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Sustainable biodiesel production on micro-scale

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Abstract

Due to the fact that fossil fuel resources are decreasing significantly and that their usage has a negative impact on the environment, there is a constant search for alternative fuels. Biofuels, especially biodiesel, attract more and more attention since they are usually considered as environmentally friendly. However, conventional methods of biodiesel production include the application of large amounts of acids or bases together with large amounts of water needed for purification. Therefore, a question mark can be put on the term environmentally friendly. The most common industrial process of biodiesel production is transesterification of different oils with methanol in a batch reactor using acids or bases as catalysts. Alternative production paths are constantly being explored. One of the solutions to maximize production efficiency and minimize the production costs is the use of enzymes as catalysts in a continuous process. Advantages of continuous biodiesel production processes are being more and more explored whereby application of microreactors results with many advantages comparing to conventional, batch and macroscale processes. In this paper, a short overview of different microreactor types for biodiesel production has been presented.

Keywords: *microreactors, biodiesel, transesterification*

1. Introduction

Pursuant to the Biofuels for Transport Act (OG65/09, 145/10, 26/11 and 144/12), biodiesel, as one of the biofuels used for transport, is defined as a fatty acid methyl ester (FAME), produced from vegetable or animal oil, of diesel quality, to be used as biofuel. The main advantages of biodiesel compared to conventional fuels are increased biodegradability, increased lubricity, high flash point, non-toxicity, and reduced emissions of hydrocarbons, sulphur, carbon monoxide and particulate matter [1-4]. The main disadvantages of biodiesel production and application are especially high raw material prices (75% of the total costs of biodiesel production [5]), stability in storage and after exposure to atmospheric conditions, increased NOx emissions, low calorific value and poor low temperature properties [6-9]. There are a variety of methods used in biodiesel production (Fig. 1).

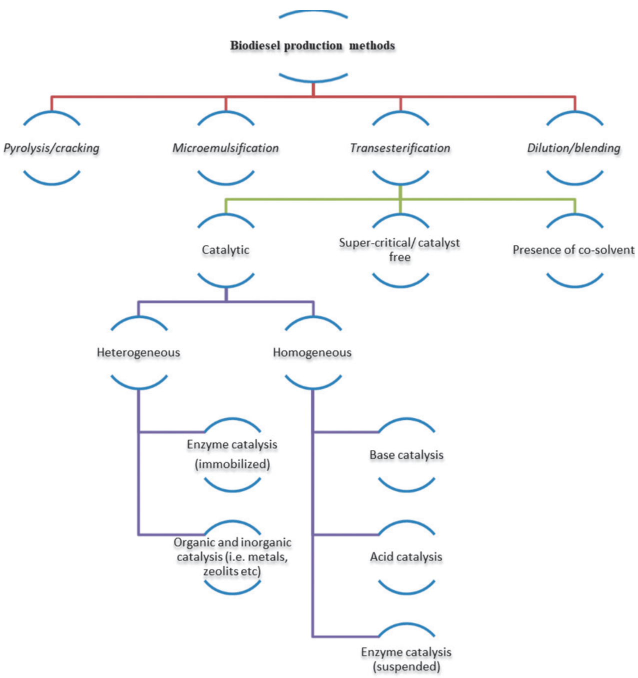

Fig. 1. Different methods for biodiesel production

Microemulsification [7] is based on blending animal and vegetable oils with solvents and microemulsions or surfactants, to form a microemulsion biodiesel fuel. *Pyrolysis* [10-14] is based on heating dried biomass without oxygen in a reactor at a temperature of about 500 °C with subsequent cooling. *Blending* is based on blending vegetable oils as biodiesel directly with conventional diesel fuels in a suitable ratio. Currently, *catalytic transesterification* is the most important method for the industrial production of biodiesel [15-19].

On the industrial scale, transesterification (or alcoholysis) is nowadays mostly performed in batch reactors. Different biomass and feedstock like edible vegetable oil, animal fats, waste edible oil remaining after roasting and non-edible oil [20] in combination with short-chain alcohols (methanol and/or ethanol) can be used as substrates for the biodiesel production.

Based on the source of biomass biofuels, in general, can be divided into four generations as shown in Fig. 2. Biodiesel is mostly produced by feedstock from the first and second generation.

