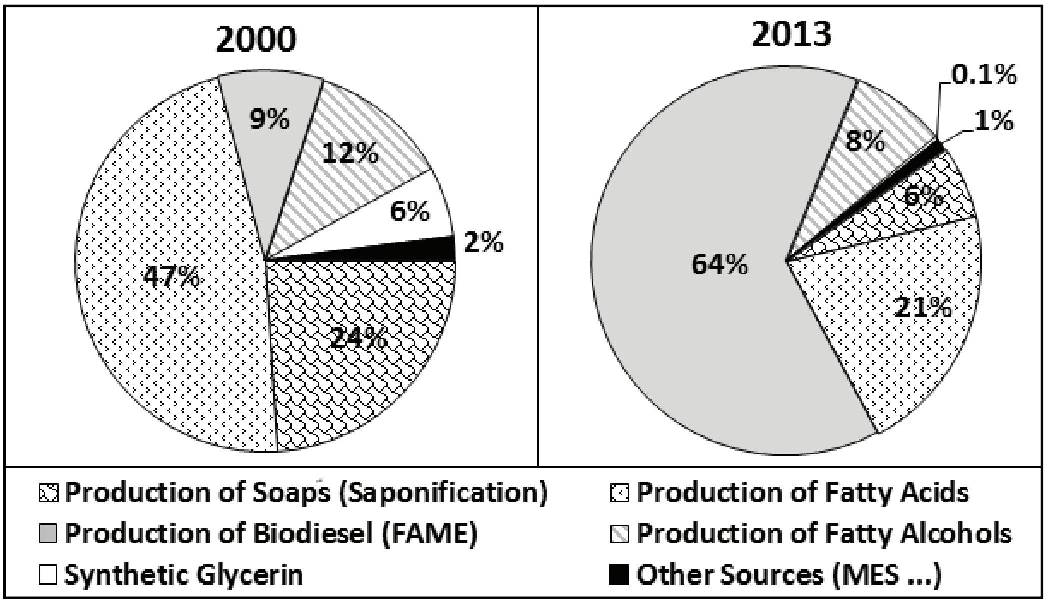

Figure 1: Glycerin in 21st century: Radical change of supply sources [04]

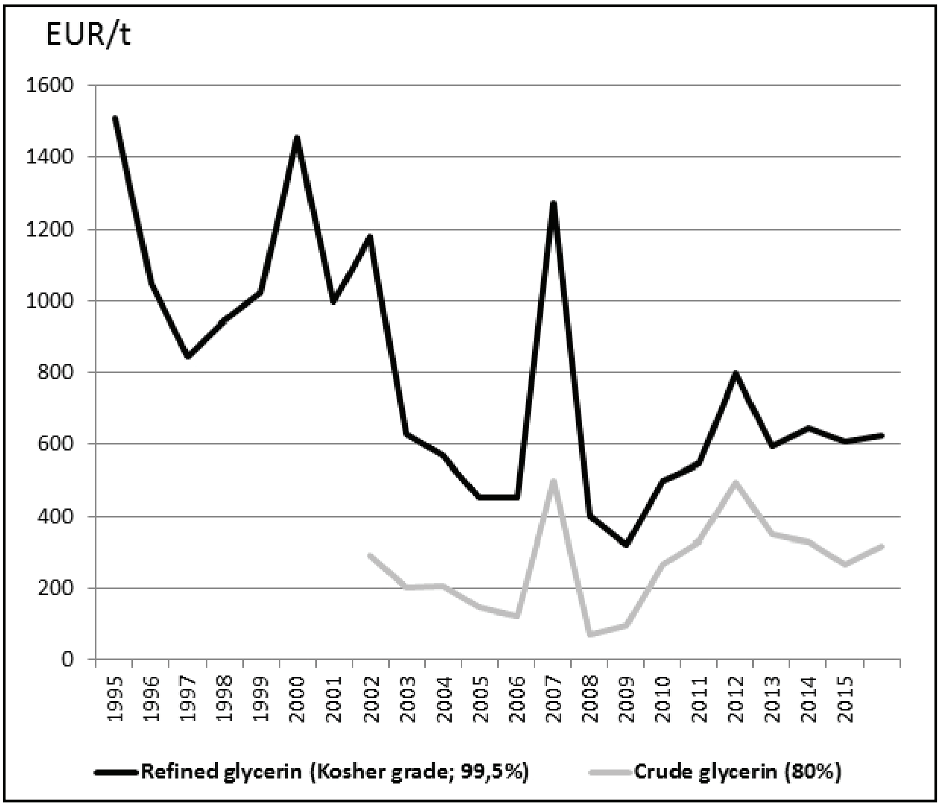

Figure 2: European spot prices of glycerin (CFR Rotterdam) [16]

Most recent prognostic studies predict growth in global consumption of glycerin up to 2020 by very high compound annual growth rates (CAGRs), ranging from 6.3 to 6.8% [08, 01]. The largest sector demand for refined glycerin will remain the production of pharmaceuticals and toiletries, but uses of highly purified glycerin in the food industry & soft drinks industry will grow extremely fast, at CAGR of about 8.5%. However, the highest growth at CAGR of over 10% will record uses of refined glycerin in catalytic processes to produce chemical intermediates.

