Continuous reciprocating plate and packed bed multiphase reactors in biodiesel production: Advancements and challenges

Ivana B. Banković-Ilić[1], Marija R. Miladinović[1] and Vlada B. Veljković[1,2]

[1]University of Niš, Faculty of Technology in Leskovac, Serbia
[2]Serbian Academy of Sciences and Arts, Belgrade, Serbia

Abstract
Biodiesel, a renewable and environmentally friendly alternative to conventional fossil fuels, has gained significant attention over the last two decades. Continuous production of biodiesel offers efficiency, productivity, and scalability advantages. This paper provides a concise overview of continuous reactor systems for biodiesel production, focusing on two specific systems—the reciprocating plate reactor and the packed bed reactor—subjects of the authors' extensive research. A thorough comparison of these reactors, spanning biodiesel yield, reaction kinetics, and conversion efficiency, underscores their advantages. The reciprocating plate reactor demonstrates superior mixing characteristics, which improve mass transfer and reaction kinetics. Conversely, the packed bed reactor offers a higher catalyst-to-feedstock ratio and longer residence time, enhancing conversion efficiency. Both reactors exhibit favourable performance for continuous biodiesel production. This research can contribute to understanding continuous biodiesel production using innovative reactor designs. The comparative analysis between the reciprocating plate and packed bed reactors offers valuable insights for process optimization and reactor selection based on specific requirements such as feedstock availability, reaction kinetics, and economic considerations. These insights pave the way for the implementation of sustainable and efficient biodiesel production processes in the future.

Keywords: Transesterification, methanolysis, hydrodynamics, mass-transfer, continuous reactors.

Available on-line at the Journal web address: http://www.ache.org.rs/HI/

1. INTRODUCTION

The rising worldwide interest in clean energy sources has driven extensive research in biodiesel production. Biodiesel, a sustainable and energy-efficient fuel, addresses current energy usage and supply concerns. It can be blended with conventional diesel, offering a safe, non-toxic alternative, significantly reducing carbon dioxide emissions without requiring major engine modifications. Biodiesel production involves transesterification of vegetable and algal oils or animal fats with alcohol in the presence of a catalyst. Various factors, such as reactor type, feedstock and catalyst properties, alcohol-to-oil ratio, temperature, time, and mixing intensity, affect the quality and yield of biodiesel [1].

Traditional batch reactors have limitations like poor heat and mass transfer, high operating costs, long reaction times, variable product quality, and challenges in scaling up production. Continuous reactors have emerged as a viable solution, providing controlled operation, improved kinetics, and enhanced product quality. They allow precise control over process parameters, resulting in higher conversion rates, reduced reaction times, and improved yield. In addition, they facilitate the use of solid catalysts, offering benefits such as reduced waste generation and catalyst reusability. Moreover, continuous reactors optimize contact between reactants and catalyst surfaces, improving overall reaction efficacy. They enable process intensification by integrating multiple steps within a single system, leading to streamlined operations, reduced energy consumption, and increased process efficiency. This integrated approach increases the

1

economic viability of biodiesel production and reduces environmental impact, making continuous reactors highly attractive for large-scale production [2-5].

This paper comprehensively reviews recent advancements in continuous multiphase reactors for biodiesel production, emphasizing their benefits and drawbacks. The review critically analyses existing literature and identifies key challenges and opportunities. It focuses explicitly on reciprocating plate reactors (RPRs) and packed bed reactors (PBRs) as promising multiphase reactors for biodiesel production. Comparing their characteristics and performance will contribute to the knowledge base of continuous reactor technologies. The findings will assist researchers and industry professionals in reactor selection and process optimization, ultimately enhancing the sustainability of biodiesel production.

2. BASIC TYPES OF REACTORS USED IN BIODIESEL PRODUCTION

Biodiesel can be produced through four main steps, which refer to the transesterification reaction between the reactants under defined reaction conditions and then three consecutive separation unit operations [3], *i.e.*:

- the reaction between the reactants,
- product separation by settling, filtration, floatation, decantation, sedimentation, or centrifugation,
- removal of unreacted alcohol and excess water from biodiesel by evaporation or flash distillation and
- separation of undesirable compounds, such as a residual catalyst, soap, moisture, or acylglycerols, using dry or wet washing (purification of biodiesel).

Each of these steps can be implemented in different ways, but the first, main step- chemical reaction, can be performed using one of three available modes for biodiesel production: batch, semi-continuous (semi-batch), or continuous, where each of them has its own advantages and drawbacks (Table 1) [2-5].

Table 1. Classification of reactors for biodiesel production on the basis of the operating mode

Reactor	Advantages	Drawbacks
Batch	Simplicity of design and operation Suitability for variable type and quality of feedstock Good flexibility, versatility, and easy scale-up Good mixing of reactants Easy control of the material inflow and outflow	Low selectivity and production rate Inferior heat and mass transfer High energy consumption, capital, and operating costs Requirement for large reactor volumes Requirement for high amounts of alcohol to shift the reaction forward Biodiesel separation costs Requirement for high water consumption for purification
Continuous	Reduced energy consumption Low capital requirements Uniform product quality Good reactor selectivity and flexibility Suitable for fast reactions and large-scale processes	Complex design and scale-up Low versatility
Semi-continuous (semi-batch)	Suitable for rapid reactions Uniform product quality Good temperature control Good heat transfer Easy monitoring	High operating costs Low production rate High energy consumption Labor intensive process Complex scale-up

According to the mode of operation, the phase numbers, operating conditions, reaction parameters, and the type of mixing, the chemical reactors employed in the production of biodiesel can be grouped into five categories (Table 2) [5,6].

Table 2. Advantages and drawbacks of different categories of reactors applied in biodiesel production [5,6].

Reactor type		Advantages	Drawbacks
Tubular (plug-flow)	Oscillatory flow[c]	High biodiesel yield, high mass and heat transfers, low required alcohol-to-oil molar ratio, and low operating and capital costs	Complicated design for industrial biodiesel production in continuous mode
	Packed (fixed) bed[b, c]	High biodiesel yield, simple and economically favourable processes, possible to realize high pressures and temperatures	Difficult catalyst replacement, difficult heat and temperature control, possible side-reactions
	Trickle bed[b,c]	Low catalyst destruction without the need for separation, simple operation under high temperatures and pressures, continuous separation of products	Channelling and flooding, difficult control of reaction parameters, complex scale-up process
	Fluidized bed[b, c]	High mixing intensity, high heat, and mass transfers, uniform distribution of temperature, and convenient catalyst replacement	High-pressure drop, high catalyst attrition, erosion of the reactor wall, expensive equipment for regeneration, high operating and capital costs
	Micro-channel[c]	Easy control of temperature and phase separation, good energy efficiency	Low contact between phases
Rotating	Stirred tank- batch	Low capital and operating costs, easy to maintain, simple design	Complexity of the reaction kinetics, complex operating conditions, difficult temperature control, non-uniform product quality, large reactor volume, less efficient compared to continuous reactors, high capital and labour costs
	Stirred tank- continuous	Simple temperature control, constant heat release rate	Difficult process control
	Rotating - spinning tube[c]	Improved heat and mass transfers	Energy consumption for rotation
	Rotating - spinning disc[c]	Good control of side reaction, reduced cost of downstream purification	
Microwave [c]		Short reaction time, efficient heat transfer, and clean products	Difficult control of power and temperature, low reproducibility of the process
Cavitational[c]	Ultrasonic	Decreased reaction time, temperature, alcohol-to-oil molar ratio, and catalyst amount	High cost of the downstream process, complex scale-up, particle erosion, cavitational blocking
	Hydrodynamic cavitation	Simple design, operation, maintenance, and scale-up	Lower conversion degree for pressures above the optimal
	Shockwave power	Stable formed emulsion	
Simultaneous reaction-separation	Membrane[c,b,sc]	Small amount of wastewater, membrane resistance to organic solvents, low energy consumption	Plate-and-frame membranes: a possibility of plugging at flow stagnation points, difficult cleaning, high cost: Inorganic membranes: brittleness, complicated sealing at high temperatures, difficult scale-up, low selectivity, high cost
	Reactive distillation[c]	Safe process, low capital and operating costs, low emissions	
	Annular centrifugal contactors[b,c]		Transesterification cannot be completed due to uncontrolled and extremely low residence time

[c]Continuous, [b]batch, and [sc]semi-continuous mode.

2. 1. Tubular reactors

Plug-flow reactors (PFRs) are the simplest chemical reactors utilized in continuous flow reactions, where reactants enter at one end and exit at the other. Their design ensures turbulent, constant-velocity flow through a narrow, tubular channel without back-mixing. PFRs, often incorporating a fixed-bed catalyst, promote uniform reaction progress and

allow for radial mixing of immiscible fluids, enhancing efficiency. Suitable for steady-state flow, high pressure, and small solid particles, PFRs are scalable from laboratory to industrial scales. Advantages include simple construction, easy cleaning, and uniform product quality, but challenges include a large length-to-diameter ratio, slow mixing, and high dispersed phase holdup, requiring careful consideration of kinetics, mass transfer, and pressure drop in design and operation.

2. 1. 1. Oscillatory flow reactors

Oscillatory flow reactors (OFRs) use periodic reactant oscillation for enhanced mixing and improved reaction efficiency. Whether horizontal or vertical, tubes with pistons or diaphragms generate oscillatory flow. Baffles inside create vortex mixing, turning interbaffle spaces into stirred tanks, resembling an ideal plug flow reactor (PFR). This motion enhances mixing and mass transfer and improves reaction kinetics and conversion. RPCs, a type of OFRs, will be discussed further in Chapter 3.1. OFRs boost biodiesel production through improved mixing, enhanced mass transfer, and reduced reaction times. Oscillatory motion enhances reactant dispersion, promoting contact with the catalyst for higher reaction rates and conversion. This design allows for scalability from lab to industry, but energy consumption must be balanced with efficiency and conversion benefits.

In recent decades, OFRs have been investigated in continuous biodiesel production as a potential alternative to conventional batch or continuous flow reactors [7-12]. Highina *et al.* [9] achieved a 96 % yield using Jatropha oil and methanol in a continuous oscillatory baffled reactor. Palm fatty acid distillate yielded 94.2 % under optimized conditions [10]. Solar-powered rotating flask OFR produced 93.7 % yield from coconut waste cooking oil [11]. Zheng *et al.* [12] obtained similar conversion in batch and continuous mesoscale OFRs. Azhari *et al.* emphasized the importance of mixing, heat, and mass transfer to scale OFRs [7]. García-Martín *et al.* [8] found a higher yield (72.5 %) in batch OFR compared to STR (63.5 %) using a blend of waste cooking and olive/sunflower oil. The composition of fatty acid methyl esters (FAME) and physicochemical properties were similar in both reactors.

It is clear that OFRs can potentially improve biodiesel production, but their practical implementation and commercial viability are still being researched. More studies are needed to understand their benefits and limitations in large-scale production.

2. 1. 2. Packed-bed reactors

Packed-bed reactors (PBRs), known as fixed-bed reactors, consist of a column filled with solid catalyst particles or a combination of catalyst particles and an inert support material. The reactants flow through the packed bed, allowing the transesterification reaction. The structure and size distribution of catalyst and inert particles determine the transport phenomena, the surface area, and the interparticle space. The process of particle packing is determined by the physical properties of the solid particles that do not require any downstream separation process and treatment method. High oil conversion and favourable economic process variables are the most important advantages of PBR for its application in biodiesel production. The use of PBRs in biodiesel production will be described in more detail in Chapter 3.2.

