Biodiesel production by the electrocatalytic process: a review

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Abstract

Biodiesel—an impressive alternative fuel with favourable physico-chemical properties having environmental benefits—is prepared from vegetable oil. However, the cost is one of the main hurdles in commercializing it. Its production by conventional transesterification processes needs high ambient temperature and a specialized catalyst. Due to the multifaceted adversities of many of the catalysts, there is active consideration for an electrocatalytic process that does not require elevated temperature. In addition, an electrocatalytic process is carried out in the presence or absence of a catalyst or co-solvent. In this review, various parameters such as electrolysis voltage, stirring rate, electrode type, water content, co-solvent type, reaction temperature, reaction duration, oil-to-methanol molar ratio and concentration of NaCl affecting the electrocatalytic transesterification process are presented.

Graphical Abstract

Keywords: electrolysis; electrocatalytic reactor; electrodes; transesterification; biodiesel
Introduction

Biodiesel—an alternative fuel prepared from vegetable oil—has the merit of renewability, biodegradability and eco-friendliness [1, 2]. Recently, biodiesel has received attention since fossil fuels are being depleted rapidly, besides causing a considerable negative impact on the environment [3]. Approximately 80% of the expenditure in producing biodiesel goes to the cost of raw materials, namely vegetable oil or animal fat. As a compromise on cost, non-edible oils derived from woody plants are being considered as a raw material [4]. The high viscosity, density and free-fatty-acid (FFA) content of woody plant oils and waste cooking oil (WCO) make them less attractive as a raw material. Consequently, dilution, blending, microemulsion, pyrolysis (thermal cracking) and transesterification processes have been attempted. Among these, transesterification is considered the best process [5, 6]. In the transesterification process, short-chain alcohol (methanol or ethanol) in the presence of a catalyst is used, resulting in the formation of fatty-acid methyl or ethyl esters (FAME) with glycerol as a by-product from the triglycerides present in the vegetable oils or animal fats [7]. In the above process, NaOH or KOH is employed as the catalyst at a reaction temperature of 50–65°C. In such event, there is every likelihood of saponification if the oil has an unusually high FFA content. Saponification grossly interferes with the transesterification process by diverting the alkali into soap formation instead of generating esters. To avert such a contingency, often an acid catalyst is used with which the reaction rate is relatively slow. It also demands more alcohol in quantitative terms. Therefore, heterogeneous catalysts and enzyme catalysts have been used, expressing varied performance rates [8, 9].

Catalysts that are currently in use are metal oxides, molecular sieves, activated alumina and sodium carbonate. Besides, lipolytic enzymes are also being used, although the cost is prohibitive. Most often, the enzymes are immobilized due to certain advantages such as enhanced stability of the enzymes and easy separation from the reaction mixture. The metal oxides find extensive application in various catalytic systems due to their unique properties such as a high specific surface area, strong base strength and high concentration of basic sites [10]. Some of the salient features of metal oxides as catalysts are related to the complementary structure, strong affinity between the metal and oxygen, and the presence of rich basic or acidic sites. Catalytic properties of metal oxides are due to the adsorption of reactants on unsaturated metal sites, oxygen atoms or both, followed by the addition or removal of hydrogen or oxygen. Such structural benefits of the metal oxides are considered favourable for utilizing them as catalysts in chemical reactions [11, 12]. Heterogeneous catalysts and immobilized lipase catalysts have the advantages of being environmentally friendly, safer and cheaper, and with easy recovery besides being renewed and reused in many cycles. The heterogeneous-base catalysts have proved to be successful in biodiesel production, although they suffer limitation due to their sensitivity to high FFA content or to low-grade feedstock [13].

Nanostructured materials have recently received attention in view of their extraordinary physical and chemical capabilities as compared to their corresponding macroscopic materials. Nanocatalysts ably bring the reactants and catalyst site into close contact, mainly due to the disproportionately high ratio of surface to volume. This characteristic enables the heterogeneous nanocatalytic system to bring out reaction rates equal to those of a homogeneous catalytic system [14].

In order to eliminate the problems associated with the above transesterification process, the electrocatalytic process is introduced [5, 15]. An electrocatalytic process is one in which electrons are transferred between the electrode and the reactants, which is an alternative technology without any major impact on the environment. This process has high efficiency with low cost and is applicable in many sustainable-energy technologies [16]. The oxygen reduction reaction (ORR) [17, 18], oxygen evolution reaction (OER), hydrogen evolution reaction (HER) [19] and hydrogen oxidation reaction (HOR) [20] are significant in the energy-oriented electrochemical-conversion processes. Biodiesel production through the electrocatalytic process from used frying oil as the raw material was first investigated by Guan and Kusabe in 2009 [21]. The electrocatalytic process was observed to be advantageous in oils containing high FFA and water (>5%) and it effectively circumvented the saponification [22]. The electrocatalytic process is relatively inexpensive and does not require any heating [23].