GLYCERIN MARKET IN SERBIA AND NEIGBORING COUNTRIES

Today, Serbia has at its disposal a certain amount of crude bio-glycerin from FAME production, but in 2014 this quantity was not greater than 300 t. Production of refined glycerin does not exist, and the needs of the domestic market for glycerin are covered from imports. In recent years, annual imports of refined glycerin ranged from 2,000 to 2,100 t, whereas import of crude glycerin was negligible. Major domestic consumers of refined glycerin are production of nitroglycerin, tobacco industry as well as manufacturers of soaps, toiletries and cleansers.

By adoption of (i) Ministerial Council Decision 2012/04/MC-EnC within the Energy Community (EC) in October 2012, and (ii) National Renewable Energy Action Plan in June 2013, the Republic of Serbia took over obligations arising from the provisions of the Renewable Energy Directive (RED) 2009/28/EC with regard to achieving the percentages that are targeted in 2020 for the overall share of energy from renewable sources and for the share of energy from renewable sources in transport. The bulk of mandates within EC member states continue to come from the EU-27, where the RED Directive specified a 10% renewable energy content in sector of road transport by 2020 [17].

Serbia has an obligation to reach by 2020 some 27% of energy consumption from renewable sources. It is uncertain how Serbia will meet this target and increase share of renewable energy in total energy consumption for over 5% in only five years.

Each EC member state has the freedom to decide how they will achieve that target through rise of energy from renewable sources in electrical energy generation, in the sector of heating and cooling, as well as in the transport sector. Above mentioned the National Renewable Energy Action Plan includes the projection that by 2020 the share of renewables in the transport sector will reach mandatory level of 10%. Having in mind projections of domestic consumption of energy in sector of transport, that means that domestic consumption of renewables might reach in 2020 a level of over 135,000 to 245,000 t of oil equivalent (toe) [10]. Most of this renewables will be biofuels.

Targets of Serbia for energy from renewable sources in transport sector refer to the „consumption", and not for the „production". On us is whether the targeted „consumption" we want to achieve through use of renewables of domestic origin or by import.

Orientation of Serbia on imports of biofuels automatically means the reduction of market for domestic suppliers of motor fuels (at level that corresponded to the quantity of imported biofuel intended for blending). For JSC "NIS", who is manufacturer, wholesaler and exporter of petroleum products, and also the owner of a chain of gas stations in Serbia and neighboring countries, this situation also means the reduction of its market potential for placement of motor fuels in the region.

Therefore, from an economic point of view, it is quite realistic to expect the re-start of domestic production of biofuels in existing plants. However, it is important to underline that domestic production of biofuels starts from an almost negligible level, but the capacities for production of around 100,000 tpy were constructed but they are not in operation.

On the other hand, there are two "weak points" related to the development of biofuel production in Serbia.

First is the fact that according to all reliable forecasts, the producer prices of conventional fuels in the next 5-6 years will not exceed a level that allows the competitiveness of biofuels . It would be unrealistic to count with high-level production and sale of FAME in Serbia if its price is 0.62-0.64 EUR per liter [01], while you can buy petroleum diesel at price of 0.49-0.52 EUR per liter [05] .

Second, the biofuel industry is generally very dependent on legal regulations and incentives. In the past few years much has been done in Serbia on the first assignment, but up to now practically nothing happened on the implementation of this latter assignment.

Serbia already has the plants of industrial scale for the production of FAME, three of which are facilities of smaller size in operation with total capacity of around 6,500 tpy. There are also two larger FAME plants, one of which is idled (100,000 tpy located in Šid), and the other one which is still not completed (35,000 tpy located in Kruševac) [12]. Besides, over 1,000 individual farmers throughout Serbia are producing FAME for their own use in small on-farm production systems.

On the other hand, Serbia still has no facilities for the production of bioethanol or any of the advanced biofuels [12]. Moreover, there are no indications that such kind of facility could be built in Serbia in the near future. Therefore, it is highly probable that fulfillment of national targets on use of bio-renewables in transportation sector up to 2020 will be almost exclusively realized through the development of production and consumption of biodiesel consumption (production). Bearing in mind benchmarks regarding use of renewables in transport sector which were imposed by the European Commission, then the expected development of „road" diesel fuel consumption (production) in Serbia [13] and marginal percentages of biodiesel blending [10] the domestic needs for biodiesel in 2020 will be at a level of 113,000-179,000 t, and in 2025 at a level of 183,000-203,000 t [10].

In addition, the significant amounts of bio-glycerin are already available in neighboring countries. Table 1 shows current quantities of crude bio-glycerin that might be considered as available at regional level.

Table 1: Availability of bio-glycerin in neighboring countries (in tpy)

Country	FAME capacity (2014)	FAME production (2014)	Bio-glycerinavailability* (2014)	Glycerin exports (2012-2014)
Romania	277,000	160,000	16,000	15,035 (2014)
Bulgaria	408,000	40,000 (2013)	4,000 (2013)	1,000-1,500
Hungary	162,000	190,000	19,000	17,650-19,300
Croatia	62,000	35,000	3,500	10,460 (2014)
FYR Macedonia	20,000	6,500	650	630 (2014)
Greece	812,000	140,000 (2013)	14,000 (2013)	16,835 (2014)
T O T A L :	**1,741,000**	**571,500**	**57,150**	**61,610-63,760**

*Based on fact that FAME production generates about 10% (w/w) of bio-glycerin
Remark: Other neighboring countries currently do not have production of FAME.