2. 1. 3. Trickle-bed reactors

Trickle-bed reactors (TBRs) consist of a tube with a sieve plate or wire mesh as a support for a packed bed near the bottom and can be used for biodiesel production due to its flexibility and simple operation. This configuration provides intimate contact between the liquid reactants and the solid catalyst. The liquid phase trickles through the catalyst bed downward in the form of drops or film based on pressure or gravity forces, while the gas phase can flow concurrently or countercurrent through the reactor, which operates in continuous or semi-continuous mode.

TBRs are not extensively utilized in biodiesel production but have been explored for certain aspects [13-15]. The advantages of TBRs for biodiesel production are high liquid-solid contacting area due to the trickling flow, facilitating the efficient mass transfer and reaction kinetic rate, reduced catalyst requirements due to high contact efficiency, and lowering the cost of the overall process. However, the choice of catalyst is critical for achieving its high activity and

stability in TBRs. In addition, proper reactor design, including the selection of packing material, reactor dimensions, and flow distribution devices, is essential to ensure uniform flow distribution, avoid channelling, and maximize contact between the reactants and the catalyst. Further research and development are needed to explore the full potential of trickle-bed reactors in biodiesel production and optimize their performance for large-scale implementation.

2. 1. 4. Fluidized-bed reactors

Fluidized-bed reactors (FBRs) are column-type reactors where an upward liquid flow fluidizes a bed of solid particles. The temperature inside the reactor is more uniform, and the heat and mass transfers are greater than in PBRs. Chen *et al.* [16] obtained a 91.8 % biodiesel yield from waste cooking oil in an FBR using *Pseudomonas mendocina* cells as a biocatalyst immobilized in magnetic microspheres. The catalyst showed good reusability (87.5 % biodiesel yield after 10 cycles).

2. 1. 5. Microchannel reactors

Microchannel reactors (MCRs) are small-scale reactors with millimetre-sized interconnected channels, operating based on microfluidic principles for controlled and efficient chemical reactions. Their high surface area-to-volume ratio enhances heat and mass transfers, allowing for precise control of reaction conditions. MCRs can be scaled up for continuous, high-throughput biodiesel production by stacking or parallelizing multiple channels. However, short diffusion paths necessitate micro-mixers for the improved liquid contact. Specialized fabrication techniques and careful handling are required to prevent blockage or damage. Oily feedstock properties may also require pretreatment for smooth operation.

There are several studies in the literature about biodiesel production in MCRs with high achieved yields (higher than 95 %) by using various raw oil materials (sunflower, palm, cotton seed, soybean oils, or pork lard), methanol, and homogeneous or solid catalysts (KOH, NaOH, H_2SO_4, CaO, or enzyme) [17-21]. Further studies are needed to optimize the reactor design, catalyst selection, and process conditions to maximize possibilities for the use of microchannel reactors for efficient biodiesel production.

2. 2. Rotating reactors

2. 2. 1. Stirred-tank reactor

Stirred-tank reactors (STRs) are cylindrical vessels with a central shaft containing one or multiple impellers. They can operate in batch or continuous mode. To enhance mixing, especially in large multiphase reactors, it is recommended to use vertical baffles on the inner wall or different types of stirrers, such as turbine, impeller, monolithic, and foam.

Batch stirred-tank reactors (BSTR) are commonly used for industrial biodiesel production, with reactor productivity linked to conversion time. Continuous STRs offer advantages for large-scale production due to perfectly mixed flow, simpler temperature control, and consistent heat release rate, conversion rate, and selectivity. While most biodiesel literature focuses on batch processes, CSTRs have gained attention in the last three decades. Studies on homogeneously-catalysed oil transesterification and the use of CaO as a solid catalyst have shown promises. However, a single CSTR may not achieve the same biodiesel yield as a BSTR, suggesting the need for a series of continuous reactors, particularly for large-scale plants with glycerol separation as a byproduct.

2. 2. 2. Rotating/spinning tube reactors

Rotating/spinning tube reactors (R/S-TR) can be categorized into 3 groups that are rotating-tube reactors (RTRs), rotating-bed reactors (RBRs), and spinning tube-in-tube reactors (STTRs). These centrifugal reactors use rotation to induce centrifugal forces, thus enhancing mixing and mass transfer, and providing turbulent flow for improved reaction kinetics and conversion of oil and alcohol. They are versatile for use in laboratories as well as in industrial-scale biodiesel production.

RTRs have such a cylinder geometry so to provide low shear stresses, improving heat and mass transfer. RBRs, on the other hand, use a rotating bed for micromixing and improved mass transfer, depending on parameters like rotating

speed, which affects efficiency. Concentric rotating tubes in STTRs enhance micromixing and interfacial contact, reducing reaction time. Lodha *et al.* [25] achieved a 97.6 % biodiesel yield with the use of RTR. RBR demonstrated high yields (over 973 %) in continuous biodiesel production using homogeneous (KOH) [26] or solid (K/γ-Al$_2$O$_3$) [27] catalysts. The COSTELLO Company utilized an STTR reactor for industrial biodiesel production [28].

2. 2. 3. Spinning-disc reactors

Spinning-disc reactors (SDRs) are a distinctive class of reactors in which the reactants are introduced into a dynamically rotating disc or a series of stacked discs. The radius and thickness of the liquid film in the reactor are controlled by a defined rotating speed, generating strong shear stresses and turbulence, leading to enhanced mass transfer and reaction kinetic rates. This reactor type provides excellent control of side reactions, increases the product yield, reduces further purification costs, and shows significant advantages of good heat and mass transfers. Soybean oil was converted with methanol (methanol-to-oil molar ratio of 6:1) into biodiesel (97 % yield within 2 to 3 s) in an SDR using NaOH (1.5 %) as a catalyst at 60 °C and 2400 rpm [29].

2.3. Microwave reactors

Microwave reactors (MRs) use microwave energy to generate heat directly within the reaction mixture, enabling rapid and uniform heating. Microwaves selectively interact with polar molecules, such as water and certain organic compounds, leading to efficient heating.

Microwave irradiation can effectively produce biodiesel *via* two main routes: extraction of oil from raw materials and transesterification of oil into biodiesel. Continuous MRs were applied for the ethanolysis of soybean [30] and cottonseed oils [31] using microwave powers of 1000 W and 270 W when 84 and 99.5 % ester yields were obtained, respectively. Microwave irradiation was combined with ultrasound for the *in situ* transesterification of microalgae over a KF/CaO catalyst, providing a biodiesel yield of 93 % [32].

2. 4. Cavitational reactors

Cavitational reactors utilize the cavitation phenomenon to enhance chemical reaction rates, by forming and collapsing vapor-filled cavities or bubbles in a liquid and generating intense localized conditions of high temperatures and pressures that can improve the reaction efficiency. Generally, in this reactor type acoustic (ultrasonic reactors, URs) or flow energy (hydrodynamic cavitation reactors, HCRs) or shockwave power (shockwave power reactor, SPR) are used to intensify the transport process, i.e., mixing intensity *via* micro eddies, acoustic liquid microcirculation, or shock waves. Thus, during the alcoholysis of oils, a very fine emulsion of two immiscible reactants is generated due to cavitational collapse near the liquid interface. The reaction rate was increased due to the increase in surface area between the reactants and the catalyst.

2. 4. 1. Ultrasonic (sonochemical) reactors

Acoustic cavitation is based on changes in the pressure (positive or negative) of the bubbles due to their expansion or constriction during the passage of sound waves, which intensifies the chemical reaction. Three main steps make up every ultrasound-assisted reaction: converting electrical energy into mechanical energy, transmitting acoustic energy into medium, and converting energy to the final form (chemical transformation). Batch [33,34] or continuous [35,36] ultrasonic reactors (URs) are usually applied for biodiesel production. However, the continuous mode is more suitable when large amounts of vegetable oil have to be processed in a relatively small reactor volume [37].

2. 4. 2. Hydrodynamic cavitation reactors

Hydrodynamic cavitation reactors (HCRs) use pressure changes generated by a pump and a constriction channel with some orifice, valve, or vent. This specific geometry causes cavity formation in a flowing liquid, induces intense mixing and localized high temperatures and pressures, and increases the reaction rate. Many cavities are formed when the pressure drops below the vapor pressure in the liquid at the reaction temperature. Compared to conventional reactors,

HCRs are a more efficient alternative due to reduced energy consumption. Batch HCRs were used for transesterification of non-edible oils from Thumba (*Citrullus colocyntis*) [38] and *Nagchampa* [39], achieving 80 and 92.1 % biodiesel yield, respectively, while Javadikia *et al.* [40] transesterified sunflower oil into biodiesel with 88 % yield in a continuous HCR.

2. 4. 3. Shockwave power reactors

Shockwave power reactors (SPRs) are rotating hydrodynamic reactors with spinning rotors with dead-ended cavities and a low-pressure zone at the bottom of the cavities. They utilize shockwaves generated by the rapid compression and expansion of gases. The resulting shockwaves propagate through the liquid medium, inducing intense mixing and enhancing reaction rates (shockwaves process). Hydro Dynamics, Inc. offers different models of SPRs for continuous biodiesel production with a capacity of 3 to 495 kt/year [41].

2. 5. Simultaneous reaction-separation reactors

A simultaneous reaction-separation reactor, called a reactive separation reactor, combines chemical reaction with product extraction from unreacted reactants in a single step. It is incredibly convenient for applications in equilibrium reactions, such as transesterification reactions so that the separation of products shifts the reaction in the direction of product formation. Several reactor designs can fulfil his task.

2. 5. 1. Membrane reactors

Membrane reactors (MRs) combine chemical reactions with membrane separation and integrate a reaction chamber with a selectively permeable membrane in a single unit. The membrane continuously separates the products from the reactants, allowing selective transport of specific components while retaining others, thus enhancing reaction kinetic rates and improving product separation. Due to feedstock impurities or reaction byproducts and potential membrane degradation over time, membrane fouling can affect the reactor performance inducing the requirement of periodic cleaning or replacement.

The membrane type depends on various parameters, such as the separation method, membrane cost, and reaction conditions. This reactor design is a relatively new concept in biodiesel production, although a higher biodiesel quality can be provided compared with conventional methods. MRs can be divided into inert, where the membrane is physically separated from the catalyst and does not participate in the reaction, and catalytic, where the membrane acts as a catalyst, or the catalyst is dispersed in the membrane. The first reactor type with a tubular ceramic TiO_2 membrane was used for continuous methanolysis of palm [42] and canola [43] oils. In the latter, an agarose membrane was used in batch biodiesel production from *Eruca sativa* Gars oil [44], while a polypropylene nonwoven fabric membrane was used in continuous biodiesel production from soybean oil [45].

2. 5. 2. Reactive distillation reactors

Reactive distillation reactors (RDRs) combine the reaction and distillation steps in a single unit, enabling improved reaction efficiency, product purity, and simplified process flow. They contain catalysts or reactive packing materials that facilitate the desired reactions while allowing simultaneous separation of reaction products by distillation. The reactive distillation process is appropriate if the boiling points of the reactants and products differ.

Petchsoongsakul *et al.* [46] used two solid catalysts as a packed bed, Amberlyst-15 at the top and CaO/Al_2O_3 at the bottom of an RDR, for the continuous production of biodiesel from used cooking oil through a combination of esterification and transesterification processes. Similarly, Noshadi *et al.* [47] used an RDR for continuous methanolysis of used cooking oil to biodiesel (94 % yield) over 12-tungstophosphoric acid hexahydrate as a catalyst under optimal operating conditions (67.9:1 methanol-to-oil molar ratio and 10 % of the catalyst).

2. 5. 3. Annular centrifugal contactors

Annular centrifugal contactors (ACCs), or annular centrifuges, are separation devices that perform liquid-liquid extraction or reaction processes, using centrifugal force to separate immiscible liquids based on their density difference.