Transesterification under moderate conditions is not possible without the catalyst. The selection of the catalyst depends on the feedstock used. Homogeneous, heterogeneous and enzymatic catalysts can be used in the biodiesel production. Homogeneous catalysts in the alkali-based process (with NaOH and/or KOH) or in the acid-based process (with sulphuric acid) are commonly used in industrial production. The disadvantages of the alkali-based process include the undesirable saponification side reactions that lead to the formation of emulsions and lower ester yield. Acid-catalyzed transesterification requires higher amounts of the catalyst but function better at higher alcohol-to-oil ratios. Regarding downstream, more process steps are required in acid-catalyzed production, which is more energy and economically demanding. Moreover, acids can cause equipment damage. Generally, huge amounts of wastewater are generated during chemically-catalyzed biodiesel production, which is environmentally unfriendly [21].

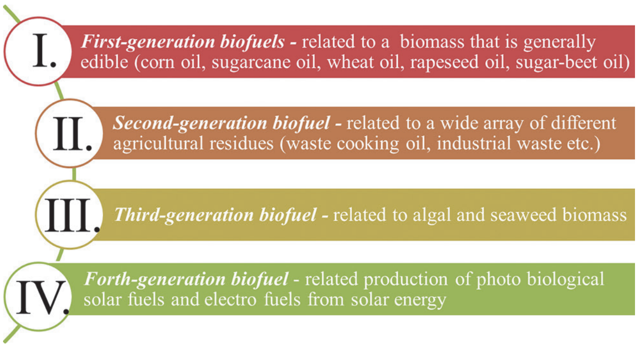

Fig. 2. Generations of biofuels production

Due to high costs and low reaction rates in these processes, the formation of by-products in parallel, side reactions, necessity to neutralize the catalyst and high energy consumption, possibilities of applying some other catalysts are being explored. Significant process improvements are predicted by the implementation of transesterification using enzyme as a catalyst. The application of enzymes in the transesterification process, comparing to acids and bases as catalysts, has several advantages. Besides the fact that enzymatic processes are performed under mild conditions, enzymatic biodiesel production leads to the production of food-grade glycerol without soap formation.

Some of disadvantages and limitations in biodiesel production by the method of transesterification together with the suggested solutions are listed in Table 1.

In order to overcome the mentioned limitations and to improve the process, advantages of continuous production of biodiesel in microreactors are being widely explored. Intensive mass and heat transfer in microreactors, which is a result of the high surface-to-volume ratio of the reactor, leads to a higher reaction rate and consequently to considerable savings in energy and raw material consumption. The high surface-to-volume ratio is a result of the reactor's structure, regarding the fact that a microreactor is a build-up of microchannels, whose dimensions are 10 μm – 500 μm, whereby microchannels are made by cutting on a solid plate. Flow in microchannels is mostly laminar due to their small diameter which consequently allows more precise regulation of the process. In addition, their reduced dimensions significantly reduce implementation and operational costs [25]. Xie et al. [26] outlined the main features of biodiesel production in microreactors compared to the conventional reactor systems such as the smaller volume of the reactor, reduction in the total size of the plant, higher surface area-to-volume ratio, higher productivity, higher efficiency of mixing and heat transfer, savings in capital costs and production costs and less energy consumption.

The enzymatic process for the production of biodiesel is simpler and more environmentally friendly than the chemical one [27-29]. The basic advantages of enzymatic processes in relation to the chemical procedures are mild reaction conditions (temperature 30 to 60 °C), separation of a large part of glycerol without further purification and without creating chemical waste, and the ability of lipase to catalyse the process of esterification of free fatty acids present in oils so that the requirements for purity of the starting materials are significantly milder. Using enzymes as catalysts in the transesterification reaction does not generate by-products as soaps, which significantly facilitates additional purification procedures and results in quality biodiesel. By using biocata-

Table 1. Disadvantages and limitations of biodiesel production by transesterification and possible solutions

Disadvantages and limitations	Solution
Reaction rate can be limited by a mass transfer between immiscible alcohol and oil phases	Application of microreactors
The transesterification reaction is a reverse reaction	Application of continuous removal of the product or increasing the alcohol to oil molar ratio
The majority of commercially used processes are based on biodiesel production in batch reactors [22]	Exploiting the advantages of continuous production processes by implementation of microreactors
The price of biodiesel is 1.5- to 3-fold higher than the price of diesel derived from fossil fuels [1,23]	Making the process more sustainable. Search for a) novel catalysts (obtained from waste materials, such as e.g. flying ash) and biocatalysts; c) lowering the cost of enzyme production by genetic engineering or search for novel microorganisms producers, d) application of immobilized enzymes using novel materials for immobilization; e) use of feedstock such as non-edible oil, waste frying oil, and oil with high FFA content
Long reaction time (the catalytic processes with acids and alkalis can take from 2 to 24 h) [24]	Application of supercritical conditions (temperatures up to 300 °C and pressures higher than 40 MPa) or addition of solvents that shortens the process of biodiesel production to just a few minutes

lysts, there is no need to rinse product in the final stage of biodiesel synthesis and purification, which reduces the amount of wastewater that poses a serious environmental problem in conventional biodiesel production.