The Croatian exports obviously include some re-export. Data on Bulgarian exports in 2014 are not available.

AVAILABILITY OF CRUDE BIO-GLYCERIN IS EQUATION INVOLVING SEVERAL UNKNOWNS

Global biodiesel industry consists today from facilities to produce FAME and so-called "renewable diesel" (which is also known as Hydrotreated Vegetable Oil or abbreviated HVO).

The first manufacturing plant to produce HVO was started on December 2007 in Finland by the petroleum company „Neste Oil". HVO is produced by the hydrotreating vegetable oils and/or animal fats. The process of HVO manufacturing does not yield bio-glycerin, but other by-products such as naphtha (for petrochemical industry), LPG and propane. HVO has emerged as an attractive alternative to FAME in recent years. With this process the same kinds of vegetable oil feedstock that are used in FAME production are reacted with hydrogen in a process called hydrotreating — a common process in the petroleum industry. The primary advantage of HVO over FAME is that the product is chemically equivalent to petroleum diesel, so it can be used in diesel engines in higher concentration with no modifications (usually up -to 30%). A disadvantage is higher capital costs of hydrotreating equipment when compared with equipment required to produce biodiesel, and thus HVO production requires larger scale to be economical. Today in Europe manufacturing of HVO have the Netherlands, Finland, Italy, Sweden, Germany, Spain and France. World production of biodiesel has grown throughout the entire first decade of the 21st century. Globally, increase of biodiesel production has been realized in production by both FAME and HVO, although from 2010 this increase can mainly be attributed to rising HVO production. This trend is even more evident In Europe, where production of FAME experienced "peak" back in 2010, and since than the production of biodiesel (FAME + HVO) is maintained on an ongoing level only due to increased HVO production.

Table 2: Production of biodiesel (FAME/HVO) in 2014 (in million t)

	FAME		**HVO**		**Total Biodiesel**	
	2010	2014	2010	2014	2010	2014
World	17.25	22.00	0.15	2.70	17.40	24.70
EU-28	9.35	8.10	0.15	1.45	9.50	9.55

The global biofuel industry is nowadays under great pressure. Crude oil and petroleum products prices collapsed towards the end of 2014 and into 2015, which very soon caused a huge enlarging of the margins between prices of biofuels and petroleum products. Slowly but surely such circumstances have reduced blending of biodiesel worldwide. Many European plants to produce FAME are either mothballed or running at low capacities due to a lack of demand. Although energy legislation still pushes the market participants to fulfill national mandates on blending biofuels, and although European Commission responded promptly and increased biodiesel premiums, some of market participants decided rather to pay penalties than to blend uncompetitive FAME.

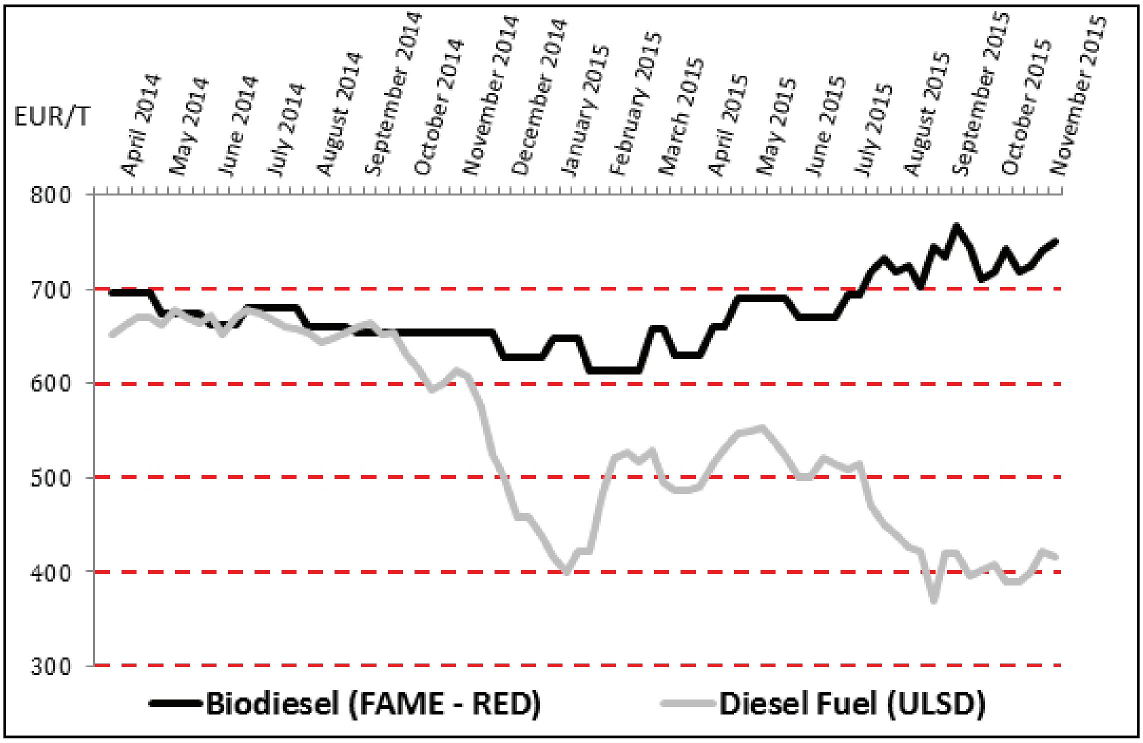

Figure 3: Historic prices of biodiesel (FAME - RED) and petroleum diesel fuel (ULSD) (spot prices FOB Rotterdam) [01, 14]