The device consists of an annular channel or rotor, where the two immiscible liquids are introduced through two separate inlets at the top of the ACC. They flow through narrow annular spaces between the casing wall and the rotating rotor, where chemical reactions occur, and are separated due to the rotational motion and centrifugal forces acting on them.

By using a continuous ACC, a 98 % biodiesel yield was obtained *via* ethylation of Jatropha oil catalysed by sodium ethoxide at optimal conditions (6:1 ethanol-to-oil molar ratio, 1 % C_2H_5ONa, and 60 °C) [48]. Although the biodiesel yield was 57 %, which was lower than the yield achieved in a batch reactor under optimized conditions, this process was appropriate for small-scale units.

3. SPECIFIC CONTINUOUS REACTORS FOR BIODIESEL PRODUCTION

Several reviews on continuous-flow biodiesel production technologies *via* transesterification processes can be found in the literature, focusing on reactor type, operation conditions, reactant sources, catalyst type, and reaction mechanisms [4,28,49,50]. Different authors have divided continuous reactors into about 20 types in different manners. Many of these types were described in Section 2. However, the present study is directed toward exploring two continuous reactor types employed in biodiesel production, RPRs and PBRs. Both reactors are tubular, consisting of a column that contains a set of reciprocating plates or a fixed bed of solid particles, respectively. Generally, the configurations of these reactors are designed to enhance biodiesel production in terms of biodiesel yield, improved separation of final products with increased purity, and optimized energy consumption. The ensuing analysis delves into a detailed examination of the performance of these 2 reactor types.

3. 1. Biodiesel production in RPRs

Reciprocating plate reactors (RPRs) occupy an important place in the group of multiphase contactors, characterized by relatively low energy consumption and a high interfacial mass transfer rate. This column-type reactor can be classified in the subgroup of oscillatory flow reactors due to the reciprocating motion, *i.e.* periodically moving up and down the vibration set consisting of a number of perforated plates that are equally spaced and attached to a vertical carrier connected to the driving motor. An experimental system with an RPR is shown in Figure 1.
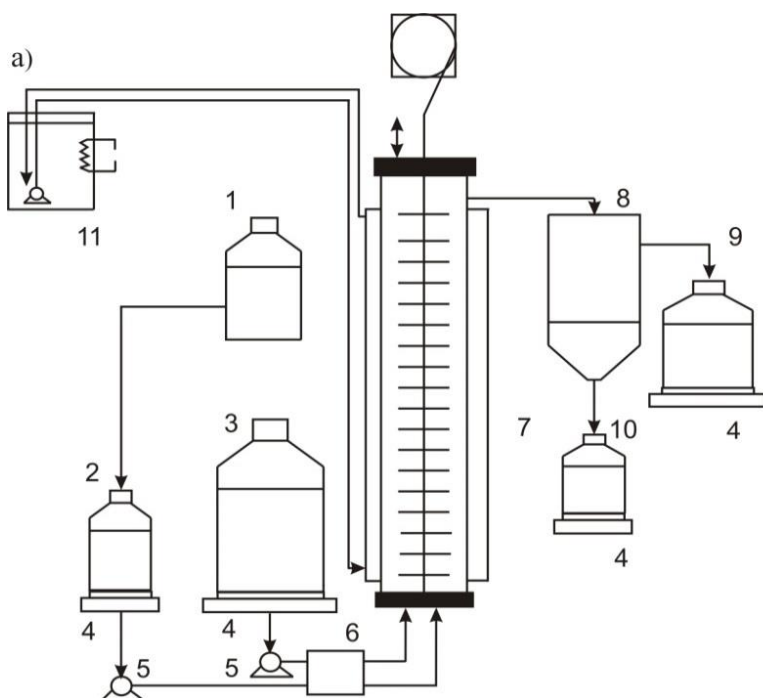

Figure 1. Experimental setup containing an RPR for laboratory-scale biodiesel production: 1 - vessel for preparing a catalyst solution in alcohol, 2 - tank for the catalyst solution in alcohol, 3 - tank for vegetable oil, 4 - scales, 5 - peristaltic pumps for transporting the vegetable oil and the catalyst solution in alcohol, 6 - oil and alcohol preheater, 7 - RPR, 8 - gravity separator, 9 - oil-ester phase tank, 10 - glycerol-alcohol phase tank, and 11 - water bath with recirculation.

In such a simple construction, the positive effects of mechanical mixing are maximized, and the adverse effects are minimized. In addition, several advantages of RPRs over the other column-type reactors can be noted such as a large and frequent renewal contact area between the phases, the radial and axial uniformity of dispersion [51], reduced axial mixing [52], and simple scale-up [51]. Small drops with long retention times in the liquid-liquid system are created by the energy of reciprocating motion.

Studies of hydrodynamic characteristics of the RPRs were mainly based on investigations of the pressure variation at the column bottom (PVCB), power consumption, flow regime, drop size, dispersed phase holdup, and axial dispersion [53-62]. Also, mass-transfer characteristics in RPCs, such as the specific interfacial area (SIA) and the liquid volumetric mass transfer coefficient (LVMTC), have been investigated in many studies [57,63-70]. The PVCB value is needed to know how to size the device for liquid transport, while the power consumption value is required to size the driving motor and calculate operating column costs. The axial dispersion coefficient has an important effect on RPR productivity. The interfacial mass transfer rate and the design of RPRs depend on the dispersed phase holdup and drop size, which influence the interphase mass transfer rate of the reactants per unit volume of dispersion, *i.e.* the LVMTC.

Due to their beneficial hydrodynamic and mass-transfer properties, RPRs have been investigated over the last three decades for commercial use as multiphase extractors or reactors in the chemical, petrochemical, and pharmaceutical industries. For instance, two immiscible reactants, like vegetable oil and alcohol, in biodiesel production can readily react with a relatively low energy input due to a maximized interfacial surface area [71-74].

3. 1. 1. Hydrodynamic characteristics of RPRs

Pressure variations at the column bottom (PVCB) result from the influences of inertia, friction, gravity, and buoyancy forces [58,75]. The first two forces appear due to the reciprocating plate movement, their mechanical contact with the reactor wall, and the contact of the liquid phase with moving and stationary column parts. A quasi-steady-state flow model was the base for calculating the PVCB value and power consumption [76].

These values in single- and multiphase systems in RPRs depend on the column geometry (height, diameter, plate number, and free fraction plate area), operating conditions (amplitude and frequency of reciprocating movement, temperature, and superficial velocities of continuous and dispersed phases), physical properties of the phases, the type and concentration of solid particles, and hydrodynamic flow conditions. In addition, power consumption depends on the liquid flow regime through the plate openings, which changes with the change in the viscosity of the liquid.

Applications of RPRs in the alcoholysis of edible or non-edible oils in producing biodiesel have been rarely investigated [73,77]. These studies focused on some hydrodynamic (PVCB, power consumption, mean drop size, drop size distribution, and dispersed phase holdup) and mass-transfer (SIA) properties of a continuous concurrent RPR in the case of the KOH-catalysed methanolysis of commercial sunflower oil. The obtained results can be crucial for designing continuous RPRs in producing biodiesel from vegetable oils. The influences of the vibration intensity and reaction conditions (reaction temperature and methanol-to-oil molar ratio) on the performance of the RPR in both non-reactive (sunflower oil as the continuous phase and methanol as the dispersed phase) and reactive (methanol-sunflower oil-KOH) systems were studied.

Investigations of PVCB and power consumption related to single-phase (sunflower oil) and two-phase (methanol/sunflower oil without catalyst) systems showed their increase with increased vibration intensity due to increased frictional losses. Decreases in density and viscosity of the dispersion with a temperature increase from 20 to 30 °C for the same methanol-to-oil molar ratio reduced the time-averaged and total PVCB and power consumption values. Also, a change in the methanol-to-oil molar ratio from 3:1 to 6:1 at a constant temperature affected the physical properties of the dispersion and reduced the PVCB and power consumption.

Gas holdup, as a crucial hydrodynamic characteristic of multiphase reactors, determines the mean gas retention time and the specific gas-liquid interfacial area. There is a 'critical' vibration intensity at which the gas holdup reaches its minimum value, depending on the type of plates, physical properties of the liquid, and the gas velocity, after which it increases. The gas holdup increases proportionally with the increased gas velocity up to the 'critical' value due to the increased resistance to the gas flow through the plate openings [56,62,78]. At a gas velocity of 3 cm s^{-1}, the gas holdup

reaches its maximal value and does not further change with the increase in the gas velocity [60]. The physical properties of the liquid phase affect the gas holdup. Comparing the gas holdup in different solutions of *n*-butanol, glycerol, and sodium sulphite, the lowest value was determined in water and the highest value in the *n*-butanol solution due to the prevented coalescence of bubbles. In non-Newtonian solutions of carboxymethyl cellulose (CMC), the gas holdup depended on the CMC molar mass and concentration in the solution as a result of changes in the rheological properties of the liquid phase [57].

The dispersed phase holdup for a non-reactive system (methanol/sunflower oil) in RPR with a diameter of 2.54 cm and 63 perforated plates was found to be independent of operating temperature, but it was greater at a higher methanol-to-oil molar ratio (6:1 *vs.* 3:1) [73,77]. In this case, the effect of increasing the vibration amplitude (from 1 to 2.35 cm) and frequency (from 2 to 3 Hz) on dispersed holdup was not observed. However, it increased nonlinearly with an increase in the vibration intensity up to 5 cm/s due to the intensification of drop breakage and then remained almost constant due to a slight drop size reduction.

With increasing the vibration intensity, the size of drops formed in RPRs depends on the energy input for their dispersion, so it reduces with increasing the total power consumption above the critical value [70]. This reduction is greater if the liquid flow is higher due to the effect of the turbulent force field on the dispersion process. The Sauter-mean drop diameter (SMDD) in non-reactive systems reduces with increasing the vibration amplitude and frequency due to the drop breakage [73,77]. The SMDD for the reactor's upper part (more than half of the height) is correlated with the time-average power consumption. It is higher than that in the reactive system (methanol-KOH/sunflower oil) under the same operating conditions due to the stabilization of small drops by emulsifiers, such as soaps, monoglycerides, and diglycerides, formed during the methanolysis reaction [79]. Drop size distributions in a reactive system are narrower and shift to smaller drop sizes along the reactor height. Also, they have higher peaks of drop size distributions at smaller drop sizes than non-reactive systems, where they are uniform in the whole reactor at vibration frequencies of 3 and 4 Hz and only in the upper part of the reactor at the vibration frequency of 2 Hz. The drop size distribution shape and peaks position are not affected by the methanol-to-oil molar ratio [73,77].

The effect of tetrahydrofuran (THF) as a co-solvent on biodiesel production by the continuous sunflower oil methanolysis catalysed by KOH was investigated in a continuous concurrent up-flow RPR [71]. THF effectively transforms non-reactive and reactive heterogeneous systems into stable homogeneous emulsions. For all co-solvent concentrations (up to 30 %) and both systems, the SMDD decreased along the reactor height in its lower part. In this zone, without the reaction between the phases, the initially large drops break up, passing through the plate perforations, while the occurrence of the reaction presents another factor in reducing the drop size. The SMDD remains constant in the upper part of the reactor, where a stable homogeneous dispersion of small drops is formed. Mainly, at any location in the reactor under the same operating conditions, the SMDD is smaller in the reactive than in the non-reactive system. The increase in the THF concentration reduces the SMDD due to the influence of THF on the drop breakage and the solubility of the reactants. The drop size distribution along the reactor is unimodal for both systems, *i.e.* with one peak located in the small drop size range for all the applied THF concentrations, and it became narrower along the reactor height. THF shifts the system into a homogeneous emulsion of small drops [71].

3. 1. 2. Mass-transfer characteristics in RPRs

The LVMTC and the interphase mass transfer rate of the reactant per unit volume of dispersion affect the efficiency of multiphase reactors, while the SIA is a significant parameter for achieving maximum reactor productivity.