1 Electrocatalytic process in transesterification

In electrolysis, a direct current (DC) electric field is passed through molten salts or dissolved ionic substances causing the decomposition of the above into simple substances [24]. The electrocatalytic reactor consists of an electrochemical cell whose electrodes are made of graphite [13, 15, 23, 25] or activated carbon [26] or carbon nanotubes [27] or graphene [28] separated by a distance in the order of 10–20 mm [13, 21–23, 25, 29] (Fig. 1). Laboratory-scale electrolysis is carried out by applying a constant voltage (10–40 V) at room temperature (25°C) [13, 15, 22, 23, 25, 29]. The mechanism of electrolytic transesterification is given in Equations (1)–(5). The electrocatalytic reactor is loaded with a mixture comprising vegetable oil, methanol, catalyst, co-solvents and an electrolyte solution (NaCl + H2O). The reaction is given in Equations (1)–(3). The chlorine and hydroxyl ions reach the anode and are oxidized into chlorine (Cl2) and oxygen (O2); the hydroxyl ions and hydrogen are formed on the cathode (Equation (4)). The methoxide ion is formed by the reaction of methanol with hydroxyl (OH−), which is strongly nucleophilic. It then attacks the carbonyl moiety in the glyceride molecules to result in methyl ester and glycerine.
Glycerine is the by-product of the transesterification reaction [13, 23, 25]

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$$  \(1\)

anodic reaction

$$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$$  \(2\)

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$$  \(3\)

cathodic reaction

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$  \(4\)

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$$  \(5\)

proton-transfer reaction

$$\text{CH}_3\text{OH} + \text{OH}^- \leftrightarrow \text{CH}_3\text{O}^- + \text{H}_2\text{O}$$  \(6\)

and transesterification reaction

$$\text{Triglycerides} + 3\text{CH}_3\text{OH} \leftrightarrow \text{FAME} + \text{Glycerol}$$  \(7\)

1.1 Electrodes

Two types of electrodes are used. They are (i) metallic electrodes prepared by conventional microfabrication and (ii) a thin layer of metal or metal oxide electrodeposited onto the surface of the substrate. A conductive thin-layer coating on the metal or metal-oxide electrodes improves the surface properties. The mechanism of electrocatalysis leads to the speeding-up of half-cell reactions on the surface of the electrode. The performance of the electrocatalytic reactor largely depends on the properties of the electrode materials [30]. Electrodes made of platinum have good conductivity and chemical stability, which effectively oxidizes the organics [31]. A Ti/Pt electrode is normally used to analyse the reactivity of glucose in all current densities [32]. A dimensionally stable anode (DSA) has a high surface area and excellent mechanical and chemical resistance, even at high current densities in strong-acid media [33]. The OER is a common problem associated with anodes made of metal or inert metal. A DSA as an electrode is ideal in the context of chlorine evolution and has also demonstrated its activity in all other electrochemical reactions and organic oxidation. Chlorine evolution affects long-term stability. This problem is overcome by employing transition metal oxides in the anode [34]. Quaternary metal-oxide anodes such as Ti, Ru, Sn and Sb are stable and electrochemically active in the oxidation of organic compounds when they are used in the absence of a soluble supporting electrolyte with Nafion® membrane as the solid-state electrolyte [35]. Lead oxide (PbO 2)-based anodes are popular in the conversion of organics with high oxygen evolution due to the effective oxidation of organic molecules. The effect is reported to be higher than that of many other traditional electrodes [36]. An electrode material of synthetic boron-doped diamond has received much attention in recent years due to its capability in dealing with inert surfaces with low-adsorption properties. It reduces corrosion even in strongly acidic media [37]. Many studies were made by combining RuO 2 with low-cost metal oxides such as SnO 2, MnO 2, NiO, VOx, TiO 2, MoO 3, WO 3 and CaO to form composite oxide electrodes [38].

Perovskite-type manganites and their derivatives offer high electronic conductivity and substantial electrocatalytic activity towards oxygen reduction at low temperatures with moderate thermal-expansion coefficients. All perovskite-related manganites show predominant electronic conduction with low-oxygen-ion diffusivity. Their transport properties and electrochemical activities are strongly dependent on the oxygen stoichiometry [39]. Polymer-based electrodes are commonly used in energy-storage devices due to their easy synthesis, low environmental effect and low cost [40]. Polyaniline (PANI), polypyrrole (PPy), polythiophene (P3HT) and their corresponding derivatives are often used as electrode materials. Composite electrodes, particularly carbon nanotubes with conducting polymers, are also considered as an effective solution for improving the mechanical and electrochemical properties of electrodes [38].