It should be underlined that problems of biodiesel industry have caused also a certain drop in global prices of the crude vegetable oils, and particularly drop in prices of waste and residual fats and oils, what is logical since the biodiesel industry is a major consuming sector of these feedstock . However, those price reductions were not sufficient to make biodiesel competitive in the motor fuel market. At the beginning of November 2015, an average EU's wholesale price for biodiesel net of duties and taxes stood at around 750 EUR per t, thus exceeding the price for off-road diesel fuel (diesel fuel which is not subject to duties and excise taxes that are applied to the retail sales of road-diesel fuel) by nearly 340 EUR per t.

Also, there are two new events that will mostly probably affect the future availability of bio-glycerin in Europe:

- In April 2015 by the European Parliament approved Directive 2015/1513/EU that says that first-generation biofuels (i.e. biofuels produced from food crops, which includes FAME) should not exceed 7% of the final energy consumption in transport by 2020 (less than 10% stated in RED Directive).

- Currently, a major turnaround is in progress in interregional trade of motor fuels. All analyzes indicate that in 2015 the United States will become a net exporter of motor gasoline, for the first time after many decades. This event will significantly change an established image according to which the European refineries marketed their own surpluses of gasoline fuels in the United States. It is likely that such kind of shift will have an impact on relations in European demand of motor fuels in favor of gasoline (and at the expense of diesel pool of refinery streams which also includes the biodiesel).

Respecting all the above stated, it could be concluded that availability of bio-glycerin has reached a historic „peak" at both worldwide level (most probably) and in Europe (definitely). Further, rise of glycerin availability will only be realized from increased production of certain oleochemicals (fatty acids, fatty alcohols and methyl ester sulfonates). However, having in mind the current share of these productions in overall global supplies of glycerin, and the fact that new production capacity of these oleochemicals is built almost exclusively in the Asia-Pacific region, it seems that a market participant who intends to consume glycerin as feedstock in the manufacturing plant which is located in Europe, should not in future count to enlarged level of glycerin availability.

PROBLEMS IN VALORIZATION OF CRUDE BIO-GLYCERIN WITHIN CHEMICAL INDUSTRY

The first and essential factor in assessing the technoeconomic viability to valorize crude bio-glycerin through its use in chemical syntheses is its origin, i.e. type of processes to produce biodiesel which yields it. This refers to conventional process using a homogeneous catalyst or a process using a heterogeneous catalyst on carrier.

Homogenous catalysts are alkaline metal hydroxides and alkoxides as well as sodium or potassium carbonates. Since these catalysts react with components of vegetable oils and fats, and methanol, this kind of production process yields crude bio-glycerin in mixture with a lot of impurities. Advantages of that production process are high yield of FAME and cheap catalysts.

Heterogeneous catalysts are systems of alkaline or alkaline -earth metal or their oxides on carriers. Main advantage of heterogeneous catalyst is that it can be recycled and re-used several times with easier separation of the final reaction product. Heterogeneous catalysis in biodiesel production, unlike homogeneous catalysis, removes the costly and time-consuming water washing and neutralization steps to separate and recover the spent catalyst. Also, contaminated water from homogeneous catalysis process is greatly reduced and the need for waste water treatment minimized.

The problems for the use of crude bio-glycerin in chemical syntheses and other industrial applications are its high contamination with toxic methanol, high content of organic salts and fee fatty acids (FFAs), as well as its substantial color (from yellow to dark brown). A crude bio-glycerin produced from biodiesel process using heterogeneous catalysts is somewhat cleaner comparing to a crude bio-glycerin produced by conventional homogenous biodiesel processes. However, it should be bare in mind that all existing operating and preserved facilities for biodiesel production in Serbia use conventional process.

Glycerol fraction formed in the process of biodiesel production generally contains 23 to 63 wt. % of crude bio-glycerin and more than 10 wt. % of methanol. The rest is mixture of water, methyl esters and lipids, inorganic salts (catalyst residues), FFAs, unreacted mono-, di-, and tri-glycerides, and a variety of non-glycerin organic compounds in small percentages. These impurities make the crude bio-glycerin obtained in the process of decanting mixtures of biodiesel plus crude bio-glycerin unsuitable for direct application in the most traditional uses of glycerin.

