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ENVIRONMENTAL ASPECTS OF THE PRODUCTION AND USE OF CORN OIL BIODIESEL

Abstract: *The present paper reviews the environmental aspects of the production and use of corn oil-based biodiesel. The environmental aspects are analyzed by considering the used-corn oily feedstocks and production technology. Besides that, the possibilities for the improvement of the biodiesel production process are emphasized. The most valuable corn-oil feedstocks are waste corn oil and corn distillers oil obtained primarily from dried distillers grains with solubles (DDGS). The use of DDGS, a by-product of ethanol production, for biodiesel production and glycerol, a by-product of biodiesel production, as a substrate for ethanol production, allows the development of an integrated ethanol/biodiesel production and contributes to the elimination or minimization of wastes and the production of the added-value products. Biodiesel is a degradable, less-toxic, safe, and generally, clean-burning fuel with exception of NOx emission that can be reduced by the appropriate methods but further investigations are desirable.*

Key words: corn oil, biodiesel, environmental aspect, ghd emission, pollution.

INTRODUCTION

The industrial growth, demographic expansion, increased transportation, and higher living standard cause the continued increase in energy demand. The most important energy sources, particularly in the transportation sector, are the fossil fuels, so the modern world is confronted with the fossil fuel depletion that leads to the increase of their price and the environmental problems connected with their consumption, such as significant greenhouse gases (GHG) emission, global warming, and climate changes. Consequently, particular attention is dedicated to the development of renewable energy sources and among them to biodiesel a very perspective fuel.

The biodiesel is a mixture of fatty acid alkyl esters (FAAE), usually methyl or ethyl esters, which is obtained from oily feedstocks rich in triacylglycerols or free fatty acids by alcoholysis and esterification reaction, respectively. The FAEE synthesis is performed in the presence of a catalyst, which can be a base or an acid. On the basis of the catalyst's solubility in the reaction mixture, this synthesis can be homogeneous (soluble) or heterogeneous (insoluble). The catalyst of the FAAE synthesis can also be an enzyme - lipase, usually used in the immobilized form. In addition, at the reaction temperature and pressure over the alcohol critical values, the alcoholysis reaction can be performed with no catalyst i.e. as a supercritical reaction. The physicochemical properties of biodiesel are prescribed by the biodiesel quality standard specifications EN14214 or ASTM D6751 in EU and USA, respectively. The various feedstocks are used for biodiesel production, such as edible vegetable oils and animal fats (first generation biodiesel), non-edible oils, used edible oils, waste oily streams and animal fats from different production processes (second generation biodiesel), and algal oils (third generation biodiesel).

A promising oil crop for biodiesel production may be corn or maize (*Zea mays* L.) that is widely cultivated, especially in the USA and China, followed by Brazil, Mexico, Argentina, India, and France [1]. It was discovered about 9,000 years ago in Central America, from where it was spread all over the world, with the generation of a large number of types and varieties adaptable to different growing conditions [2]. Today's corn is the result of long-term spontaneous and continuous mutation through cultivated breeding during the development of civilization and the application of different selection methods. By the natural selection, a number of varieties have also been created for different purposes. Corn is grown in different climatic conditions, from moderate to tropical. It does not tolerate frost and thrives best when the mean daily temperature is about 15 to 25 °C. Performance of corn cultivation depends significantly on the proper selection of varieties and timely applied agricultural measures.

Corn is primarily used as a fodder, raw material in the food and alcoholic beverage industries, for the bioethanol fuel production, and since recently for the paper, packaging, and plywood production. Generally, large corn quantities are used in the production of starch and ethanol wherein a by-product is the corn oil

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that is “fastest expanding oily feedstock for biodiesel production” [3].

The present paper deals with the environmental assessment of corn oil-based biodiesel production and use from the technological point of view. The aim of the work was to analyze the ecological impacts of corn oil-based biodiesel production in terms of the used oily feedstocks and the production technology. Furthermore, the possibilities for the improvement of the current biodiesel production processes are discussed.

CORN OIL BIODIESEL PRODUCTION

Oily feedstocks

Various corn oil-based feedstocks can be used for biodiesel production, such as corn oils originated from different plant parts (neat corn oil), waste frying corn oil (WFCO), and corn distillers oil (CDO). Neat corn oil can be extracted from whole ground kernels and germs. Kernels are rarely used for the oil recovery due to the low oil content (3-5%) [4]. The most often used methods are the extraction with ethanol [5]. The germ or embryo is part of the corn kernel, rich in the oil (35-56%) [6], which is used for the commercial production of corn oil. Germs can be obtained by a wet- or dry-degerming milling process. The former process, primarily used for starch production, is more effective since 50% more germs is separated, compared to the latter process [7]. However, this process is environmentally unfavorable due to the requirement of a large amount of water, the presence of other kernels portions in the output stream, and the need of an appropriate pretreatment for the oil release [8]. The germs obtained by the wet-milling process are used for producing edible corn oil. The corn germ oil for biodiesel production is usually obtained from germs obtained by the dry-degerming milling process, which is applied in the most ethanol facilities because of its high ethanol yield, low capital, energy and water investment, and simplicity [7].