The LVMTC, $k_l a$, increases with increasing vibration intensity as a result of greater power consumption and intensified reduction of gas bubbles [61,65-67,80-82], especially at higher vibration intensities [82]. The LVMTC increases to a maximum value as the gas flow rate increases due to higher energy transferred from the gas to the liquid. By adding Raschig rings (2.5 vol.%) in each interspace between the plates, the LVMTC increases by 30 % due to the effect of the solid phase on the bubble-breaking process [66]. The geometrical characteristics of an RPR affect the LVMTC. With an increase in the number of reciprocating plates under the same conditions of aeration and mixing, the LVMTC increases [68] due to more intensive energy dissipation, preventing bubble coalescence [65]. As the hole diameter and

free area of the plates increase, the VMTC decreases, probably due to the reduced power consumption [65,66]. The LVMTC in RPRs can be correlated with power consumption, *i.e.* vibration intensity, gas or liquid velocities, and geometric characteristics of the reactor [57].

The SIA depends on fluid-dynamic conditions in the multiphase reactor as well as on the properties of the phases. Variation of the SIA with the vibration intensity depends on the fluid flow regime in the reactor [70], so at low vibration intensities, either it increases due to the decrease in bubble size [66] or remains unchanged at constant bubble size and gas holdup [70,83]. At higher vibration intensities, SIA increases with increasing vibration intensity due to the increased gas holdup and reduced bubble size. The effect of gas velocity on the SIA depends on the flow regime. At low gas velocities, SIA increases with the increase in the vibration intensity due to the enhanced bubble break up. At higher gas velocities and larger amounts of gas in the column, gas bubbles increase in size and become densely packed, which favors their coalescence and increases the SIA due to the increased gas holdup [62,66,70,83]. Raschig rings (2.5 vol.%) placed in the interplate spaces increased the SIA by about 30 % [66], while the addition of spheres in the interplate spaces did not have any effect [57]. Geometric characteristics of the column, such as the hole diameter and the fractional free area of the plates, also affect the SIA. With their increase, the SIA decreases [66]. Correlations proposed in the literature for SIA estimation in RPRs include dependences on power consumption and gas velocity [57]. The SIA value in a 2.54 cm i.d. RPR filled with mixtures of methanol and sunflower oil (molar ratios 3:1 and 6:1) increased with increasing the methanol-to-oil molar ratio and vibration intensity, as a consequence of the influence of these parameters on the SMDD and the dispersed phase holdup.

3. 1. 3. Effects of operating conditions on FAME yields and reaction kinetics in RPRs

Stamenković et al. [77] examined the sunflower oil methanolysis with KOH as a catalyst (1 % of the oil weight) in a continuous reactor under atmospheric pressure. Optimal conditions for single-step (one reactor and one separator) and two-step (two reactor-separator in series) reactor systems were determined: vibration amplitude of 1 cm, vibration frequency of 2 Hz, temperature of 30 °C, and methanol-to-oil molar ratio of 6:1. Residence time in each reactor of both system was 13 minutes. The results obtained in the laboratory-scale experiments were successfully implemented in a semi-industrial plant for methanolysis of rapeseed oil achieving a 98 % biodiesel yield at the separator outlet. Overall, this investigation shed light on the optimal operating conditions for the sunflower oil methanolysis catalysed by KOH and demonstrated the scalability of the process for industrial application.

FAME concentrations at several THF concentrations were below 10 % in the initial part of the reactor because of the mass-transfer limitation [71]. At the reactor exit and low THF concentrations, the maximum FAME concentration reached about 80 % when the reaction approached the equilibrium. At the THF concentration of 30 *%* of the oil mass, the FAME concentration increased quickly along the reactor height due to negligible mass transfer limitations. In the upper reactor part, the FAME concentration achieved the maximum at the exit. The reaction also approached equilibrium, indicating that the reactor height could be lower. Thus, the overall biodiesel production process should be conducted in two RPRs in a series.

At lower THF concentrations (0, 1, and 10), FAME concentration varied in a sigmoid manner along the reactor height indicating different kinetic regimes along the reactor [71]. The overall triacylglycerol (TAG) reaction rate is controlled by the rate of mass transfer in the lower and by the chemical reaction in the upper part of the reactor, *i.e.* the lower region was TAG mass transfer controlled followed by the region controlled by the irreversible second-order reaction. At the highest THF concentration (30 %), the curve becomes exponential, indicating the reaction-controlled regime without mass transfer limitations, *i.e.* the irreversible and reversible second-order reaction kinetics can be used to describe the process in this case. By simulating the methanolysis process and comparing the developed kinetic models with the experiment, three equations were suggested for the TAG conversion degree calculation for the mass transfer-controlled regime, the reaction-controlled regime with the irreversible pseudo-second-order reaction, and the reaction-controlled regime with the reversible second-order reaction. The study of Banković-Ilić *et al.* [71] was the first attempt to investigate the kinetics of methanolysis of vegetable oils in the presence of a co-solvent in a continuous up-flow RPR

and presented a good basis for studying alcoholysis of cheap oily raw materials (non-edible oils, used cooking oils, waste animal fats, etc.) in the presence of homogeneous base catalysts.

Further research into this trend was performed by Miladinović *et al.* [84], who conducted biodiesel production from a waste pig-roasting lard using methanol as a reactant and KOH as a base catalyst at 60 °C in a continuous RPR (diameter: 2.54 cm, height: 200 cm, 63 plates). The influential process factors, such as the methanol-to-lard molar ratio (4.5:1 to 7.5:1), catalyst loading (0.5 to 1.0 %, based on the lard mass), and height of the reactor column (13 to 192 cm) were optimized with respect to the FAME content in the ester phase using the response surface methodology (RSM). The optimal methanol-to-lard molar ratio and catalyst amount at the reactor exit (corresponding to the retention time of 10 min) were 4.5:1 and 0.9 *%* of waste lard, respectively. Also, the transesterification reaction kinetics models that defined the variation of TAG and FAME concentrations along the height of the RPR were determined indicating two models, namely the irreversible pseudo-first-order reactions or the reactions involving a changing mechanism and TAG mass transfer.

3. 2. Biodiesel production in PBRs

Packed bed reactors (PBRs) play a crucial role in the methanolysis of vegetable oil, which involves a three-phase system of methanol, vegetable oil, and a solid catalyst. When considering the choice of the reactor type for this process, several factors should be taken into account and PBRs are preferred for several reasons. These reactors are relatively easy to design and construct, typically comprising a column filled with catalyst pellets or beads (Fig. 2). They are widely used due to the low operating costs and ease of operation, particularly in separating the final products from the catalyst. In a PBR, the reactants are continuously fed into the reactor while the product continuously flows out, leaving the catalyst behind. As a result, high-purity biodiesel and glycerol can be obtained as final products. When using solid catalysts with poor mechanical properties, PBRs are clearly advantageous over CSTRs in which aggressive agitation can lead to the catalyst destruction and leaching of active species, contaminating the final products.
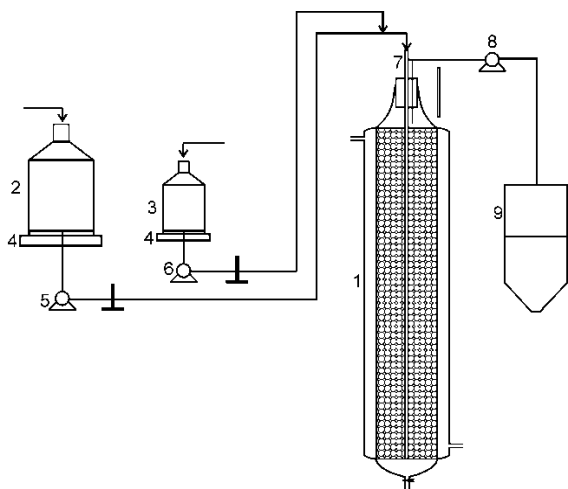

Figure 2. Experimental setup containing a PBR for laboratory-scale biodiesel production: 1 - PBR with catalyst particles, 2,3 - tanks for vegetable oil and alcohol, 4 - scales, 5,6 - pumps for transporting the reactants, 7 - glass tube for introducing and thermostating reactants, 8 - pump for transporting the reaction mixture from the reactor, and 9 - gravity separator

Different types of PBRs have been employed for oil methanolysis, including rotating PBRs, packed bed membrane reactors (PBMRs), TBRs, PBRs with a recycle, and MCRs. For example, a rotating PBR was used for the methanolysis of soybean oil [26] providing enhanced mixing and mass transfer by centrifugal acceleration and resulting in shorter reaction times, higher FAME yields, and greater production capacity. However, it should be noted that a rotating PBR is not recommended for oil methanolysis with solid catalysts with low mechanical strength, as centrifugal acceleration can cause catalyst leaching [27].

A PBMR was employed to obtain high-quality FAMEs [42] using the advantages of a dual-functionality membrane that acts as both a reactor and a separator, thereby increasing the reaction rate and yield. The small molecules of FAMEs,

methanol, and glycerol can permeate through the membrane pores, while the permeation of larger TAG molecules is prevented. Removal of the products through the membrane shifts the reaction equilibrium towards product formation. The selective permeation FAMEs and exclusion of unreacted TAGs and other impurities lead to high-quality FAMEs that do not require further purification. In one study, a ceramic membrane (TiO_2/Al_2O_3) packed with KOH supported on palm shell activated carbon was an efficient catalyst for transesterifying soybean oil with methanol in a PBMR [42]. PBMRs have also been investigated using shaped KF/Ca–Mg–Al hydrotalcite [85] and KF/Ca-Mg-Al hydrotalcite/honeycomb ceramic monolithic [86] catalysts.

Another type of three-phase reactor explored in oil methanolysis is TBR, in which gas and liquid phases flow concurrently or countercurrent through a packed bed of catalyst particles. Methanol is typically heated to its vapor temperature and used as a continuous upward gas phase, while oil and condensed methanol flow downwards by gravity through the catalyst bed. This arrangement enhances the contact area between methanol and oil, promoting the methanolysis reaction on the catalyst surfaces. Oil methanolysis has been investigated in conventional [13,14] or modified [14] TBRs. A 98 % biodiesel yield was achieved by countercurrent transesterification of sunflower oil with vaporized methanol above the boiling point and CaO particles in a packed bed [13]. Similarly, Meng *et al.* [14] obtained a 94.5 % biodiesel yield using a packed bed of base heterogeneous Ca/Al composite oxide catalyst to convert rapeseed oil and methanol at the boiling point and atmospheric pressure. Also, a countercurrent TBR with palm oil methanol vapor and a CaO-based extrudate catalyst produced a 92.3 % biodiesel yield [15].

PBRs with a recycle offer advantages regarding product stream division and improved mass transfer rates. Hernández-Montelongo *et al.* [87] conducted esterification of FFA in canola oil with methanol using cation exchange resins in a PBR with recycling to produce biodiesel. This configuration involved recycling the reaction mixture to the feed stream and approximating the PBR to a CSTR by ensuring a high volumetric ratio of the recycling flow to the reactor inflow. This setup facilitated a higher methanol concentration within the reactor that shifted the reaction equilibrium towards the products.

MCRs have also been investigated for heterogeneously catalysed methanolysis, offering enhanced biodiesel production through improved conversion, reduced reaction time, and improved biodiesel quality [21]. Chueluecha *et al.* [88] conducted palm oil methanolysis in a micro-channel reactor using CaO as a catalyst achieving a high FAME content of 99 % at the methanol-to-oil molar ratio of 24:1, a short retention time of 8.9 min, and 65 °C. Another study [17] explored iso-propanol as a co-solvent in micro-channel reactors. The addition of a co-solvent (14.5 %) reduced the methanol-to-oil molar ratio to 20:1 and the retention time to 6.5 min while maintaining the same high FAME content as in the previous study.