To convert crude bio-glycerin into the product of commercial value is necessary to conduct the operations of removing water, methanol and its salts, and undissolved impurities (there are 5-7 wt. % of insoluble salts in crude bio-glycerin from process of transesterification with homogeneous alkali catalyst). Or in other words, it is necessary to carry out the process of refining (purification) which is realized in two steps:

1) Getting demethylated bio-glycerin=Flash evaporation+Acidulation+Filtration (eventually with the addition of auxiliary chemical agents)
2) Preparation of refined glycerin=Membrane filtration+Reverse osmosis+Drying+Disti

llation. The process of flash evaporation, besides elimination of water, also removes most of the methanol, which is an easy-volatile organics. Acidulation includes treatment with HCl or H2SO4 to neutralize the traces of the catalyst and causes hydrolysis of the soaps present in the crude bio-glycerin. That leads to the formation of insoluble salts, which are then removed (partially by decantation, and completely by filtration). Filtration with the addition of chemical agent that react with impurities gives de-methylated bio-glycerin with glycerin content of 80-90 wt. %.

The minimum conditions for bio-glycerin to have any commercial value are glycerol content over 80 wt. %, and methanol content below 1 wt. %. In fact, bio-glycerin which does not fulfill these conditions can be used only as an energy source (incineration for heat production, fuel for steam boilers, and agent for improving the combustion properties of biogas in anaerobic digesters), then as an additive for certain types of cattle fodder (improves the ruminant's feed to weight gain ratio), and from recently as an auxilliary agent for cements of enhanced performance (replacing petrochemical amines and glycols).

Further purification of demethylated bio-glycerin leads to obtaining refined glycerin:

- Technical grade glycerin, 95.5 to 98.0% purity, suitable for production of chemicals and use in many other industrial applications, with exception of uses in food industry, pharmaceutical industry and industry of toiletries and cosmetics;
- Pharmaceutical grade glycerin (USP, Ph. Eur.), 99.5% and 99.7% purity, derived from vegetable oils and animal fats, suitable for food products, pharmaceuticals, toiletries and cosmetics;
- Kosher/Halal grade glycerin, high-purity, derived 100% from vegetable oils suitable for use in Kosher and Halal foods.

Treatment to reach Pharmaceutical or Kosher/Halal glycerin through process of purification when it starts from crude bio-glycerin is complex and it requires serious CAPEX and OPEX, primarily those in distillation section.

Crude glycerin which is a by-product in production of fatty acids and fatty alcohols ("splitter crude glycerin") is not contaminated with methanol and catalyst's salts, and also has a much lower content of other organic impurities. This glycerin is usually completely converted into refined products, and mostly to those of Pharmaceutical or Kosher/Halal quality. CAPEX and OPEX correlated to process of "splitter crude glycerin" purification are significantly lower than those in treatment of crude bio-glycerin.

Crude bio-glycerin, even with the content of glycerin over 80%, cannot be treated in a traditional oleochemical refinery for purification of the "splitter crude glycerin", since it could damage the equipment and pipelines. It must be treated in the purposely-built refinery where purification usually goes up to an improved technical quality (> 97 wt. %).

The conversion of crude bio-glycerin into technical glycerin provides to owner of biodiesel factory certain advantages through eliminating the high costs of the toxic waste treatment and increasing the value of the products intended for market. Of course, there is a possibility of further purifying up to the Pharmaceutical or Kosher/Halal quality, but economic viability of this technological operation is highly problematic - it exists only within large-scale biodiesel factories where the profitability is expected to benefit from a high integration of all material and energy streams and lowered CAPEX and OPEX per unit of final products.

Crude bio-glycerin from FAME plant based on esterification of waste fats or used cooking oil (UCO) is glycerin of worst quality in terms of its further conversion to the refined grades. Due to the high content of saturated fatty acids, this crude bio-glycerin has a high melting point, high viscosity and often even contains solid particles. An analysis from 2011, aimed to estimate the cost of crude bio-glycerin purification up to 98 wt. % (by combination of evaporation, acidulation, filtration/centrifugation, and column distillation), calculated the lowest OPEX for glycerin purification at level of 0.15 USD per kg [04]. Measured in current prices, it is about 0.16 USD per kg.

High investment expenditures (CAPEX) effectively minimize the economic viability of construction of process units for glycerin refining within small and medium biodiesel (FAME) factories. It is estimated that, in general, there is no economic viability for construction of glycerin refinery within biodiesel factory with a capacity < 10,000 tpy.

Smaller FAME producers, however, may find an economic interest in agglomerating all their own available quantities of crude bio-glycerin in a single location to enable an economically sized refinery for purification feed glycerin up to the products of technical quality. This refined glycerin would found applications as raw-material in the traditional and newly-developed syntheses of organic chemical industry.

APPLICATIONS OF BIO-GLYCERIN IN CATALYTIC SYNTHESIS TO PRODUCE VARIOUS VALUE ADDED ORGANIC CHEMICALS

There are two approaches for conversion of crude bio-glycerin into value-added organic chemicals, and substitution of deficient or expensive petrochemicals: (a) Biotechnological conversion, and (b) Catalytic conversion. This paper discussed only catalyzed conversions, since biotechnological conversions of bio-glycerin into organic chemicals still have not been transferred into industrial practice, according to the authors' best knowledge.

Catalytic conversions of bio-glycerin can be further divided into traditional and newly-developed processes.