Carbon materials are in use in many electrochemical applications due to their high electrical and thermal
conductivity, diversified crystallinity, morphology, porosity, reasonably high corrosion resistance and low thermal expansion. Besides, carbon electrodes can be made from biomass at a relatively low cost. Carbon exists in various allotropic forms such as diamond, graphite, amorphous carbon, graphene and fullerenes, and as nanotubes. Carbon is mainly used as an electrode, either directly as an electrocatalyst or as a conductant for electrochemically active materials [41, 42]. 3D porous carbonaceous electrodes are favoured in electrocatalytic applications due to their advantages such as high electronic conductivity, tuneable molecular structures, abundance, enhanced accessibility to active sites and transport properties of reaction-relevant species, increased electron transfer through the entire electrode and strong tolerance with acidic and alkaline media [43]. Pure carbon is inert in many electrochemical reactions. Surface or sub-surface modifications of carbon are carried out to increase the binding energies of reactants and reaction intermediates onto carbon, which naturally enhances the performance of electrochemical reactions [44]. The doping of non-metals and transition metals into the carbon matrix is an effective way to alter the electronic properties of carbon and create active sites for electrochemical reactions, especially HER. Non-metal atoms such as N, B, S and P-doped carbons such as carbon-black, hollow-sphere and graphene-like structures are the potential materials for HER. Boron-doping in a carbon matrix is significantly less effective than doping with N and S [45]. Dual heteroatom-doped carbons are also used in the development of advanced bifunctional catalysts [46]. A composite of mesoporous carbon with N, S co-doped graphene nanosheets (MC/NSG) showed better performance in electrocatalytic activity in ORR and OER reactions than un-doped mesoporous carbon with graphene (GC). MC/NSG has many mesopores with an average pore size of 4 nm, high surface area of 1730 m²g⁻¹ and a surface area of 1032 m²g⁻¹ [47].

Currently, metal- and metal-oxide-based bifunctional electrocatalysts are developed to overcome the problems of the intrinsic sluggish kinetics of two reactions (ORR and OER) so as to enhance the scope for commercialization. These catalysts have become promising alternatives due to their structural and compositional active sites of oxygen. For instance, Pt-based materials have been considered as state-of-the-art catalysts for ORR, while RuO₂ and IrO₂ are highly efficient in the OER reaction. However, RuO₂ and IrO₂ show poor performance in OER and Pt shows inferior activity for the OER. In addition, transition-metal-oxide-based catalysts are poor in ORR reactions, which is possibly related to the strong bond strength between OOH*/OH* intermediates. The active sites manifesting poor electronic conductivity hamper the performance [48–50]. In order to improve the performance of electrochemical reactions, doping with electron donors or decoration with conducting materials are possible improvements [51]. Metal nanoparticles encapsulated in carbon nanotubes (CNTs) offer a unique host–guest electronic interaction that can modify the redox properties of the surrounding carbon layer and thus lead to the formation of catalytic functionalities in ORR and OER reactions. Various transition-metal nanoparticles (M = Fe, Co, Ni) encapsulated in nitrogen-doped multiwall carbon nanotubes (MWCNTs) are evaluated for their performance in ORR and OER reactions.

Among them, Co/N-CNT catalysts exhibit high efficiency and proper performance under alkaline conditions. They have a higher half-wave positive potential (0.84 V) than Fe/N-CNTs (0.81 V). All the above catalysts show enhanced ORR catalytic activity compared to MWCNTs, whereas Ni/N-CNT catalysts exhibit poor activity in terms of the onset potential (0.91 V) and half-wave potential (0.73 V) [52].

A carbon-doped RuO₂-based electrode layer is reported to improve the homogeneity of the electrochemical reaction. It is known to reduce the ionic resistance of the metal oxide, expand the active sites and increase the electrical conductivity with a consequent increase in the power and energy densities of the electrochemical device [53]. In addition, ruthenium oxide is highly electrically conductive due to its low resistivity (10⁻³ Ω cm). Nanostructured porous carbon has micropores and mesopores with long-range disordered structures [54]. Three categories of pores are known with respect to interlayer-spacing values such as micropores (d < 2 nm), mesopores (d = 2–50 nm) and macropores (d > 50 nm) [55]. Nanostructured carbon materials are advantageous relative to other carbon materials due to their nanodimensions. These consist of fullerene, graphene, carbon nanotubes (CNTs) and their derivatives including quantum dots, nanofibres, nanoribbons, nanospheres, nanocapsules and other nanostructured morphologies. Carbon quantum dots (CQDs) and graphene quantum dots (GQDs) are considered for employment as electrode materials due to their excellent physical and electrochemical properties such as redox properties, high electrical conductivity, low toxicity, biocompatibility, size-tunability and high stability [56, 57]. CQDs are in the size range of 1–10 nm and are in the category of zero-dimensional carbon materials [58, 59] with both sp²- and sp³-hybridized carbon atoms, whereas GQDs have sp³-hybridized carbon only [60]. CQDs are known for their photoluminescence, low toxicity, chemical inertness, excellent biocompatibility, good multiphoton excitation, water solubility and environment friendliness [61, 62]. CQDs have large specific surface areas and unique electron-transfer abilities with excellent electrochemical reactions [63, 64]. In addition, preparations of CQDs from biomass exhibit an ideal choice for generating a variety of low-cost and sustainable carbonaceous materials. Recently, carbon-based electrocatalysts derived from biomass have been employed in electrochemical-conversion processes. Pd/CQDs composite exhibited high performance in methanol oxidation due to the electrochemically active area of glassy carbon electrode (GCE),
which increased from 0.12 cm$^2$ for Pd/GCE to 0.22 cm$^2$ for Pd/RCQDs/GCE [65].