Several approaches have been used for recovery of corn germ oil, such as pressing, extrusion, as well as various solvents extraction. Traditionally, corn germ oil is recovered by *n*–hexane extraction and pressing followed by *n*-hexane extraction of the obtained cake. Due to the environmental, health, and safety risk, *n*-hexane extraction is needed to be replaced with the environment friendly methods. Accordingly, the U.S. Environmental Protection Agency issued rigorous instructions for hexane emissions by plants for vegetable oil extraction in 2001 [9]. For minimizing the environmental impact of the corn oil extraction, the substitution of hexane as extracting agent is required. Alcohols, supercritical (SC) fluids (especially SC-CO_2) and water are promising, environmentally-friendly solvents; the enzyme-assisted aqueous extraction has also attracted an attention for the same reasons [10].

Waste cooking oils are advantageous feedstocks for biodiesel production due to their environmental desirability. Namely, their disposal onto landfills can cause certain environmental problems, such as water and soil pollution. Their valorization helps to reduce waste, to minimize the footprint of the technology and to add value through the production of valuable products. Up to date, WFCO has rarely investigated for biodiesel production [11] but the increased use of corn oil in food processing will certainly contribute to its significance in the future biodiesel production.

The most interesting corn oily feedstock for biodiesel production is CDO. It is obtained from the by-products of the ethanol production process. One of them, called whole stillage (WS), is obtained after fermentation and ethanol separation. Although the various fraction of whole stillage can be used as a feedstock for oil recovery, the most often is used distiller dried grain with solubles (DDGS or distiller dried grain DDG). Considering the composition and annual production of DDGS, its importance is underestimated and it is mainly used in the preparation of animal feed [12]. Bearing in mind that DDGS contains 8–10% of the oil (based on dry mass), which is higher than the amount needed for animal feed, it can be a valuable feedstock for the biodiesel production. The investigations of the oil recovery from DDGS have started at the end of the XX century, and hence, no many literature data are presently available. The most often used methods for oil recovery are the extraction with SC-CO_2 [13,14] and ethanol [15] while the use of *n*-hexane is limited to WS fractions with a lower oil content. Regarding the environmental and economic aspects, these fractions are not considered as biodiesel feedstocks because of *n*-hexane flammability and toxicity and low oil content.

It is obvious that the environmental impact of oily feedstocks for corn biodiesel production could be minimized by using WFCO and DDGS as raw materials as well as environmentally favorable solvents for the oil extraction. The use of DDGS allows the development of a new integrated process that has a positive both ecological and economic effects.

Production technology

The present commercial biodiesel production is generally based on the homogeneous base-catalyzed alcoholysis. However, this process is environmentally unfavorable because of the need for a complex purification of crude biodiesel that involved a number of washing steps generating a large amount of wastewater [16,17].

A lower environmental impact on biodiesel production can be achieved by developing new and improving current production processes. The biodiesel perspectives generally include the development of emerging technologies based on the process intensification concept aiming at overcoming the drawbacks of the conventional processes. Emerging technologies are based on the catalyst selection, new reactor type design, lower energy inputs, easy process control, and reduced “footprint” requirements.

The use of heterogeneous catalysts and enzymes and the conduction of the biodiesel synthesis at supercritical conditions of alcohol without catalyst are environmentally more acceptable. Among them, the heterogeneous processes are promising, which can be further improved by the development of high-active, easiely available, stable, and eco-friendly catalysts, prepared either from waste materials (shells of oyster, cockle, sea snail, and mollusc, and waste eggshell) or from biomass [18]. Their use not only adds a value to these wastes but also enables the development of a sustainable process. Furthermore, the development of continuous processing technologies based on the heterogeneous catalysis minimizes or eliminates the numerous downstream separation and purification steps. It is expected that these technologies gain a wider acceptance in the near future [19]

An encouraging approach from environmental and economic aspects is the development of integrated and *in situ* processes that have numerous advantages.

Integration of biodiesel production into the existing ethanol production facilities is an advanced method that allows adding value to the by-products from the ethanol production. The schematic presentation of the biodiesel production process from DDGS as mostly oily feedstock is shown in Figure 1.