Despite numerous advantages, enzymatic methods are still not competitive with chemical processes. The main obstacle for the introduction of enzymatic production processes is the high cost of enzyme and its reduced activity and stability in the presence of polar alcohol such as methanol and ethanol. Some of these deficiencies could be resolved by applying microreactors, which are still underexplored in terms of the enzyme-catalysed process of biodiesel.

2. Biodiesel production on a microscale

For some time now microreactors have been tested for biodiesel production [26,30,31]. Thanks to their flexibility in design different varieties of microdevices emerged for biodiesel synthesis. Their main goal was to enhance mass transfer to carry out the reaction in short residence time. Microreactors are known to considerably increase the dispersion of two phases as needed for the biodiesel reactants (alcohol and oil). This provides a much higher interface area that by the elimination of mass-transfer hindrance has shown to lead to shorter reaction time [32]. The capillary microreactor was the first one reported for biodiesel production and those that followed had more complex and advance design [33]. The most used microstructured devices for biodiesel production are listed in Table 2.

that, lipases are among the least expensive enzymes. Mostly used lipases for biodiesel production are from genus *Candida* and *Thermomyces lanuginosus* [34].

Overview of some transesterification processes performed on a microscale is presented in Table 3.

There are several different parameters that affect transesterification process on a microscale. They are presented in Fig. 3.

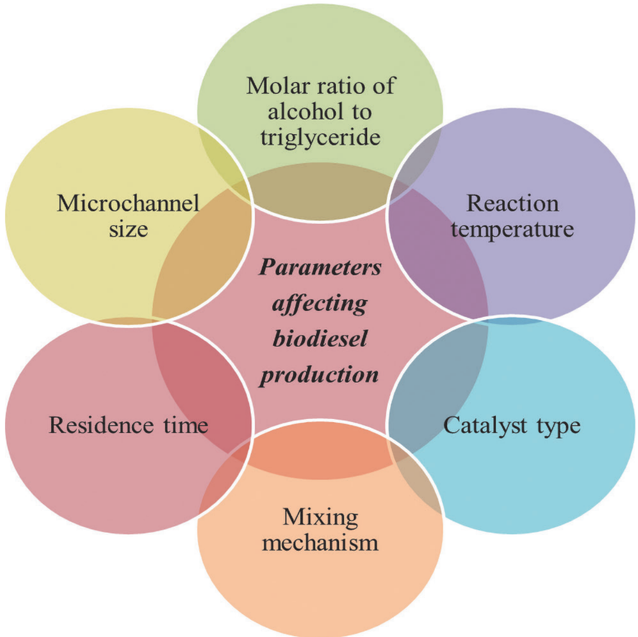

Fig. 3. Parameters affecting biodiesel production in microreactors

Table 2. Microstructured devices for biodiesel production

Microtube reactors	- a simple channel ecched in a plate - by connecting multiple plates together, complex systems can be built up - the reaction starts by introducing reactant(s) and catalyst(s) into the reactor separately
Microstructured devices	- characterized by multifunctionality - they combine chemical reaction, efficient heat exchange, and phase separation - micromixers (i.e., tear drop or swirl, zig-zag flow obstacles, nozzle injections, different obstacles, etc.
Membrane microreactor	- not truly a microreactor but it combines the advantages of the membrane reactor and the microreactor - the plate-type and tubular-type.
Oscillatory flow reactor	- the net flow of process fluid, an oscillatory motion is superimposed creating a flow pattern which helps in efficient mixing and mass transfer - the degree of mixing is independent of the net flow thus allowing long residence times to be achieved - the controlled oscillatory motion enhances radial mixing.