2 Effect of reaction parameters affecting biodiesel yield

The parameters affecting the biodiesel yield in electrocatalytic processes are voltage, stirring rate, electrode type, water content, co-solvent type, reaction temperature, reaction duration, oil-to-methanol molar ratio and concentration of NaCl. A comparison of the performance of electrocatalytic processes in biodiesel production is presented in Table 1.

2.1 Effect of electrode materials

Generally, ion-exchange resins are suitable catalysts for esterification and transesterification, and can be used as strong-acid and basic catalysts. Therefore, hybrid ion-exchange resin-grafted electrodes are used in electrocatalytic systems for biodiesel production. The hybrid electrodes consist of stainless-steel (SS) woven wire cloth coated with an anion- or cation-exchange resin pastes, which are called hybrid anion-exchange chromatography (AEX) and cation-exchange chromatography (CEX). Both electrodes are made using a pore-filling method across the porous SS wire mesh. The two electrodes are placed inside the cell at a distance of 30 mm. Electrolysis is carried out at 40°C for an applied voltage of 20 V employing SS mesh and hybrid electrodes of anion-exchange (hAEM) and cation-exchange (hCEM) resin. The hybrid electrode coated with hCEM did not give a favourable result (conversion rates <15%) when used as a cathode and conversion was <22% when used as an anode (Fig. 4a and b) [22]. The above result indicates the reverse-bias conditions occurring in the electrochemical cell that are similar to the operation mode of bipolar membranes in the electrodialysis process [66, 68].

The efficiencies of SS mesh (SS 316 L) electrodes are higher than those of the hybrid electrode (hAEM) as the SS 316 L has lower electrical resistivity (7.4 × 10$^{-7}$ ohm-m) than epoxy resins (10$^{10}$–10$^{13}$ ohm-m) [69]. Ion-exchange resins made of polymeric materials have low electrical conductivity, as resins have moderate catalytic activity [70]. Therefore, hybrid electrodes do not dissociate efficiently at 20°C (20 V) in mixtures containing triglycerides and methanol. The same hybrid electrodes (hAEM) give a high conversion rate at 40°C (20 V) in the ethanolic solution. This revealed that the performance of hAEM in the electrolysis process is not effective at 20°C, whereas it performed well at 40°C. Thus, the electrocatalytic process could not eliminate heating as being practised in conventional transesterification. In addition, the above study did not mention the role of anion- or cation-exchange resin and the name of the resins used as electrodes. Generally, anion-exchange resins consist of a polymeric matrix with various functional groups (OH$^-$, RO$^-$ or HCO$_3^-$) containing weak basic anions of tertiary amino groups. Most of the weak basic anion exchangers are of amino groups whereas strongly basic resins have quaternary amino groups. Both are in the form of a gel or macroporous ammonium groups. The cation-exchange resins are a cross-linked polymer with negatively charged structural units and is capable of undergoing exchange reactions with cations Na$^+$ (Kayexalate) or Ca$^{2+}$ (calcium resinum) or K$^+$ [72, 73].