Traditional processes

Traditional catalytic syntheses include several chemicals, but of more serious commercial value are only nitroglycerin (as component of almost all explosives and smokeless gunpowder as well as cardiovascular or therapeutic agent for the treatment of bronchial asthma in medicine) and glycerol esters (a commercially the most important is glycerol-triacetate). Today, productions of nitroglycerin and glycerol esters participate in global consumption of glycerin with 1.5% and 6%, respectively.

The market analysis of Serbia and the neighboring countries is made, which confirmed sufficient regional demand to absorb the entire output of nitroglycerin or glycerol-triacetate from an industrial facility of economically reasonable size. The production of nitroglycerin was established long time ago within company "MB-Namenska" at location near town of Lucani. This same company had also a facility to produce glycerol-triacetate (it is generally known by trade name Triacetin®), but it was destroyed during NATO bombing campaign in 1999.

Glycerol-triacetate (Triacetin®)

Triacetin® has many usages, but over one-third of demand can be attributed to tobacco industry where it is used as a binder for cellulose acetate tows that bundle forms a cigarette filter. Other more important applications include its use as binder for foundry sands, gelling agent for gunpowder and explosives, and plasticizer (for cellulosic materials, printing inks, textile dyes, adhesives etc.) [03]. Food grade Triacetin® is used as an auxiliary agent (humectant, plasticizer or solvent) in formulations of various pharmaceuticals and cosmetics (for instance, Triacetin® is irreplaceable component of several erectile-dysfunction drugs, such as "Viagra" and "Cialis") and as food additive (known by code E-1518 it is primarily used as a humectant). The most recent application of this commercially most important glycerol ester is its role in partial replacement of the health-risky phthalates within PVC industry [09].

Global market for Triacetin® is around 150,000 tpy. The estimated demand and production in Europe (excluding Russia) are around 37,000 and 31,000 tpy, respectively [19].

There is not a single manufacturer of Triacetin® in Central, Eastern and South-Eastern Europe. Serbia imports about 200 tpy for the needs of local tobacco factories, plus ~ 50 tpy for other uses. Only seven neighboring countries, plus Greece, import additional 2,800 tpy .

Global demand of Triacetin® will continue to grow by CAGR ranging from 6% to 8%, which could be an expected growth for a product of "green chemistry", but is also an extraordinarily dynamic growth for one traditional organic compound.

The current prices of technical grade Triacetin® (98 wt. %) range from 1,200 to 1,300 EUR per t. Food grade Triacetin® (99.5 wt. %) price is approximately 10-15% higher. Relatively high prices allow the economic viability of even smaller production capacities, ranging from 500 to 1,000 tpy [03].

Triacetin® plant with capacity of 600 tpy consumes annually about 450 t of technical glycerin (or roughly 550-750 tpy of crude bio-glycerin). This is approximately the amount of crude bio-glycerin potentially generated by two local FAME plants in operation. Other material inputs of production process are glacial acetic acid and efficient heterogeneous catalyst. In Serbia there is a facility to produce 100,000 tpy of acetic acid within petrochemical complex "MSK" Kikinda.

Production plant consists of two sections: refining of crude bio-glycerin and production of glycerol-triacetate (reaction system and distillation columns). Around 850,000 EUR. estimates total CAPEX for construction of 600 tpy Triacetin® plant.

There are domestic technological recourses for process and plant designing and selecting an optimal catalyst for the process. Establishing of Triacetin® production in Serbia, which would be based on use of bio-glycerin refined up to technical grade (98 wt. %), is estimated as a viable project.

Newly-developed processes

Drop of glycerin prices, as a consequence of the "boom" in deliveries of bio-glycerin from a dynamically growing biodiesel industry, has opened many opportunities for the valorization of glycerin surpluses through the thermochemical and catalytic conversion towards various chemicals. It is clear that a large number of specialty and fine chemicals can be produced on the basis of reactions involving glycerin, and well-known chemical database Beilstein registers more than 1,500 of such derivatives. Logically, the number of those derivatives that have more serious commercial value is incomparably smaller. Glycerin predominantly substitutes petrochemical propylene in catalytic processes that are commercialized up to now and transferred into industrial practice. Most of these catalytic conversions are at the same time also so called thermochemical processes. The catalytic conversion of bioglycerin into bio-methanol, glycerol ethers or syngas opens up a perspective for enlargement of renewable energy sources, such as bio-dimethyl-ether (Bio-DME), glycerol-tert-butyl-ether (GTBE) or hydrogen (H2). Today, productions of newly-developed organic intermediates participate in global consumption of glycerin with approximately 17%.

Table 3. contains one concise SWOT Analysis, where the crucial strengths, opportunities, weaknesses and threats for each of these glycerin-based chemicals are identified. This analysis included seven newly-developed glycerin-based chemicals that have already been commercialized through the construction of industrial plants or larger pilot plants. A special attention is focused on projects (products) suitable for realization in Serbia. The main conclusion of SWOT Analysis is that at present time for Serbia was only meaningful realization of the project "BioGlycerin-to-MPG". Primers for this claim are given below.