From the catalyst point of view, when comparing the number of transesterification reactions catalysed by chemical or by the enzymatic catalyst, up to now, most of the processes were oriented towards the application of chemical catalysts. Despite the advantages of enzymatic methods, as mentioned before, they are still not competitive to chemical processes [33]. Lipases have attracted the most attention for biodiesel production since they can catalyse hydrolysis, esterification and transesterification. Besides

One of the most important parameters that has a significant effect on biodiesel productivity is the *molar ratio of alcohol to triglyceride*. Since transesterification is an equilibrium reaction, the excess of alcohol is needed to shift the reaction towards the formation of esters [30]. On the other hand, excess of alcohols makes the recovery of glycerol difficult. A second important parameter for biodiesel production on the microscale is a *microchannel size*, since reducing the channel size higher yield of es-

Table 3. Production of biodiesel by transesterification on a microscale

Microreactor type	Substrate	Catalyst	Residence time	Yield (%)	Reference
Microtube	Soybean/methanol	NaOH	10.36 min	91	[35]
Microtube	Waste cooking oil/methanol + *n*-hexane/tetrahydrofuran at 62 °C	Kettle limescale	10 min	97.03	[36]
Microtube	Oleic acid/methanol and carbon dioxide as solvent at 60 – 120 °C and 10 mPa	H2SO4	1 min	90	[37]
Microtube	Sunflower oil/methanol at 75 °C	NaOH	1 min	99.9	[38]
Microtube	Soybean/methanol	KOH	3 min	99	[39]
Microtube	Sunflower oil/methanol	Lipase	2 h	95	[40]
Microchannel with circular obstruction	Sunflower oil/methanol at 50 °C	KOH	12 s	99.99	[41]
Four active micromixer and magnetic field	Soybean/methanol	KOH	8 s	98.1	[42]
Microreactor with micromixers	Soybean/ethanol	KOH	4.9 s	96.1	[43]
Membrane microreactor	Triolein/methanol	Lipase	19 min	80	[44]
Oscillatory flow reactor	Sunflower oil/methanol at 50 °C	NaOH	30 min	98	[45]
Jacketed stainless steel tubes	Jatropha oil/methanol	NaOH	5 min	94	[46]
Zig zag channel shape	Soybean oil/methanol	KOH	28 s	99.5	[47]

ters can be achieved. The *reaction temperature* is especially important for reactions catalysed by enzymes since most of them have specific temperature optimum. For lipase from *Thermomyces lanuginosus* temperature optimum is around 40 °C. Reactions that are performed at higher temperatures are faster than those performed at room temperature (Table 3). *Mixing mechanism* has a significant impact on mass transfer which is especially important when immiscible phases (like oil and alcohol) are part of the reaction mixture. In order to enhance mixing different structures can be incorporated as part of the microchannel: micromixers (i.e. teardrop or swirl), zig-zag flow obstacles, nozzle injections, etc.

Although the transesterification can be performed in the absence of biocatalyst (in that case the high temperature and pressure are required), the addition of *catalyst* allows moderate reaction conditions. Catalysts can be divided into homogenous and heterogeneous. Base and acid catalysts belong to the homogeneous group and are used commercially while heterogeneous (i.e. enzyme lipase) still need to undergo significant research.

3. Biodiesel purification on a microscale

Once biodiesel is produced, it must be purified. The purity of biodiesel according to the HRN EN 14214, must be ≥ 96.5%. Classical purification processes that are used in industry include removal of alcohol excess, glycerol, soap, unreacted triglycerides and catalyst. The first step is usually sedimentation, based on the difference in density of biodiesel and glycerol (Fig. 4a). The upper layer (biodiesel) is then removed and due to the solubility of glycerol in the aqueous phase, biodiesel at the end contains small amounts on impurity [48]. Wet washing (purification of biodiesel by water) is currently the most commonly used purification method for industrial biodiesel production. The biggest disadvantage of this approach is the generation of large amounts of waste-water [49]. In addition, it results in a loss of biodiesel during the washing phase. An alternative method would be dry washing that includes different absorbents, adsorbents, solvents and ion exchangers based on a variety of resins or applications of deep eutectic solvents [40].

When all the mentioned processes are performed on a macroscale and as batch processes (Fig. 4a) a lot of additional equipment is necessary to fulfill every step. The biggest advantage of a microreactor is the possibility to integrate all of the mentioned steps on a few chips (Fig. 4b). As presented by Šalić et al. [39], an integrated system, with enzymatic production of biodiesel on the first chip and purification on the second, can easily be assembled and successfully applied.