A trimetallic nanoalloy (PtIrRu) electrode was employed in transesterification of Amalfi-coast waste lemon-seed oil, which gave a conversion of 98.2% under optimum voltage (15 V), NaCl concentration (0.3 wt.%), methanol-to-oil molar ratio (10:1), water content (2 wt.%), reaction temperature (20°C) and duration (2 h) [66]. This study did not give details of the fabrication of the electrocatalytic reactor, especially the distance between the two electrodes. Electrical conductivity has a bearing on the nature of the electrode materials and the distance between them [74]. Thus, the PtIrRu electrode gives higher conversion than SS mesh and hybrid electrodes due to the high surface area of the electrode and high electrical conductivity of the metal nanoparticles with a short distance between the electrodes. In addition, Pt has low electrical resistivity (10.60 × 10$^{-4}$ ohm-m), high electrochemical stability, high adsorption capability of organic and inorganic molecules, and low energy consumption for HER and OER reactions in aqueous media. In this study, Pt is combined with iridium (Ir) and ruthenium (Ru), and thus the metallic alloys improve the electrocatalytic behaviour. Modification of the electronic structure and a decrease in the interatomic distance shifts the d-band structure of Pt by doping with Ir and Ru, resulting in enhanced catalytic activity due to the reduction in the adsorption and dissociation energies for different species, e.g. H$_2$ [75–77]. Ir-based alloys as electrocatalysts show good electrochemical activity for electrochemical reactions. In addition, Ru is an alternative low-cost and stable material as compared to Pt, which shows a comparable hydrogen-bond strength (~65 kcal mol$^{-1}$) [78]. In addition, the size of the PtRuIr alloy is 2.5 nm, which enhances the catalytic property due to its high surface-to-volume ratio and high conductivity [79]. The surface layers of metal nanoparticles have many corners and edges with a relatively high density of low-coordination sites. These surface properties enhance the interaction between catalysts and the intermediate molecules (methoxide or ethoxide ions and triglycerides) in an electrolyte solution [80]. Thus, the metal-alloy nanoparticles exhibit high electrocatalytic activity compared to SS mesh and hybrid electrode materials (hAEM and hCEM), but are more costly than SS mesh and hybrid electrodes. Recently, a electrocatalytic reactor was made using graphite-plate electrodes (22 × 22 mm) that were separated by various distances of 5, 10, 15 and 20 mm.
| Vegetable oil                  | Electrodes                     | Catalyst                  | Co-solvent | Electrolyte | Electrocatalytic reaction conditions                                                                 | Biodiesel yield (%) | Reference |
|-------------------------------|--------------------------------|---------------------------|------------|-------------|------------------------------------------------------------------------------------------------------|---------------------|-----------|
| Waste cooking oil (WCO)       | Graphite plates                | Zeolite/ chitosan/KOH     | Acetone    | NA          | Catalyst 1 wt.%, oil-to-alcohol ratio 1:7, electrolysis voltage 40 V, water 2 wt.%, room temperature, stirring rate 100 rpm, duration 3 h | 93                  | [13]      |
| Used cooking oil              | Graphite plates                | Chitosan                  | Tween 80, THF | NaCl        | Catalyst 10 wt.%, electrolysis voltage 18 V, duration 4 h, water 2 wt.%, co-solvent-to-methanol molar ratio (100:1) | 59.1 (without co-solvent) | [25]      |
| Used cooking oil              | Graphite plates                | CaO-900-600               | Absence of solvent | NA          | Catalyst 20 wt.%, oil-to-methanol molar ratio 1:6, electrolysis voltage 18.2 V, duration 1 h, room temperature | 98.58               | [15]      |
| Soybean oil                   | Graphite plates                | CaO-900-600               | Absence of solvent | NA          | Catalyst 20 wt.%, oil-to-methanol molar ratio 1:6, electrolysis voltage 18.2 V, duration 1 h, room temperature | 97.35               | [15]      |
| Waste cooking oil             | Platinum electrodes            | Absence of catalyst       | THF        | NaCl        | Oil-to-methanol molar ratio 1:24, electrolysis voltage 18.6 V, duration 2 h, THF/methanol molar ratio 0.25, NaCl (> 1.1 < 1.2) | >97                 | [16]      |
| Corn oil                      | Platinum electrodes            | Absence of catalyst       | THF        | NaCl        | Oil-to-methanol molar ratio 1:24, electrolysis voltage 18.6 V, duration 2 h, THF/methanol molar ratio 0.25, NaCl (> 1.1 < 1.2) | >97                 | [16]      |
| Waste oil                     | Graphite electrodes            | Zeolite                   | THF        | KOH         | Catalyst 2 wt.%, oil-to-methanol molar ratio 1:9, THF 10 wt%, electrolysis voltage 10 V, duration 4 h | 90                  | [23]      |
| Canola oil                    | SS wire-mesh and hybrid electrode (ion-exchange resin-catalyst) | Without addition of external catalyst | Absence of solvent | NaCl        | Oil-to-methanol molar ratio 1:10, NaCl 0.3 wt%, deionized water 1 wt%, electrolysis voltage 20 V, reaction temperature 40°C, duration 1 h | 87 (hybrid electrode); 81 (plain SS electrode) | [22]      |
| Amalfi-coast waste lemon-seed oil | Trimetallic nanoalloy (PtIrRu) | Absence of catalyst       | Absence of solvent | NaCl        | Oil-to-methanol molar ratio 10:1, NaCl 0.3 wt.%, water 2 wt.%, electrolysis voltage 15 V, reaction temperature 20°C, duration 2 h | 98.2                | [66]      |
| Waste cooking oil             | Graphite                       | NaOH and KOH              | Acetone    | NaOH+H₂O    | Catalyst 1 wt.%, acetone 10 wt.%, methanol-to-oil molar ratio 1:7.5, distance between electrodes 1 cm, electrolysis voltage 40 V, water 2.0 wt.%, reaction temperature 20°C, stirring rate 300 rpm, duration 2 h | NaOH (98)            | [67]      |

Table 1: Comparison of the performance of electrocatalytic processes in biodiesel production as reported.
to produce biodiesel from WCO. The maximum conversion (98%) is achieved at a distance of 10 mm. However, the study revealed that the distance between the two electrodes was not a major issue in biodiesel conversion [67]. Graphite electrodes with different dimensions (0.8 × 130 mm) are used in an electrocatalytic cell for biodiesel production from soybean oil. The dimensions of electrodes differ from those in the above study. Graphite electrodes give high conversion in soybean oil (97.5%) [15] and WCO (98%) [67] at an ambient temperature of 25°C whereas the plain SS electrode (81%) and hybrid electrode (87°C) give low efficiencies at 40°C [22]. Therefore, selection of the electrode material is a significant factor for electrocatalytic reactions.