3. 2. 1. Flow regime and external mass transfer limitations in PBRs

Analysis of heterogeneously catalysed oil methanolysis in PBRs involves consideration of various phenomena, primarily focusing on mass transfer between phases and liquid phase flow. At a steady-state operation, catalytic PBRs typically exhibit ideal plug flow behaviour under specific conditions that have to be met [89]. These conditions include ensuring that the reactor diameter and the catalyst bed length are at least ten-fold and several hundred-fold higher than the catalyst particle diameter, respectively, for low flow rates. In addition to the reactor geometry and dimensions, operational conditions significantly influence the abovementioned phenomena. Parameters such as bed height, feed flow rate (reactants), residence time, molar ratio, and catalyst size and amount all have an impact [90].

Given that heterogeneously catalysed oil methanolysis in a PBR involves a liquid-liquid-solid system, it is essential to consider the possibility of external mass transfer limitations. Marinković *et al.* [91] conducted experimental investigations on a PBR using a methanol-to-oil molar ratio of 18:1 at 60 °C. They measured the FAME content at various heights within the catalyst bed and volumetric flow rates of the reaction mixture while maintaining a constant retention time of 4.2 h, corresponding to a weight hourly space velocity (WHSV) of 0.10 h^{-1}. By varying the volumetric flow rate from 0.05 to 0.16 cm^3 min^{-1}, they achieved a constant FAME content (97.8 %) at the reactor outlet. This observation indicated that the external diffusion did not limit the rate of oil methanolysis. Miladinović *et al.* [92] ensured a constant ratio of catalyst mass to the liquid flow rate by increasing the catalyst mass proportionally with the liquid flow rate, thus

maintaining the same retention time for the reactants. They observed that the FAME content at the reactor outlet remained independent of the liquid flow rate within the range of 1.75 to 3.5 cm^3 min^{-1}, corresponding to retention times from 1.0 h to 2.0 h and different ratios of the liquid flow rate to catalyst mass (*i.e.* different WHSVs). Consequently, external liquid-solid mass transfer limitations could be neglected.

3. 2. 2. Effects of operating conditions on FAME yields and process optimization in PBRs

Residence time in a reactor is inversely proportional to the flow rate of reactants. According to the literature [93], reducing the flow rate of linseed oil resulted in an increased oil residence time and a higher FAME yield (methanol-to-oil molar ratio 7.5:1, co-solvent (diethyl ether)-to-methanol molar ratio 1.25:1, and 30 °C). Similarly, a prolonged residence time of waste cooking oil in the bed of agglomerated Zr-SBA-15 catalyst led to a higher FAME yield [94]. However, when increasing the feed flow rate from 0.6 to 1.2 cm^3 min^{-1}, there was an initial rise in the FAME content from 85.5 to 95.2 %, while a further increase from 1.2 to 1.7 cm^3 min^{-1} resulted in a decline in the FAME content from 95.2 to 70.5 % [95].

The relationship between the feed flow rate and the volume or mass of the catalyst bed can be described by the liquid hourly space velocity (LHSV) [96] and the WHSV [91,92]. In the study by Zarabudin *et al.* [96], the LHSV was varied from 6 to 30 h^{-1}, corresponding to residence times ranging from 1 to 4 min. The researchers concluded that the highest conversion rate (99.9 %) was achieved at an LHSV of 8 h^{-1}, corresponding to a residence time of 3 min. Miladinović *et al.* [92] observed that decreasing the WHSV led to increased FAME contents. The lowest WHSV (0.188 kg/kg$_{cat}$h) resulted in the longest retention time of 2 h and the highest conversion rate. It allowed for a longer contact time between the catalyst and the feed, enhancing the overall conversion process. Regarding the retention time in a PBR, Bausri *et al.* [97] noted a gradual increase in the FAME yield as the residence time increased from 0.5 to 2.5 h while maintaining a constant catalyst bed length and methanol-to-oil molar ratio. However, Sakthivel *et al.* [98] discovered that the FAME yield initially increased with an increasing retention time up to a specific value, beyond which it started to decline. This result could be attributed to a reverse reaction occurring at longer residence times. These findings highlight the importance of optimizing the residence time concerning the flow rate and catalyst bed characteristics to achieve the desired conversion and FAME yield.

The methanol-to-oil molar ratio is a critical factor influencing the FAME content in a PBR. Various studies have examined the effect of the methanol-to-oil molar ratio in the range from 3:1 to 60:1 [99]. An increased methanol-to-oil molar ratio generally leads to higher FAME contents or TAG conversion due to an increased driving force for methanol adsorption [27]. However, some studies have observed that this positive effect reaches a threshold value of the methanol-to-oil molar ratio, beyond which further increases result in a decrease in the FAME content [95,100]. This decline could be attributed to the generation of glycerol, which dissolves in methanol and inhibits further methanol adsorption on the catalyst active sites. Ren *et al.* [95] found that production of glycerol increased at higher methanol amounts. At methanol-to-oil molar ratios lower than 9:1, glycerol was not detected in the effluent, either due to its low solubility in the reaction system or because it was adsorbed on the catalyst (resin). In the case of resin as a catalyst, it was explained in literature [101] that a high methanol concentration had an inhibitory effect on the FAME production due to easier diffusion of lighter methanol molecules through the catalyst pores compared to heavier TAG molecules. Thus, a high methanol concentration hinders TAG adsorption on the catalyst active sites. Similarly, increasing the pre-added methanol amount up to a particular value positively influenced the ester content. However, the excess of methanol had the opposite effect by occupying the catalyst active sites [14]. Nonetheless, in another study [93] it was argued that a high amount of methanol could mask the effects of other parameters. On the other hand, other authors [99] suggested that a high methanol-to-oil molar ratio is necessary for an efficient transesterification in a PBR at a low flow rate of reactants, where the laminar flow regime limits the mass transfer between the liquid phases and to the solid catalyst. Moreover, a higher excess of methanol increases the polarity of the reaction mixture, which can cause the leaching and dissolution of glycerol and glyceride derivatives from the active sites on the CaO surface. This may explain why the impact of the methanol-to-oil molar ratio on the FAME content is more pronounced at longer retention times [100].

Continuous methanolysis in PBRs is performed at different temperatures and pressures depending on the reaction system (reactants-catalyst). For base catalysts, Miladinović *et al.* [100] observed a significant influence of the reaction temperature on the FAME content within a range of 40 to 60 °C at atmospheric pressure. Bausri *et al.* [102] demonstrated that exceeding 60 °C decreased the biodiesel yield. In the case of methanolysis of waste frying oil catalysed by KOH/fruit shell of *Jatropha curcas* in a PBR at atmospheric pressure, temperatures above 60 °C caused methanol evaporation, reducing the methanol-to-oil ratio and leading to a decline in TAG conversion. Studies employing acid catalysts, such as Zr-SBA-15/bentonite, investigated a higher temperature range (150-210 °C) and pressure (7 MPa) [94]. In a PBR system utilizing resins as catalysts for the interesterification of palm oil and ethyl acetate, Akkarawatkhoosith *et al.* [103] found that temperatures in a range of 80-120 °C affected not only the fatty acid ethyl esters (FAEE) content but also the reaction rate.

Optimization of reaction conditions in PBRs typically involves considering the above-mentioned parameters, that is, the residence time, catalyst bed height, feed flow rate, reaction temperature, and methanol-to-oil molar ratio. These parameters and their interactions on the FAME content/yield are evaluated statistically and optimized using factorial designs. The significance of these parameters varies depending on the reaction system, including the type of oil feedstock, alcohol, and catalyst. For instance, Díaz *et al.* [104] used a Box-Behnken design to evaluate the effects of flow rate, methanol-to-oil molar ratio, and co-solvent/methanol-to-oil molar ratio on the FAME yield when Li/Pumice was used as a catalyst. They found that the methanol-to-oil molar ratio had the most significant effect on the FAME content, while the effects of the other analysed parameters were not significant. Similarly, for the CaO-catalyzed linseed oil methanolysis with diethyl ether as a co-solvent carried out in a PBR, the flow rate and co-solvent-to-methanol molar ratio had the most significant effect on the FAME content [93]. Miladinović *et al.* [92] used a full factorial design (3^3) to evaluate the effect of methanol-to-oil molar ratio, WHSV, and the catalyst bed height on the FAME content. All three factors and their interactions had a significant effect, with the catalyst bed height showing the strongest influence due to its relationship with the retention time. Optimal values were determined as 40 cm the catalyst bed height, 0.188 kg/(kg$_{cat}$ h) WHSV, and 6 : 1 methanol-to-oil molar ratio. Sakthivel *et al.* [98] reported that residence time, reaction temperature, and molar flow rate significantly affected the biodiesel yield from *Jatropha curcas* oil. The significance of packed bed height, ethanol-to-oil molar ratio, and volumetric flow rate on the FAEE yield from palm oil catalyzed by radiation-induced Kenaf as a catalyst was also evaluated [105], with optimal values determined as 9.8 cm for the packed bed height, 50:1 for the ethanol-to-oil molar ratio, and 0.38 cm^3 min^{-1} for the volumetric flow rate. In the palm oil methanolysis catalysed by potash/orange peel in a PBR [106] the reaction temperature was found to have a higher significance with respect to the FAME yield than the catalyst amount and the methanol-to-oil molar ratio. RSM optimization proposed an optimum temperature of 60 °C, catalyst loading of 2.5 %, and a methanol-to-oil molar ratio of 12:1, resulting in a 95.6 % biodiesel yield. Conversely, Talha and Sulaiman [107] found that the reaction temperature had an insignificant effect on the FAME yield in the in-situ transesterification of solid coconut waste in a PBR with the CaO/PVA catalyst. The highest biodiesel yield of 95 *%* was achieved with the catalyst loading of ~2.3 % and a methanol-to-solid ratio of 12:1 at 61 °C. Similarly, Zik *et al.* [108] optimized the catalyst loading, temperature, and methanol-to-oil molar ratio for producing biodiesel from used cooking oil over a CaO/nanocrystal cellulose/polyvinyl alcohol catalyst in a PBR. The optimum conditions were determined as 65 °C, 6:1 methanol-to-oil molar ratio, and 0.5 *%* catalyst amount, resulting in a 98.4 % biodiesel yield.

3. 3. Comparison of RPRs and PBRs for biodiesel production

The choice between the RPRs and PBRs for biodiesel production depends on the process conditions, reaction kinetics, feedstock and catalyst characteristics, scalability, and economic considerations. Each reactor type has unique advantages, and the optimal choice can be determined by evaluating these factors in the context of the biodiesel production process. Compared to PBRs, RPRs offer superior mixing efficiency, improved heat and mass transfers, better catalyst utilization, handling different feedstock, including oils of various viscosities, better reaction control, and simple scalability, making them suitable for both small- and large-scale biodiesel production. On the other hand, PBRs require less energy for mixing, promote higher conversion rates, increase biodiesel yield due to providing sufficient reaction times for complete

conversion of the reactants, better stability for solid catalyst particles, convenience for homogeneous feedstock, and often have a smaller footprint than RPRs, making them more suitable for space-constrained environments. Both reactor types can be scaled up for large-scale production, although RPRs have a slight advantage in terms of scalability due to their design. Also, economic considerations (capital and operating costs, maintenance requirements) should be carefully evaluated to determine the appropriate option between the two offered.