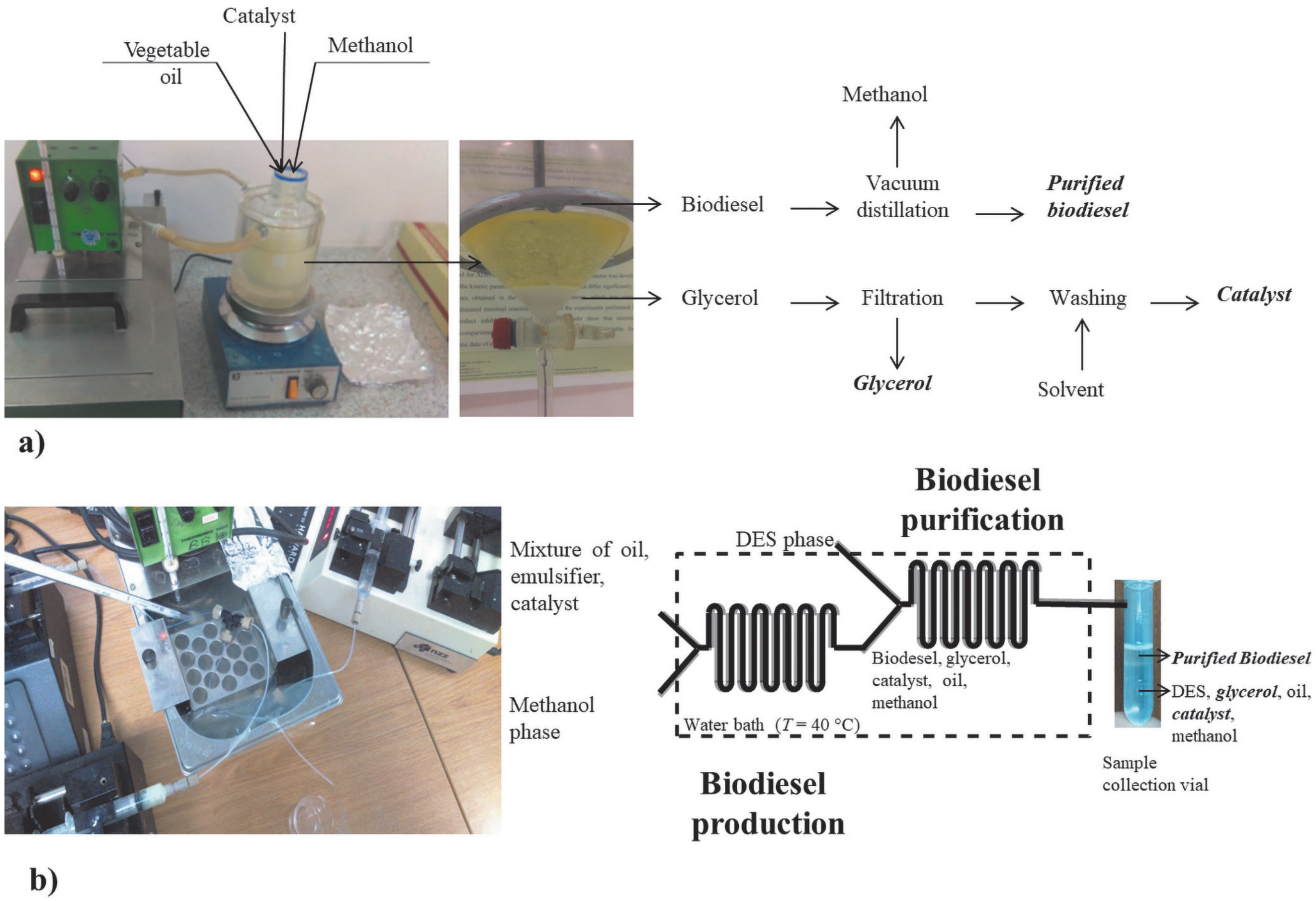

Fig. 4. Comparison of different steps in enzymatic biodiesel production and purification in a) a batch reactor and b) in a microsystem

Development of the integrated systems, which would include production and purification of biodiesel, glycerol purification and catalyst recovery, is one of the goals of future research in the area of biodiesel production on a microscale.

4. Conclusion

The application of microreactors for biodiesel production is promising and prospective technology. Although this technology still needs some improvements especially in the area of reactor production costs and biodiesel production capacity, obtained results (the high FAME yield, the high productivity, the short residence time etc) are in favour of microreactors. Nowadays we are in an era where the application of the small microreactor based portable factories that could be used in households or restaurants for biodiesel production from waste cooking old is not far away. Their development is for sure less complicated and expensive than classical scale-up of the batch biodiesel production process so progress in this area is expected in the near future.

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