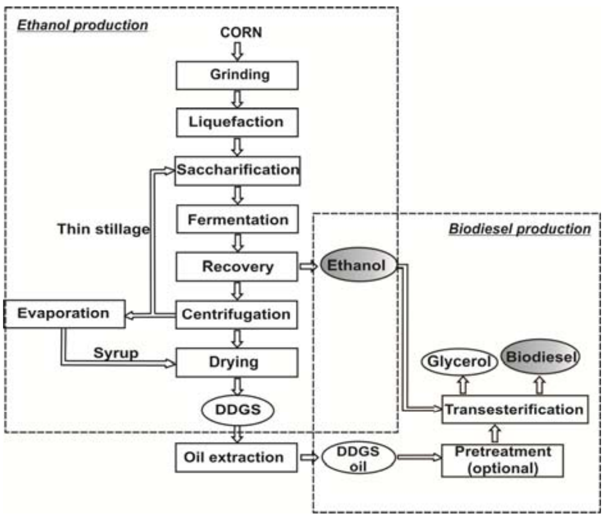

Figure 1. *Integrated production of corn based ethanol and biodiesel*

Corn oil from DDGS is already recovered in some ethanol plants and used for biodiesel production [20]. The incorporation of the necessary equipment does not affect ethanol production and has many environmental and economic advantages. Among them, the most significant is the exploitation of by-products streams, the use of existing infrastructure, the reduced transportation, the energy savings, as well as the obtaining of a fully agricultural biodiesel fuel. In this way, this approach reduces the negative environmental impact related to land use for new plant building, transportation of raw materials, lower use of non–renewable energy sources, and replacement of highly toxic methanol with ethanol. Furthermore, the overall process results in significant capital savings and higher cost efficiencies compared to conventional biodiesel processes.

Another approach for the improvement of corn-based biodiesel production is the development of the integrated process where glycerol, a by-product of biodiesel production, is used as a substrate for ethanol production, which is schematically presented in Figure 2 [21]. The use of heterogeneous catalysts or immobilized enzymes with high stability is desirable for the biodiesel synthesis in order to develop a continuous process or enable their multiple uses with/without an appropriate treatment. The fermentation residue can be used for the production of biofertilizers that can be used in corn cultivation.

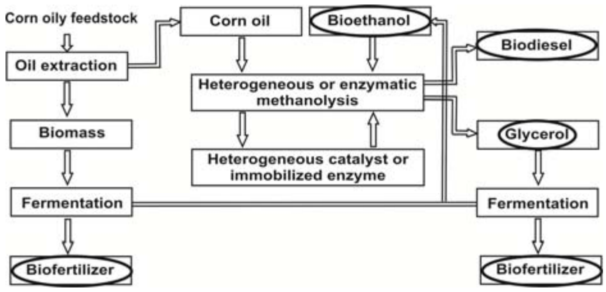

Figure 2. *Integrated process of heterogeneous or enzymatic biodiesel production*

The *in situ* transesterification is a novel technology for producing biodiesel from corn oil, which is designed with the aim of avoiding the use of a large solvent amount for the oil extraction from corn germs, thus reducing the environmental impact and the overall cost. As a feedstock in the *in situ* biodiesel production from corn, the germ separated in the processing of the whole corn kernels or milled and treated whole kernels are used [22]. Besides the positive environmental impact of this process, the obtained esters yield is higher compared to the conventional two-step extraction/alcoholysis process.

THE USE OF CORN OIL BIODIESEL

The environmental impact of the corn oil biodiesel use has rarely been investigated. However, many researches have been aimed at the assessment of these implications for biodiesel obtained from other feedstocks [23]. Since the biodiesel physicochemical characteristics are prescribed by the standard specifications, it is expected that the environmental impacts of corn oil biodiesel are similar or even the same with those of biodiesel originated from other oily feedstock. The use of corn oil biodiesel reduces the emission of GHG, sulfur, particulate matters, and hydrocarbons [24], consequently lowering the negative impacts on air, water, land, biodiversity, and climate changes. Based on different approaches taking into account the emissions of the six climate gases defined in the Kyoto Protocol, it was estimated that biodiesel reduces the GHG emissions by 22-59 %, compared to fossil diesel [25]