To gain a comprehensive assessment and better understanding of the potential of RPRs and PBRs as innovative technologies in the biodiesel production industry, it is crucial to conduct a thorough examination of these reactors using a SWOT analysis (Strengths, Weaknesses, Opportunities, and Threats). It is a practical tool for identifying and assessing the internal and external factors that can impact the successful deployment of either reactor type. Understanding the strengths of these reactor technologies allows for leveraging their unique advantages. Similarly, identifying weaknesses helps in addressing potential challenges and finding strategies to alleviate them. Furthermore, recognizing the opportunities offered by each reactor type enables stakeholders to explore new possibilities for enhancing biodiesel production. Concurrently, identifying potential threats helps to proactively manage risks and ensure the long-term viability of the chosen reactor technology in the industry. As presented in Tables 3 and 4, this analysis provides valuable insights into the advantages and disadvantages of each of the 2 discussed reactor types. By carefully evaluating these factors, stakeholders in the biodiesel production industry can make informed decisions regarding the implementation of these technologies.

Table 3. SWOT analysis of RPRs for biodiesel production

STRENGTHS	WEAKNESSES
Efficient mixing	Complex design and operation
Scalability	Susceptible to fouling and plugging
Catalyst utilization	
Heat transfer	
OPPORTUNITIES	**THREATS**
Advancements in materials and manufacturing	Competition from alternative reactor systems
Research and development	Availability and cost of catalysts

Table 4. SWOT analysis of PBRs for biodiesel production

STRENGTHS	WEAKNESSES
High catalyst loading	Limited mixing
Longer residence time	Potential pressure drop
Catalyst stability	Potential catalyst fouling
Compact design	Mass transfer limitations
Cost-effectiveness	Process control
Versatility	
OPPORTUNITIES	**THREATS**
Advanced in materials and catalyst	Competing reactor technologies
Process optimization	Feedstock variability
	Evolving regulatory environment

4. CONCLUSIONS

Despite the significant advantages of continuous reactors, their implementation in biodiesel production still poses specific challenges. Reactor design, catalyst selection, reaction conditions, and process optimization are key factors that must be carefully considered to ensure efficient and reliable operation. Furthermore, the scale-up of continuous reactor systems from laboratory to industrial scale requires a comprehensive understanding and optimization of various parameters. Continuous reactors have immense potential for revolutionizing biodiesel production, offering improved

productivity, product quality, and process efficiency. With further research and development, continuous reactor systems can pave the way for a more sustainable and environmentally friendly energy future.

Both reciprocating plate reactors and packed bed reactors show promise for biodiesel production. Their continuous flow operation, improved mass or heat transfer properties, and potential for efficient control over reaction conditions make them attractive options for enhancing the efficiency and scalability of biodiesel manufacturing processes. However, the specific implementation and adoption of these reactor types will depend on various factors, including cost considerations, process optimization, and further research and development.

REFERENCES

[1] Živković SB, Veljković MV, Banković-Ilić IB, Krstić IM, KonstantinovićSS, Ilić SB, Avramović JA, Stamenković OS, Veljković VB. Technological, technical, economic, environmental, social, human health risk, toxicological and policy considerations of biodiesel production and use. *Renew Sust Energ Rev*. 2017; 79: 222-247. https://doi.org/10.1016/j.rser.2017.05.048

[2] Awogbemi O, Von Kallon DV, Application of tubular reactor technologies for the acceleration of biodiesel production. *Bioengineering*. 2022;9(8): 347. https://doi.org/10.3390/bioengineering9080347

[3] Fonseca FAS, Vidal-Vieira JA, Ravagnani SP. Transesterification of vegetable oils: Simulating the replacement of batch reactors with continuous reactors. *Bioresour Technol.* 2010; 101(21): 8151-8157. https://.doi.org/10.1016/j.biortech.2010.05.077

[4] Gopi R, Thangarasu V, Vinayakaselvi MA, Ramanathan A. A critical review of recent advancements in continuous flow reactors and prominent integrated microreactors for biodiesel production. *Renew Sust Energ Rev*. 2022; 154: 111869.https://doi.org/10.1016/j.rser.2021.111869

[5] Tabatabaei M, Aghbashlo M, Dehhaghi M, Panahi HKS, Mollahosseini A, Hosseini M, Soufiyan MM. Reactor technologies for biodiesel production and processing: A review. *Prog Energy Combust Sci.* 2019; 74: 239-303. https://doi.org/10.1016/j.pecs.2019.06.001

[6] Mohiddin MNB, Tan YH, Seow YX, Kansedo J, Mubarak NM, Abdullah MO, Chan YS, Khalid M, Evaluation on feedstock, technologies, catalyst and reactor for sustainable biodiesel production: A review. *J Ind Eng Chem.* 2021; 98: 60-81. https://doi.org/10.1016/j.jiec.2021.03.036

[7] Ghazi ATIM, Resul MFMG, Yunus R, Yaw TCS. Preliminary design of oscillatory flow biodiesel reactor for continuous biodiesel production from Jatropha triglycerides. *J Eng Sci Technol.* 2008; 2(3): 138-145.

[8] García Martín JF, Barrios CC, Alés Álvarez F-J, Dominguez Sáez A, Alvarez Mateos P. Biodiesel production from waste cooking oil in an oscillatory flow reactor. Performance as a fuel on a TDI diesel engine. *Renew Energy.* 2018; 125: 546-56. https://doi.org/10.1016/j.renene.2018.03.002

[9] Highina BK, Bugaje IM, Ngala GM. Performance evaluation of continuous oscillatory baffled reactor arrangementon production of biodiesel from Jatropha oil using heterogeneous catalyst. *World J Renew Energ Eng*. 2014; 1: 1-7. http://www.scenrp.com/World%20Journal%20of%20Renewable%20Energy%20&%20Engineering/Current%20Issue.php

[10] Kefas HM, Yunus R, Rashid U, Taufiq-Yap YH. Enhanced biodiesel synthesis from palm fatty acid distillate and modified sulfonated glucose catalyst via an oscillation flow reactor system. *J Environ Chem Eng.* 2019; 7: 102993*.* https://doi.org/10.1016/j.jece.2019.102993

[11] Niyas MM, Shaija A. Biodiesel production from coconut waste cooking oil using novel solar powered rotating flask oscillatory flow reactor and its utilization in diesel engine. *Therm Sci Eng Prog*. 2023; 40: 101794. https://doi.org/10.1016/j.tsep.2023.101794

[12] Zheng M, Skelton RL, Mackley MR. Biodiesel reaction screening using oscillatory flow meso reactors. *Process Saf Environ Prot*. 2007; 85(5): 365-371.https://doi.org/10.1205/psep07030

[13] Son SM, Kusakabe K. Transesterification of sunflower oil in a counter-current trickle-bed reactor packed with a CaO catalyst. *Chem Eng Process.* 2011; 50: 650-654. https://doi.org/10.1016/j.cep.2011.04.001

[14] Meng YL, Tian SJ, Li SF, Wang BY, Zhang MH. Transesterification of rapeseed oil for biodiesel production in trickle-bed reactors packed with heterogeneous Ca/Al composite oxide-based alkaline catalyst. *Bioresour Technol.* 2013; 136: 730-734. https://doi.org/10.1016/j.biortech.2013.03.081

[15] Jindapon W, Ruengyoo S, Kuchonthara P, Ngamcharussrivichai C, Vitidsant T. Continuous production of fatty acid methyl esters and high-purity glycerol over a dolomite-derived extrudate catalyst in a countercurrent-flow trickle-bed reactor. *Renew Energ*. 2020; 157: 626-636. https://doi.org/10.1016/j.renene.2020.05.066

[16]　Chen G, Liu J, Yao J, Qi Y, Yan B. Biodiesel production from waste cooking oil in a magnetically fluidized bed reactor using whole-cell biocatalysts. *Energy Conv Manag*. 2017; 138: 556-564. https://doi.org/10.1016/j.enconman.2017.02.036

[17]　Chueluecha N, Kaewchada A, Jaree A. Biodiesel synthesis using heterogeneous catalyst in a packed-microchannel. *Energy Conv Manage.* 2017; 141: 145-154. https://doi.org/10.1016/j.enconman.2016.07.020

[18]　Santana HS, Tortola DS, Silva JL Jr, Taranto OP. Biodiesel synthesis in micromixer with static elements. *Energy Conv Manag.* 2017; 141: 28-39. https://doi.org/10.1016/j.enconman.2016.03.089

[19]　Sun P, Sun J, Yao J, Zhang L, Xu N. Continuous production of biodiesel from high acid value oils in microstructured reactor by acid-catalyzed reactions. *Chem Eng J.* 2010; 162: 364-370. https://doi.org/10.1016/j.cej.2010.04.064

[20]　Yamsub A, Kaewchada A, Jaree A. Pork lard conversion to biodiesel using a microchannel reactor. *Korean J Chem Eng.* 2014; 31:2170-2176. https://doi.org/10.1007/s11814-014-0120-5

[21]　Natarajan Y, Nabera A, Salike S, Tamilkkuricil VD, Pandian S, Karuppan M, Appusamy A. An overview on the process intensification of microchannel reactors for biodiesel production. *Chem Eng Process: Process Intensif*. 2019; 136: 163-176. https://doi.org/10.1016/j.cep.2018.12.008

[22]　Darnoko D, Cheryan M. Continuous production of palm methyl esters. *J Am Oil Chem Soc*. 2000; 77: 1269-1272. https://doi.org/10.1007/s11746-000-0199-x

[23]　Kouzu M, Fujimori A, Fukakusa R, Satomi N, Yahagi S. Continuous production of biodiesel by the CaO-catalyzed transesterification operated with continuously stirred tank reactor. *Fuel Process Technol*. 2018; 181: 311-317. https://doi.org/10.1016/j.fuproc.2018.10.008

[24]　Sun Y, Zhang J, Sun Z, Zhang L. Biodiesel production using calcium-based catalyst from venus shell: Modeling of startup production in an industrial reactor. *Environ Prog Sustain Energy.* 2019; 38(3): 1-9. https://doi.org/10.1002/ep.13053

[25]　Lodha H, Jachuck R, Suppiah Singaram S. Intensified biodiesel production using a rotating tube reactor. *Energ Fuel.* 2012; 26: 7037-7040. https://doi.org/10.1021/ef301235t

[26]　Chen YH, Huang YH, Lin RH, Shang NC. A continuous-flow biodiesel production process using a rotating packed bed. *Bioresour Technol.* 2010; 101: 668-673. https://doi.org/10.1016/j.biortech.2009.08.081

[27]　Chen YH, Huang YH, Lin RH, Shang NC, Chang CY, Chang CC, Chang CC, Chiang PC, Hu CY. Biodiesel production in a rotating packed bed using K/γ-Al$_2$O$_3$ solid catalyst. *J Taiwan Inst Chem Eng.* 2011; 42(6): 937-944. https://doi.org/10.1016/j.jtice.2011.05.007

[28]　Qiu Z, Zhao L, Weatherley L. Process intensification technologies in continuous biodiesel production. *Chem Eng Process.* 2010; 49: 323-330. https://doi.org/10.1016/j.cep.2010.03.005

[29]　Chen KJ, Chen YS. Intensified production of biodiesel using a spinning disk reactor. *Chem Eng Process.* 2014; 78: 67-72. https://doi.org/10.1016/j.cep.2014.02.009

[30]　Scares L, Franca A, Oliveira L. Feasibility of biodiesel production in a continuous flow microwave reactor with static mixing. In: *8th international conference on mechanical and aerospace engineering (ICMAE)*. Prague, Czech Republic: IEEE, 2017. pp. 581-585.