2.2 Effect of electrolysis voltage

The electrocatalytic mode of biodiesel production from canola oil using methanolic or ethanolic solution across a series of cell voltages from 10 to 40 V at 20°C and 40°C was investigated [22] (Fig. 2a–d). The conversion was made using an SS mesh electrode and the efficiency was relatively low at 20°C as compared to 40°C. However, when the electrocatalytic reaction was carried out using a hybrid electrode coated with the anion-exchange resin (hAEM), the biodiesel yield remained the same at both reaction temperatures at 20 V. The FAME-conversion rate decreased at high voltages (20–40 V) at 20°C due to hydrogenation and saponification of the reaction mixture [4, 22]. The electrocatalytic conversion of the canola oil was 60% at 40 V at a reaction temperature of 40°C when a plain SS mesh electrode was used. The study revealed that the reaction temperature (40°C) had a limited impact on the biodiesel yield by hAEM [22]. The above study indicated the need for a high voltage as well as a high temperature (40°C), which are not favoured in large-scale commercial operations. The effects of different voltages (20–55 V) were investigated when biodiesel was made from WCO. The yield of esters was >92% at 40 V [24]. The maximum FAME-recovery efficiency (98%) was observed at 40 V [67]. The electrodes needed such a high voltage (40 V) [22, 67] due to the continuous formation of hydroxide ions on the cathode material. The interaction of hydroxyl ions and methanol makes transesterification easy [24, 67]. In addition, a high catalytic voltage affects the chemical-bond structure of methyl esters. Besides, a high voltage may cause excessive ionization at the anode. Power consumption is directly proportional to the anode surface area. The power consumption can be minimized by reducing the surface area of the anode [74].

Further studies conducted using a low voltage [15, 21] indicated that the hydroxide-ion concentration was influenced by the reaction rate [13, 21] and the FAME yield increased with an increase in the electrolysis voltage [13] from 5 to 18.6 V. A yield of 88.7% was obtained at 18.6 V using Pt electrodes when the NaCl concentration was 0.56% by weight [21]. The yield of FAME and the generation

![Graph showing the effect of electrolysis cell voltages and temperatures on the conversion of canola oil in a methanolic reaction mixture at (a) 20°C and (b) 40°C. (c) and (d) Photographs of the reaction products with stainless steel (SS) mesh and hAEM electrodes at 40°C (Source: https://doi.org/10.3389/fmats.2017.00022)](https://doi.org/10.3389/fmats.2017.00022)
of OH– ions were directly proportional [13]. In addition, the increase in electrolysis voltage significantly affected the FAME production. Electrolytic voltages of 10, 18.2 and 20 V were applied in the transesterification of soybean oil using the catalyst CaO-900-600 in which a biodiesel yield of 86.57% was obtained in 60 min at 18.2 V with calcium oxide as a solid-base catalyst [15].

From the above studies, it is known that the electrolysis voltage, oil-to-methanol molar ratio and catalyst are inter-related. Graphite electrodes consumed a high voltage in a low oil-to-methanol molar ratio (1:7) [13] whereas Pt electrodes offered high efficiency with low energy consumption in a high alcohol-to-oil molar ratio [21]. Graphite electrodes achieved high conversion efficiency in the presence of a highly effective catalyst (CaO-900) by a low oil-to-methanol molar ratio (1:6) and electrolysis voltage (18.2 V). CaO may participate in the electrochemical reaction that may increase the oxidation and reduction process. This takes place either at the surface of the electrode or at the body of the electrode itself. Hydroxide ions (OH–) are continuously produced at the cathode, which may in turn increase the potential of the cathode. The hydroxyl ions formed may react immediately with methanol and oil to produce methyl esters. The catalysts with high catalytic activity promoting high electrical conductivity of the electrodes easily dissociate triglyceride molecules along with methanol or ethanol. The electrical conductivity of the reaction mixture is proportional to the concentration of the catalyst present in the solution [15, 21].

### 2.3 Effect of electrolysis time

A high yield of biodiesel (34.2%) was achieved from WCO using 10 wt.% of chitosan at 4 h and the recovery decreased to 5.1% when using cooking oil for a reaction duration of 6 h [25]. The biodiesel yield from WCO was observed to increase gradually with the concentration of the electrolyte. However, invariably, the electrical conductivity of the reaction mixture is proportional to the concentration of the catalyst present in the solution [15, 21].