Mono propylene glycol (MPG)

Mono propylene glycol (MPG) is also known as 1,2-propanediol (1,2-PD), and it belongs to the category of medium-tonnage organic chemicals. Industrial grade MPG (min. 95 wt. %) has many uses, but its main sectors of demand are unsaturated polyester resins (for the production of coatings and glass fiber reinforced plastics) and functional fluids (aircraft deicers, coolants and antifreeze products). Other applications include its uses as plasticizer in production of hydraulic fluid for brake systems and component in syntheses of non-ionic surfactants. MPG is also an excellent extraction solvent. Pharmaceutical grade MPG is at least 99.5% pure by weight and it finds uses in health-sensitive products such as food, fodder, personal consumer goods, cosmetics, and pharmaceuticals.

Conventionally, the commercial MPG production rote is propylene-based, via propylene-oxide, and therefore it is sensitive to the price of crude oil (or naphtha) and long-term deficiency of propylene. In newly-developed glycerin-based process of MPG production in gaseous phase, glycerin is reacted over a heterogeneous catalyst with hydrogen via a two-step reaction in the same reactor. Glycerin is first dehydrated to acetol, and MPG is then formed by the in-situ hydrogenation of acetol. First step is catalyzed by acid and second-step by metal, so that the commonly used are bi-functional catalysts (Cu-ZnO-Al2O3 or similar).

The main problem with use of crude bio-glycerin for production of MPG is excessive content of Na or K salts. Using of synthesis in gaseous phase opens the possibility of integration with crude bio-glycerin refining as a means of reducing energy consumption and capital expenditures.

Although n-propanol and iso-propanol are being created as by-products of the reaction of glycerin to MPG, they are produced in such small quantities that it is more profitable to simply dispose of them as waste instead of investing in additional purification equipment. The current worldwide market for MPG is around 2 million tpy. Global capacity to produce MPG is around 2.76 million tpy, of which around 30% is located in Europe [15]. Today, three industrial plants worldwide (US, China and Belgium) use "Glycerin-to-MPG" process, and they together consume about 170,000 tpy of technical glycerin (or roughly 200,000-280,000 tpy of crude bio-glycerin) [15].

Table 3: Summary of SWOT Analysis for Newly-Developed Glycerin-Based Chemicals

Chemicals	Strenghts	Opportunities	Weaknesses	Threats
Epichlorohydrin (ECH)	ECH is an essential feedstock for production of epoxy resins that have growing use in electronics, automotive and aircraft industry. Global ECH market overcame 1.6 x 106 tpy in 2014 and it grows by a CAGR of ~ 5%.	There are 15 glycerin-based ECH plants worldwide (4 within EU-28) that are consuming ~370,000 tpy of refined glycerin. ECH-based epoxy resins have strongly growing use in wind-generating power plants.	Negligible demand of ECH in Serbia and neighboring countries. Serbia used to be producer of epoxy resins within several plants that are all devastated during transition period. ECH manufacturing is ecologically and safety risky because of the toxicity of auxiliary and intermediate chemicals, and corrosion problems.	The prospects for the future development of ECH demand in Serbia and region of SEE & CE are modest. Globally, it is still 88% of ECH being produced starting from propylene
Mono-Propylene Glycol (MPG)	Project to produce MPG in Serbia is estimated as viable one (to see why is that, see text below)			
1.3-Propanediol (1,3-PD)	1.3-PD is feedstock for production of special polymers & copolymers, fibers, and coatings, which are all expensive and highly value added products.	Fast growing market of major derivative, polytrimethylene terephthalate (PTT), which globally consume over 80% of 1.3-PD.	Serbia annualy imports only 5-6 t of 1.3-PD. Imports of more than 100 tpy of 1.3-PD among neighboring countries realize only Greece and Romania.	1.3-PD can be used also in formulations of coolants. However, price of 1.3-PD is 15-20% higher comparing to price of MPG, as a valid alternative.
Bio-Methanol	Bio-methanol and its derivatives (Bio-MTBE and Bio-DME) are primarily intended for fuel market (as the 2nd generation biofuels). According to the EU-28 regulative on renewable energy, in fulfilling of the national RED targets these products belong to category "double counted biofuels".	None. In any case, for Serbia would be much more viable to develop production of methanol based on the use of biomass.	Serbia has 200,000 tpy methanol plant where natural gas is used both as feedstock and energy source ("MSK" Kikinda). The cost of Bio-methanol production highly depends on price of crude bio-glycerin but it is usually significantly higher than the cost of production of the NG-based methanol. A minimum economic capacity to produce bio-methanol is estimated to be over 150,000 tpy.	Except captive use of methanol in acetic acid production within "MSK" Kikinda and its use in FAME production, there are no more serious consumers of this chemical in Serbia. Gravitating region cannot provide amount of crude bio-glycerin required for operation of a minimum economic capacity
Acrolein / Acrylic Acid (ACR / AcrAc)	ACR is an intermediate to produce AcrAc, and also methionine (fodder supplement). Global demand of super-absorbent polymers (SAPs) is growing by a CAGR 8%.	"Green" AcrAc provides replacing of conventional AcrAc based on globally deficient propylene. Serbia annually imports 1,200-1,300 t of methionine	There is no demand of these products in Serbia and neighboring countries. Only Romania imports acrolein, in amount of about 1,000 tpy	Globally, about 60% of AcrAc is used in production of acrylates, whose demand is in saturation phase. Methionine market is controlled by only a few multinationals.
Acrylonitrile (ACN)	ACN is an irreplaceable intermediate to produce acrylic fibers (~38% of global demand) and ABS/SAN polymers (36%).	Fastest growing ACN's markets are production of polyacrylamides and NB copolymers, where demand grows at a CAGR of >6%.	There is no demand for ACN in Serbia and neighboring countries of SEE and CE (with exception of Hungary, which in 2014 imported ~22,300 t)	Global production of acrylic fiber is growing at a very modest CAGR of 1.5% to 2.0%. This growth will be almost 100% realized in Asia.
Glycerol Carbonate (GC)	GC is used in production of value added products, such as special types of PUR foams, epoxies, polycarbonates, and as special solvent for uses in cosmetic, personal care, and medicinal applications. High price (> 6 EUR/kg).	There are three commercially available glycerolysis-based processes where the second component is methanol, phosgene or urea, and Serbia has a production of all these raw materials	Demand of GC is still in developing phase and in 2014 global market did not overcame 11,500 t There is no demand of GC in Serbia and neighboring countries of SEE and CE.	The prospects for the future development of demand in gravitating region are negligible, since GC is used in production of sophisticated chemical products that are produced only in highly industrialized countries
Glycerin-Tert-Butyl-Ether (GTBE)	GTBE would be used as an additive for blending into reformulated diesel pool, analogous to the use of MTBE or ETBE as oxygenates in gasolines.	Already was verified that GTBE can be effectively blended into 1st generation biodiesel (FAME)	Globally still does not exist GTBE production on an industrial scale	Researches on the possibilities of GTBE use in reformulated diesel fuels are still ongoing.