[31]　Thirugnanasambandham K, Sivakumar V. Investigation on biodiesel production from cotton seed oil using microwave irradiated transesterfication process. *Environ Prog Sustain Energy.* 2015; 34: 1229-1235. https://doi.org/10.1002/ep.12094

[32]　Ma G, Hu W, Pei W, Jiang L, Song M, Mu R. *In situ* heterogeneous transesterification of microalgae using combined ultrasound and microwave irradiation. *Energy Conv Manag.* 2015; 90: 41-46. https://doi.org/10.1016/j.enconman.2014.10.061

[33]　Avramović JM, Stamenković OS, Todorović ZB, Lazić ML, Veljković VB. Empirical modeling of ultrasound-assisted base-catalyzed sunflower oil methanolysis kinetics. CI&CEQ. 2012; 18(1): 115-127.https://doi.org/10.2298/CICEQ110705053A

[34]　Avramović JM, Radosavljević DB, Veličković AV, Stojković IJ, Stamenković OS, Veljković VB. Statistical modeling and optimization of ultrasound-assisted biodiesel production using various experimental designs. *Zaštita Materijala*. 2019; 60(1): 70-80. https://doi.org/10.5937/zasmat1901070A

[35]　Gogate PR, Sutkar VS, Pandit AB. Sonochemical reactors: important design and scale up considerations with a special emphasis on heterogeneous systems. *Chem Eng J.* 2011; 166(3): 1066-1082. https://doi.org/10.1016/j.cej.2010.11.069

[36]　Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: a practical and economical approach to produce high quality biodiesel fuel. *Bioresour Technol*. 2010; 101: 5394-5401. https://doi.org/10.1016/j.biortech.2010.02.060

[37]　Veljković VB, Avramović JM, Stamenkovi OS. Biodiesel production by ultrasound-assisted transesterification: State of the art and the perspectives. *Renew Sust Energ Rev*. 2012; 16: 1193-1209. https://doi.org/10.1016/j.rser.2011.11.022

[38]　Pal A, Verma A, Kachhwaha S, Maji S. Biodiesel production through hydrodynamic cavitation and performance testing. *Renew Energy.* 2010; 35(3): 619-624. https://doi.org/10.1016/j.renene.2009.08.027

[39]　Gole VL, Naveen K, Gogate PR. Hydrodynamic cavitation as an efficient approach for intensification of synthesis of methyl esters from sustainable feedstock. *Chem Eng Process.* 2013; 71: 70-76. https://doi.org/10.1016/j.cep.2012.10.006

[40]　Javadikia H, Nosrati Y, Mostafaei M, Naderloo L, Tabatabaei M. Optimization of hydrodynamic cavitations reactor efficiency for biodiesel production by response surface methods (Case study: sunflower oil). *J Agric Mach.* 2017; 7: 260-269.https://doi.org/10.22067/jam.v7i1.51920

[41]   https://www.hydrodynamics.com/cavitation-technology/ (Accessed April 10, 2023.)

[42]   Baroutian S, Aroua MK, Raman AAA, Sulaiman NM. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. *Bioresour Technol.* 2011; 102(2): 1095-1102. https://doi.org/10.1016/j.biortech.2010.08.076

[43]   Cao P, Dubé MA, Tremblay AY. High-purity fatty acid methyl ester production from canola, soybean, palm, and yellow grease lipids by means of a membrane reactor. *Biomass Bioenergy.* 2008; 32(11): 1028-1036. https://doi.org/10.1016/j.biombioe.2008.01.020

[44]   Hou R, Zhang D, Duan X, Wang X, Wang S, Sun Z. Fabrication of $H_3PW_{12}O_{40}$/agarose membrane for catalytic production of biodiesel through esterification and transesterification. *RSC Adv.* 2016; 6: 81794-81801. https://doi.org/10.1039/C6RA17118D

[45]   Luo Q, He B, Liang M, Kong A, Li J. Continuous transesterification to produce biodiesel under HTCC/Na_2SiO_3/NWF composite catalytic membrane in flow-through membrane reactor. *Fuel.* 2017; 197: 51-57. https://doi.org/10.1016/j.fuel.2016.12.089

[46]   Petchsoongsakul N, Ngaosuwan K, Kiatkittipong W, Aiouache F, Assabum-rungrat S. Process design of biodiesel production: hybridization of ester- and transesterification in a single reactive distillation. *Energy Conv Manag.* 2017; 153: 493-503. https://doi.org/10.1016/j.enconman.2017.10.013

[47]   Noshadi I, Amin N, Parnas RS. Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: Optimization using response surface methodology (RSM). *Fuel.* 2012; 94: 156-64. https://doi.org/10.1016/j.fuel.2011.10.018

[48]   Abduh MY, Van Ulden W, Kalpoe V, Van De Bovenkamp HH, Manurung R, Heeres HJ. Biodiesel synthesis from *Jatropha curcas* L. oil and ethanol in a continuous centrifugal contactor separator. *Eur J Lipid Sci Technol.* 2013; 115: 123-131. https://doi.org/10.1002/ejlt.201200173

[49]   Carlucci C. An overview on the production of biodiesel enabled by continuous flow methodologies. *Catalysts,* 2022; 12: 717. https://doi.org/10.3390/catal12070717

[50]   Tran DT, Chang JS, Lee DJ. Recent insights into continuous-flow biodiesel production via catalytic and non-catalytic transesterification processes. *Appl Energy.* 2017; 185: 376-409. https://doi.org/10.1016/j.apenergy.2016.11.006

[51]   Lo TC, Prochazka J. Reciprocating plate extraction columns, in Handbook of solvent extraction (Lo TC, Baird MHI, Hanson C. eds.); New York, NY: John Wiley & Sons; 1983. pp. 373-389. ISBN 0-471-04164-5.

[52]   Nikolić LB, Veljković VB, Skala DU. Axial dispersion of the liquid flow in a Karr reciprocating plate column. *Hem Ind.* 2001; 55: 249-254. https://doi.org/10.2298/JSC0407581N

[53]   Aleksić M, Veljković VB, Banković-Ilić IB, Lazić ML, Skala DU. Uticaj Rašigovih prstenova i reoloških osobina tečnosti na promenu pritiska na dnu kolone sa vibracionom mešalicom. *Hem Ind.* 2002; 56:409-414. https://doi.org/10.2298/HEMIND0210409A (in Serbian).

[54]   Aleksić M, Veljković VB, Banković-Ilić IB, Lazić ML, Skala DU. Uticaj Rašigovih prstenova i reoloških osobina tečnosti na promenu pritiska na dnu kolone sa vibracionom mešalicom. *Hem Ind.* 2003; 57: 107-113. https://doi.org/10.2298/HEMIND0210409A (in Serbian).

[55]   Banković-Ilić I, Veljković V, Skala D. Gas holdup in a three phase reactors of the bubble column type. *Hem Ind*. 1994; 48: 397-402.

[56]   Banković-Ilić IB, Veljković VB, Lazić ML, Skala DU. Power consumption and gas holdup in a gas-liquid reciprocating plate column. Chem Eng Comm. 1995; 134: 17-32. https://doi.org/10.1080/00986449508936320.

[57]   Banković-Ilić I, Veljković V, Skala D. Hidrodinamičke i masenoprenosne karakteristike kolone sa vibracionom mešalicom za sisteme gas-tečnost i gas-tečnost-čvrsta faza - monografija. Leskovac: Tehnološki fakultet; 2009. ISBN 978-86-82367-80-2 (in Serbian)

[58]   Hafez M, Baird MHI. Power consumption in a reciprocating plate column. *Trans Inst Chem Eng*. 1978; 56: 229-238.

[59]   Naseva OS, Stamenković IS, Banković-Ilić IB, Lazić ML, Veljković VB, Skala DU. Sadržaj gasa u bioreaktoru sa vibracionom mešalicom - tečna faza je njutnovski fluid. *Hem Ind*. 2002; 56: 198-203. https://doi.org/10.2298/HEMIND0205198N (in Serbian)

[60]   Skala DU, Veljković VB, Janjić VV, Lazić M, Banković-Ilić IB. Gas holdup in a gas-liquid-solid reciprocating plate column. *Can J Chem Eng*. 1993; 71: 817-820. https://doi.org/10.1002/cjce.5450710521

[61]   Vasić Lj, Banković-Ilić IB, Lazić ML, Veljković VB, Skala DU. Sadržaj gasa u koloni sa vibracionom mešalicom prečnika 16,6 cm. *Hem ind*. 2005; 59: 263-266. https://doi.org/10.2298/HEMIND0510263V

[62]   Veljković V, Skala D. Hydrodynamic investigation of gas-liquid contacting in a reciprocating plate column. *Can J Chem Eng*. 1986; 64: 906-914. https://doi.org/10.1002/cjce.5450640604

[63]   Banković-Ilić IB, Veljković VB, Lazić ML, Skala DU. Mass transfer in a multiphase vibration column. I The volumetric mass transfer coefficient. *Chem Ind*. 2001; 55(9): 376-382

[64]   Banković-Ilić IB, Veljković VB, Lazić ML, Skala DU. Mass transfer in a multiphase vibration column. II. Interfacial area. *Chem Ind*. 2001; 55(9): 383-388

[65]   Lounes M, Thibault J. Mass transfer in a reciprocating plate bioreactor. *Chem Eng Commun*. 1994; 127: 169-189. https://doi.org/10.1080/00986449408936231.

[66]   Sundaresan A, Varma YBG. Interfacial area and mass transfer in gas-liquid cocurrent upflow and countercurrent flow in reciprocating plate column. *Can J Chem Eng*. 1990; 68: 951-958. https://doi.org/10.1002/cjce.5450680610

[67]   Rama Rao NV, Baird MHII. Gas-liquid mass transfer in a 15 cm diameter reciprocating plate column. *J Chem Technol Biotech*. 2003;78: 134-137. https://doi.org/10.1002/jctb.704

[68]   Skala D, Veljković V. Mass transfer characteristics in a gas-liquid reciprocating plate column. I. Liquid phase volumetric mass transfer coefficient. *Can J Chem Eng*. 1988; 66: 192-199. https://doi.org/10.1002/cjce.5450660203

[69]   Vasić Lj, Banković-Ilić IB, Lazić ML, Veljković VB, Skala DU. Oxygen mass transfer in a 16.6 i.d. multiphase reciprocating plate column. *J Serb Chem Soc*. 2007; 72: 523-531. https://doi.org/10.2298/JSC0705523V

[70]   Veljković V, Skala D. Mass transfer characteristics in a gas-liquid reciprocating plate column. II. Interfacial area. *Can J Chem Eng*. 1988; 66: 200-210. https://doi.org/10.1002/cjce.5450660203

[71]   Banković-Ilić IB, Todorović ZB, Avramović JM, Veličković AV, Veljković VB. The effect of tetrahydrofuran on the base-catalyzed sunflower oil methanolysis in a continuous reciprocating plate reactor. *Fuel Process Technol*. 2015; 137: 339-350. http://dx.doi.org/10.1016/j.fuproc.2015.03.023

[72]   Stamenković I, Stamenković O, Todorović Z, Banković -Ilić I, Lazić M, Veljković V, *et al.* The production of fatty acid methyl esters by a continuous base catalyzed methanolysis of sunflower oil. In: *The Proceedings of the 1st Conference of the Sustainable Development And Climate Changes*. Niš, Serbia, 2008. p. 251-255.

[73]   Stamenković IS, Banković-Ilić IB, Jovanić PB, Veljković VB, Skala D. Hydrodynamics of a cocurrent upflow liquid-liquid reciprocating plate reactor for homogeneously base-catalyzed methanolysis of vegetable oils. *Fuel* 2010; 89: 3971-3984. http://www.doi:10.1016/j.fuel.2010.06.026

[74]   Stamenković I, Stamenković O, Banković-Ilić I, Todorović Z, Lazić M, Veljković V, Skala D. Production of fatty acid esters by continuous alcoholysis of vegetable oils. Serbian patent RS 52398 B, 2013 (in Serbian)

[75]   Hafez M, Prochazka J. The dynamic effects in a vibrating plate and pulsed extractors I. Theory and experimental technique. *Chem Eng Sci*. 1974; 29: 1745-1753. https://doi.org/10.1016/0009-2509(74)87033-8

[76]   Jealous AC, Johnson HF. Power requirements for pulse generation in pulse column. *Ind Eng Chem*. 1955; 47: 1159-1166. https://doi.org/10.1021/ie50546a021

[77]   Stamenković I. Kontinualna homogena bazno katalizovana alkoholiza biljnih ulja u reaktoru sa vibracionom mešalicom. Doktorska disertacija, Univerzitet u Nišu, Tehnološki fakultet, Leskovac; 2014 (in Serbian).