The transesterification reaction that included n-hexane, heptane, carbon dioxide, diethyl ether, dimethyl ether, tert-butyl methyl ether, acetone, 2-propanol, tetrahydrofuran and ethyl acetate [13, 23, 25, 29, 81, 82]. Acetone has a low cost and is the best co-solvent for transesterification [82]. Acetone improves the miscibility and homogeneity of the mixture, which in turn increases the mass-transfer resistance. However, invariably, the electrical conductivity of the solution decreases at a high concentration of co-solvent [13].

Putra et al. (2014) investigated the biodiesel production from WCO using two different solvents, namely Tween 80 and THF (Scheme 1). The FAME yield was low in Tween 80 due to non-polarity with low kinematic viscosity causing the inhibition of the catalytic activities of chitosan in the transesterification and hydrolysis reactions [29]. The THF-to-methanol molar ratio (0.25) gave a biodiesel yield of 93.7% in an hour while higher ratios reduced the yield. The miscibility improved due to the addition of THF, whereas the initial electrical conductivity and mass-transfer resistance decreased [21]. Another study suggested that the addition of co-solvents THF and hexane permitted the reaction to be completed under mild conditions due to the low critical properties of the reaction mixture. Hexane as a solvent for vegetable oil was used in the continuous production of biodiesel in supercritical methanol [83].

By increasing the amount of acetone as the co-solvent (from 5 to 10 wt.%) in the transesterification mixture, the FAME yield increased marginally from 92% to 93% while the conversion decreased to 90% at high amounts (12.5 and 15 wt.%) as the high concentrations of acetone reduced the electrical conductivity of the reaction mixture [13]. The high amount of acetone in the reaction mixture did not give a significant difference in the biodiesel yield from WCO. Increasing the amount of acetone affected the separation of the biodiesel from the glycerol and residual triglycerides, and hence extended the time required for the
Hexane as a co-solvent was favourable for biodiesel conversion at a low reaction temperature due to controlled mass transfer whereas, at a high reaction temperature, no impact was observed [84]. The addition of a co-solvent accelerated the reaction rate and also reduced the molar ratio of the oil to methanol or ethanol. However, it would require specific equipment to recover the solvents and to isolate toxic volatile compounds if done on an industrial level [4]. As a result, co-solvents are seldom used [85]. In the normal process, there will be poor miscibility of oil with methanol due to the high polarity of methanol and the miscibility can be enhanced by the use of ethanol [86]. In addition, the miscibility of the reactants (canola oil, alcohol, water and NaCl) is improved by enhancing the reaction temperature and stirring rate. Allioux et al. (2017) achieved a high electrolytic-conversion rate (>80%) from canola oil without the addition of a co-solvent [22].

### 2.5 Effect of oil-to-alcohol molar ratio

The electrical conductivity of the reaction mixture containing oil and methanol at a ratio of 1:6 was relatively low before electrolysis. In addition, the active-species-formation rate and the electric current at the cathode were low at a relatively high concentration of NaCl (0.156 mS m⁻¹ at a NaCl concentration of 0.56 wt.%), which reduced the FAME conversion [21]. The electrical conductivity of the reaction mixture prior to electrolysis was very low, even with a high concentration of catalyst (0.1 wt.% and with a 1:3 oil-to-methanol molar ratio. When the oil-to-methanol ratio was increased (from 1:7 to 1:9), the electrical conductivity decreased, since it limited the concentration of the catalyst in the mixture due to the enhanced volume. The maximum yield of biodiesel was reported with an oil-to-methanol molar ratio of 1:7 with 1% by weight of catalyst zeolite/chitosan/KOH [87, 88]. Guan and Kusakabe (2009) reported that, at a high electrical conductivity (150 mS m⁻¹) and with a high molar ratio of 1:12 of oil to methanol with 0.56 wt.% of NaCl, the maximum yield of biodiesel was obtained [21]. But the electrical conductivity of the reaction mixture decreased as the molar ratio increased [66].

### 2.6 Effect of reaction temperature

Many workers did not consider the effect of the reaction temperature [13, 23, 25, 29, 67]. Allioux et al. (2017) investigated the effect of temperatures (20°C and 40°C) using
plain SS wire-mesh and hybrid electrodes. The miscibility of the components of the reaction mixture (canola oil + alcohol + water + NaCl) was also governed by the reaction temperature and the stirring speed of the electrocatalytic reactor without the addition of any co-solvent. The biodiesel conversion was observed to be better at 40°C in the plain SS electrode. The overall biodiesel conversion rate was also high with the hybrid electrode at 20°C due to the catalytic activity of the anion-exchange resin (Fig. 2a and b) [22].