Global demand of MPG grows by a CAGR of about 4%. A significant contribution to the market growth give widespread concerns concerning the toxicity of mono-ethylene glycol (MEG), in the sense that MPG has increasingly replaced MEG in applications where chemical goods come into direct contact with humans and animals. Also, MPG is mandatory to use in refrigeration systems within food industry, where there is a risk of contact with food.

The current prices of MPG industrial grade range from 1,750 to 1,850 EUR per t. Anti-freeze grade costs 8-9% less whereas the price of pharmaceutical grade is 5-6% higher [15].

Recent researches on economies of scale suggest that the minimum economic capacity to produce MPG by using "Glycerin-to-MPG" process is about 20,000 tpy. Such a capacity would consume 32,000 tpy to 42,400 tpy of crude bio-glycerin. In some parts of Europe, such as the region of Southeastern Europe, this would might mean the collection of crude bio-glycerin from the several FAME factories [15].

Serbia annually imports (and consumes) over 650 t of MPG, with a growing tendency. However, seven neighboring countries, plus Greece, annually imports over 10,000-11,000 t of MPG. In Central, Eastern and South-Eastern Europe today operates only one 15,000 tpy petroleum-based MPG plant in Romania.

Future development of "glycerin-to-MPG" production in Serbia has marketing sense, but the issue is "economy of scale". To operate above mentioned 20,000 tpy MPG plant an investor could collect around 32,000-42,000 tpy of crude bio-glycerin, what is the quantity that Serbia in the foreseeable future definitely will not have. On the other hand, it is the amount that could still be available through a certain long-term contracting delivery of bio-glycerin from some of the large-scale FAME plants that are operating in the neighboring countries.

CONCLUSION

Today, when almost total output of glycerin originates from production of biodiesel and oleochemicals, the global availability of glycerin is completely independent of its market demand. In fact, the supply of glycerin depends on dynamics of converting vegetable oil into biodiesel and oleochemicals, which is in turn a function of demand of biofuels and the key sectors of oleochemicals final demand (surfactants, synthetic materials). Thus, demand of glycerin does not have a more significant influence to its prices, which is specificity of only a small number of industrial goods. This explains the importantance of the planned glycerin-based derivative as value added product, whose price is more stable and less fluctuates than the price of glycerin.

New applications in organic chemical synthesis are still far from being absorbed surpluses of glycerin from production of FAMEs and oleochemicals. Even assuming that all industrial plants that currently use the new catalytic processes to convert glycerin into the organics are operating at full capacity, which is not the case, this sector of demand would not overcame the current share within total market of glycerin (crude + refined) of 17-18%. However, there are numerous "Bio-Glycerin-to-GreenChemicals" projects in phase of construction or designing worldwide (taking into account also the development of new biotechnological conversions of refined glycerin). Hence, there are serious chances that profitable production of "green chemicals" that depart from crude bio-glycerin or refined glycerin will quickly repress the current applications of crude bio-glycerin which are seen as low value added ones (basically incineration) and reduce the surpluses bio-glycerin to a minimum.

Development of the "green-chemistry" based on catalytic conversion of glycerin in Serbia and the region will largely depend on future prices of crude oil and its derivatives. Every more serious price reduction of fossil fuels, as it is the case today, substantially decreases the economic viability of biodiesel industry. And if domestic production of biodiesel does not exist on a more serious industrial scale, then there is no availability of glycerin to be catalytically converted into value-added chemicals.

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