[78]   Rama Rao NV, Srinivas NS, Varma YBG. Dispersed phase holdup and drop size distributions in reciprocating plate columns. *Can J Chem Eng*. 1983; 61: 168-177. https://doi.org/10.1002/cjce.5450610204

[79]   Stamenković OS, Lazić ML, Todorović ZB, Veljković VB, Skala DU. The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil. *Bioresour Technol*. 2007; 98: 2688-2699. https://doi.org/10.1016/j.biortech.2006.09.024

[80]   Banković-Ilić IB, Veljković VB, Lazić ML, Skala DU. Mass transfer in a multiphase vibration column. I. The volumetric mass transfer coefficient. *Hem. Ind*. 2001; 55: 376-382

[81]   Baird MHI, Rama Rao NV. Characteristics of a countercurrent reciprocating plate bubble column. II Axial mixing and mass transfer. *Can J Chem Eng*. 1988; 66: 222-231. https://doi.org/10.1002/cjce.5450660206

[82]   Sundaresan A, Varma YBG. Yang NS, Shen ZQ, Chen BH, McMillan AF. Axial mixing and mass transfer in gas-liquid Karr columns. *Ind Eng Chem Proc Des Dev*. 1986; 25: 776-780. https://doi.org/10.1021/i200034a031

[83]   Yang NS, Shen ZQ, Chen BH, Mc Millan AF. Pressure drop, gas holdup and interfacial area for gas-liquid contact in Karr-columns. *Ind Eng Chem Pro. Des Dev*. 1986; 25**:** 660-664. https://doi.org/10.1021/i200034a011

[84]   Miladinović MR, Stojković IJ, Veličković AV, Stamenković OS, Banković-Ilić IB, Veljković VB. Optimization and kinetic modeling of waste lard methanolysis in a continuous reciprocating plate reactor. *Chin J Chem Eng*. 2019; 27: 2481-2490. https://doi.org/10.1016/j.cjche.2019.02.019

[85]   Xu W, Gao L, Wang S, Xiao G. Biodiesel production from soybean oil in a membrane reactor over hydrotalcite based catalyst: An optimization study. *Energ Fuels*. 2013; 27:6738-6742. https://doi.org/10.1021/ef401823z

[86]   Xu W, Gao L, Xiao G. Biodiesel production optimization using monolithic catalyst in a fixed-bed membrane reactor. *Fuel*. 2015; 159: 484-490. https://doi.org/10.1016/j.fuel.2015.07.017

[87]   Hernández-Montelongo R, García-Sandoval JP, Dochain D, Gonz A. Biodiesel production in a continuous packed bed reactor with recycle: A modeling approach for an esterification system. *Renew Energy*. 2018; 116: 857-865. https://doi.org/10.1016/j.renene.2017.09.030

[88]   Chueluecha N, Kaewchada A, Jaree A. Enhancement of biodiesel synthesis using co-solvent in a packed-microchannel. *J Ind Eng Chem*. 2017; 51: 162-171. https://doi.org/10.1016/j.jiec.2017.02.028

[89]   Perego C, Peratello S. Experimental methods in catalytic kinetics. *Catal Today*. 1999; 52: 133-145.

[90]   Zahan KA, Kano M. Technological progress in biodiesel production: An Overview on different types of reactors. *Energy Procedia*. 2019; 156: 452-457. (https://doi.org/10.1016/j.egypro.2018.11.086

[91]   Marinković DM, Miladinović MR, Avramović JM, Krstić IB, Stanković MV, Stamenković OS, Jovanović DM, Veljković VB. Kinetic modeling and optimization of sunflower oil methanolysis catalyzed by spherically-shaped CaO/γ -Al$_2$O$_3$ catalyst. *Energy Conv Manag*. 2018; 163: 122-133. https://doi.org/10.1016/j.enconman.2018.02.048

[92]   Miladinović MR, Stamenković OS, Veljković VB, Skala DU. Continuous sunflower oil methanolysis over quicklime in a packed-bed tubular reactor. *Fuel*. 2015; 154: 301-307. https://doi.org/10.1016/j.fuel.2015.03.057

[93]   Hashemzadeh Gargari M, Sadrameli SM. Investigating continuous biodiesel production from linseed oil in the presence of a Co-solvent and a heterogeneous based catalyst in a packed bed reactor. *Energy*. 2018; 148: 888e895. https://doi.org/10.1016/j.energy.2018.01.105

[94]   Melero JA, Bautista LF, Iglesias J, Morales G, Sánchez-vazquez R. Production of biodiesel from waste cooking oil in a continuous packed bed reactor with an agglomerated Zr-SBA-15/bentonite catalyst. *Applied Catal B. Environ*. 2014; 145: 197-204. https://doi.org/10.1016/j.apcatb.2013.02.050

[95]   Ren Y, He B, Yan F, Wang H, Cheng Y, Lin L, Feng Y, Li J. Continuous biodiesel production in a fixed bed reactor packed with anion-exchange resin as heterogeneous catalyst. *Bioresour Technol*. 2012; 113: 19-22. https://doi.org/10.1016/j.biortech.2011.10.103

[96]   Zabaruddin NH, Mohamed NH, Abdullah LC, Tamada M, Ueki Y, Seko N, Choong TSY. Palm oil-based biodiesel synthesis by radiation-induced kenaf catalyst packed in a continuous flow system. *Ind Crops Prod*. 2019; 136: 102-109. https://doi.org/10.1016/j.indcrop.2019.04.069

[97]   Buasri A, Loryuenyong V. Continuous production of biodiesel from rubber seed oil using a packed bed reactor with BaCl$_2$ impregnated CaO as catalyst. 2018; 13(2): 320-330. https://doi.org/10.9767/bcrec.13.2.1585.320-330

[98]   Sakthivel S, Halder S, Gupta PD. Optimization of process variables for production of biodiesel in packed bed reactor using response surface methodology. *Int J Ambient Energy*. 2013; 34: 83-91. https://doi.org/10.1080/01430750.2012.740422

[99]   Ketcong A, Meechan W, Naree T, Seneevong I. Production of fatty acid methyl esters over a limestone-derived heterogeneous catalyst in a fixed-bed reactor. *J Ind Eng Chem*. 2014; 20(4): 1665-1671. https://doi.org/10.1016/j.jiec.2013.08.014

[100]   Miladinović MR, Stamenković OS, Banković PT, Milutinović AD, Jovanovic DM, Veljković VB. Modeling and optimization of sunflower oil methanolysis over quicklime bits in a packed bed tubular reactor using the response surface methodology. *Energy Conv Manag.* 2016; 130: 25-33. https://doi.org/10.1016/j.enconman.2016.10.020

[101]   Co CET, Tan MC, Diamante JAR, Yan LRC, Tan RR, Razon LF. Internal mass-transfer limitations on the transesterification of coconut oil using an anionic ion exchange resin in a packed bed reactor. *CatalToday*. 2011; 174(1): 54-58. https://doi.org/10.1016/j.cattod.2011.02.065

[102]   Buasri A, Chaiyut N, Loryuenyong V, Rodklum C, Chaikwan T, Kumphan N. Continuous process for biodiesel production in packed bed reactor from waste frying oil using potassium hydroxide supported on *Jatropha curcas* fruit shell as solid catalyst. *Appl Sci.* 2012; 2: 641-653. https://doi.org/10.3390/app2030641

[103]   Akkarawatkhoosith N, Kaewchada A, Ngamcharussrivichai C, Jaree A. Biodiesel production via interesterification of palm oil and ethyl acetate using ion-exchange resin in a packed-bed reactor. *BioEnergy Res*. 2020; 13: 542-551. https://doi.org/10.1007/s12155-019-10051-4

[104]   Díaz L, Escalante D, Rodríguez KE, Kuzmina Y, Gonz LA. Response surface methodology for continuous biodiesel production from *Jatropha curcas* oil using Li/pumice as catalyst in a packed-bed reactor assisted with diethyl ether as cosolvent. *Chem Eng Process: Process Intensif*. 2022; 179: 109065. https://doi.org/10.1016/j.cep.2022.109065

[105]   Zabaruddin NH, Abdullah LC, Mohamed NH, Choong TSY. Optimization using response surface methodology (RSM) for biodiesel synthesis catalyzed by radiation-induced kenaf catalyst in packed-bed reactor. *Processes*. 2020; 8: 1289. https://doi.org/10.3390/pr8101289

[106]   Sulaiman S, Mohamed A, Raja S, Shah S, Ehsan R. Potash derived from orange peel supported on PVA as a heterogeneous catalyst for biodiesel production in the packed - bed reactor. *Appl Nanosci*. 2022; 12(12): 3747-3754. https://doi.org/10.1007/s13204-022-02367-z

[107]   Talha NS, Sulaiman S. In situ transesterification of solid coconut waste in a packed bed reactor with CaO / PVA catalyst. *Waste Manag*. 2018; 78: 929-937. https://doi.org/10.1016/j.wasman.2018.07.015

[108]   Zik N, Sulaiman S, Jamal P. Biodiesel production from waste cooking oil using calcium oxide/nanocrystal cellulose / polyvinyl alcohol catalyst in a packed bed reactor. *Renew Energy*. 2020; 155: 267-277. https://doi.org/10.1016/j.renene.2020.03.144

Kontinualni višefazni reaktor sa vibracionom mešalicom i pakovanim slojem u proizvodnji biodizela: unapređenja i izazovi

Ivana B. Banković-Ilić[1], Marija R. Miladinović[1] i Vlada B. Veljković[1,2]

[1]*University of Niš, Faculty of Technology in Leskovac, Serbia*
[2]*Serbian Academy of Sciences and Arts, Belgrade, Serbia*

(Pregledni rad)

Izvod

Biodizel, obnovljiva i ekološki prihvatljiva alternativa konvencionalnim fosilnim gorivima, privukao je značajnu pažnju u poslednje dve decenije. Kontinualna proizvodnja biodizela ima prednosti u primeni zbog svoje efikasnosti, produktivnosti i mogućnosti uvećanja razmera reaktora. Ovaj rad predstavlja pregled kontinualnih reaktorskih sistema za proizvodnju biodizela sa naglaskom na prinos biodizela, kinetiku reakcije i efikasnost konverzije u reaktorima sa vibracionom mešalicom i pakovanim slojem. Reaktor sa vibracionom mešalicom se odlikuje superiornijim karakteristikama mešanja, boljim prenosom mase i kinetikom reakcije. Suprotno, reaktor sa pakovanim slojem se odlikuje boljim odnosom količine katalizatora i sirovine i dužim vremenom zadržavanja, što poboljšava efikasnost konverzije. Oba reaktora imaju povoljne performanse za kontinualnu proizvodnju biodizela. Ovo istraživanje može doprineti razumevanju kontinualne proizvodnje biodizela primenom inovativnih kostrukcija reaktora. Uporedna analiza reaktora sa vibracionom mešalicom i reaktora sa pakovanim slojem nudi dragocena saznanja u vezi optimizacije procesa i izbora reaktora na osnovu specifičnih zahteva kao što su dostupnost sirovina, kinetika reakcije i ekonomska razmatranja. To sve utire put za implementaciju održivih i efikasnih procesa proizvodnje biodizela u budućnosti.