2.7 Effect of pH of the reaction mixture and its electrical conductivity

The electrical conductivity of the medium and pH of the electrolytic cell were investigated by Allioux et al. (2017) (Fig. 5a and b). Sodium chloride (NaCl) as the electrolyte (0.3 wt.% of the canola oil) was well below the solubility limit. NaCl crystals completely dissociated in the mixture (water and alcohol) at the beginning of the reaction itself. The pH increased from an initial value of 5 to 9 during the reaction period irrespective of the type of electrode and temperature (Fig. 5a). The increase in pH was due to the formation of OH− from water molecules and CH3O− from methanol molecules. The pH values were observed to be stable at >10 V, which indicated that the electrochemical reactions formed reactive species and reaction products. The initial electrical conductivity was measured to be very low (355 µS cm−1) at 0 V due to the low water content (<1 wt.%) and also due to the high resistivity of the methanol and canola oil mixture. Low electrical conductivity (10 and 20 V) demonstrated the formation of methyl esters along with the consumption of water and methanol molecules. At high voltages (30 and 40 V), the electrical conductivity increased (Fig. 5b), which may be due to the formation of ions and charged soap species as a result of saponification [22]. The electrical conductivity of the reaction mixture was evaluated with varying water contents (0.1, 2 and 4 wt.%), electrolysis times (0–60 min) as well as pH. A high water content (2.0 and 4.0 wt.%) of the reaction mixture showed high electrical conductivity (~122 mS m−1) at a pH of 11.9 before the beginning of the reaction (0 min) whereas the electrical conductivity decreased as a function of the electrolysis time. The pH of the mixture increased from 7 to 12 in 20 min and then stabilized during the next 20 min, causing enhancement of the reaction. On the other hand, the electrical conductivity of the reaction mixture reduced within 20 min and subsequently remained at a constant value [21].

2.8 Effect of water content

The biodiesel yield from corn oil was 93.7% when the water content was 2% by weight in 1 h without the addition of a catalyst. In electrolysis, the most active region is closer to the cathode where the water is localized and electrolysed. When the water content was increased to 4% by weight, the biodiesel yield reduced to 54.4%, indicating that the excess water had had a negative effect on the transesterification reaction. The FAME yield started increasing sharply during the initial stage at 5–10 min and reached a peak in 20 min, registering a yield of 95.2% with a low water content (0.1 wt.%) [21].

2.9 Effect of NaCl concentration

The effect of the electrolysis duration on the yield of FAME from corn oil and WCO was investigated with a high oil-to-methanol molar ratio (1:24) with various concentrations of NaCl (0.14, 0.28 and 0.56 wt.%). At a high concentration of NaCl (0.56 wt.%), the biodiesel yield increased to 97.9% in 2 h at 0.05 A in the presence of water (2 wt.%). The reaction rate was slightly lower with a low
concentration of NaCl (0.28 wt.%), which attained a FAME yield of 94% in 2 h at 0.03 A [21]. The biodiesel production from lemon-seed oil through the electrolysis process was studied by varying the electrolysis duration with different NaCl concentrations (0.1, 0.2, 0.3 and 0.6 wt.%). The biodiesel yields gradually increased by increasing the electrolysis time in all the concentrations of NaCl. The biodiesel yield attained 89.79% in 1.5 h and further increased up to 98.20% in 2h at 0.6% by weight with an electric current of ~0.052 A. At 0.3% by weight of NaCl, the biodiesel yield increased to 95.12% in 2 h at an electric current of 0.034 A [66]. Qualitative evaluation of the biodiesel obtained from the electrolysis process showed that chlorine gas had not been liberated in any of the samples [21].

3 Conclusion

Electrocatalytic transesterification is an impressive method for the production of biodiesel. The various parameters involved are the electrolysis voltage, duration, quantity of co-solvent, water content and oil-to-methanol molar ratio. As the constituent of the cathode plays a decisive role, the search for new materials for making electrodes with high catalytic activity is being intensified. In that way, nanostructured materials have shown good results in recent years due to their extraordinary mechanical, electrical and optical properties that emerge as a result of the combination of bulk and surface properties. Biomass-derived carbon quantum dots with metal or metal-oxide nanoparticles have been tried as electrode materials in electrocatalytic reactors, which may revolutionize the biodiesel production as CQDs have excellent physical and chemical properties. They are less toxic and environmentally friendly. Research is needed to investigate the possibility of electrocatalytic processing at room temperature. Ideal electrode materials are also being identified. The addition of a co-solvent to accelerate the reaction rate is being tried but it increases the cost of biodiesel. In addition, co-solvent-assisted processes need specific equipment to recover and recycle the solvents from the finished products at industrial scales. Studies are needed to know the role of materials involved at the cathode, especially in the context of high stirring rates. Many studies conducted in a laboratory are not scalable. Pilot plant trials are needed to translate the results up to the industrial scale on the development of electrocatalytic processes in large-scale application.

Conflict of Interest

None declared.

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