The use of biodiesel reduces life-cycle CO_2 emissions by 50–75% or net CO_2 emissions by 78.45% compared to fossil diesel [26]. Therefore, biodiesel is considered as a carbon neutral fuel, as plant during photosynthesis captured nearly overall CO_2 released during biodiesel production and use. Biodiesel has no sulfur (< 0.0024 ppm) and no emission of the sulfur oxides during its combustion, so the risk of the acid rain formation is significantly lowered. Also, the biodiesel burns with a significantly lower CO emission (up to 20%) compared to fossil diesel due to higher oxygen content and improved biodiesel combustion. Although the importance of biodiesel on the reduction of life-cycle CH_4 emissions is low (the most 2.57%), it is significant because CH_4 is a particularly harmful GHG [26]. Compared to fossil diesel, NO_x emissions from the biodiesel burning are higher and generally influenced by the engine performances. The environmental concern has resulted in the development of the methods for the reduction of NO_x emissions, such as increasing the injection fuel pressure and postponing the injection timing and adding certain additives such as alcohol or emulsifiers [27]. So far, only Wang et al. [28] have indicated the co-product treatment approach in GHG emission evaluations. The presented results indicated that the calculated GHG emissions depend on the used methodology. Based on the three developed methods, named marginal, hybrid allocation, and process-level energy allocation, the GHG emissions were estimated to be 14, 59, and 45 g CO_2e/MJ, respectively, while the fourth method designated as displacement, showed that corn-oil biodiesel is burden-free.

The environmental advantages of biodiesel are its degradability and safety. The degradation degree of biodiesel is 80.4-91.2% in 30 days, which is 3.3-3.7 times higher compared to fossil diesel under the same conditions [29]. The high biodiesel flash point (above 120 ^oC) indicates its easier and safer storage and transport and lower fire hazard compared to fossil fuel. The valuable method for capturing all the environmental influences of the products during their life cycle is the life cycle assessment (LCA). LCA studies of biofuels generally include the stages from the production of feedstocks to biofuel end-of-life. However, the LCA analysis depends on the availability and quality of the data and simulation methodologies and frequently does not comprehend feedstock variations and processes differences which are important for the analysis. Therefore, a further improvement and the addition of other analysis to LCA are needed to obtain more specific LCA results [30].

CONCLUSION

Corn is a promising crop as it is produced worldwide in large quantities for use as the main ingredient in livestock feed and processing into many industrial products and biofuels, such as bioethanol and biodiesel. Corn-oil biodiesel is attractive biofuel due to its environmental and economic advantages that can be considered in term on corn-oil feedstock and production process. The use of WFCO and DDGS as a raw material for the biodiesel production and environmentally favorable solvents for the corn germ oil extraction minimizes the environmental impact of biodiesel production. The development of the new, emerging technologies aiming at lowering the environmental impact and improving the process economy allows sustainable development. The integrated bioethanol/biodiesel production process based on the use DDGS from ethanol plant as a biodiesel feedstock, glycerol from fatty ester synthesis as the substrate in bioethanol production, and *in situ* processes have the numerous environmental advantages. The use of corn-oil biodiesel significantly contributes to the reduction of exhaust emission, especially GHG, particular matter, sulfur oxides, and hydrocarbons. The NOx emission from biodiesel combustion should be further investigated in order to reflect the environmental impact of the biodiesel use.

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BIOGRAPHY of the first author

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EKOLOŠKI ASPEKTI PROIZVODNJE I PRIMENA BIODIZELA IZ ULJA KUKURUZA

Zvonko Nježić, Ivna Banković-Ilić, Olivera Stamenković, Vlada Veljković

Rezime: *U radu su prikazani ekološki aspekte proizvodnje i primene biodizela iz ulja kukuruza na osnovu pregleda i analiza analizu dosadašnjih istraživanja i dostupnih podataka. Ekološki aspekti su povezani sa korišćenim uljnim sirovinama i tehnologijama proizvodnje biodizela. Takođe, razmotrene su mogućnosti za unapređenje postupaka proizvodnje biodizela. Ekološki najpovoljije sirovine za sintezu biodizela su otpadno kukuruzno ulje i ulje nus-proizvoda prerade kukuruza, u prvom redu suve džibre iz postupka dobijanja etanola (DDGS). Upotreba DDGS-a, nus-proizvoda u proizvodnji etanola za proizvodnju biodizela i glicerola, nus-proizvoda u proizvodnji biodizela, kao supstrata za proizvodnju etanola, omogućava razvoj integrisane proizvodnje etanola i biodizela i doprinose eliminisanju ili minimiziranju otpada i dobijanje vrednih proizvoda. Biodizel je razgradivo i manje toksicno, bez posebnih zahteva prilikom transposrta i skladištenja, i generalno predstavlja "čisto" gorivo sa izuzetkom emisije azotovih oksida. Smanjenje emisije oksida azota je moguće primenom odgovarajućih metoda, ali su za njihovu primenu neophodna dalja istraživanjanja*

Ključne reči: biodizel, ekološki aspekti, emisija gasova sa efektom staklene bašte, kukuruzno ulje, zagađenje.