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Recent advances on the catalytic conversion of waste cooking oil

Mohamad R. Khodadadi ^a, Irene Malpartida^b, Chi-Wing Tsang ^c, Carol Sze Ki Lin ^d and
Christophe Len ^{a,e,*}

[a] Chimie ParisTech, PSL Research University, CNRS, Institute of chemistry for Life and Health Sciences, 11 rue Pierre et Marie Curie, F-75005 Paris, France

[b] Deasyl, S.A., Plan-les-Ouates, Geneva, Switzerland.

[c] Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, 20A Tsing Yi Road, Tsing Yi, Hong Kong

[d] School of Energy and Environment, City University of Hong Kong, Kowloon Tong, Hong Kong

[e] Université de Technologie de Compiègne, F-60200 Compiègne, France

E-mail address: christophe.len@chimieparistech.psl.eu (C. Len)

Abstract: The recovery of waste cooking oil has long been known for second life uses without chemical modification. However, the concepts of bioeconomy and circular economy are much more recent and include a ranges of tasks such as recovery, storage, use, chemical modification. International research into the use of modified and unmodified waste cooking oil and their potential uses has been the subject of incessant research in both academia and industry. The main purpose of this review is to present the recent breakthroughs obtained in the field of recovery of used cooking oils for the last decade. The review discusses advances

obtained in major production pathways recently explored splitting in the following categories:

(i) transesterification of waste cooking oil including biodiesel production with heterogeneous/homogeneous base and acid catalysis, magnetic heterogeneous catalysis, biocatalysis and alternative technologies such as electrolysis, continuous flow, microwave irradiation, ultrasound irradiation; (ii) transesterification of waste cooking oil including catalytic biolubricant production; (iii) interesterification; (iv) hydrolysis and (v) hydrodeoxygenation, hydrocracking and hydrogenation. This review also briefly overviews current understanding of waste cooking oil valorization and the underpinning mechanism.

Keywords: Biodiesel, Biolubricant, Hydrolysis, Hydrodeoxygenation, Interesterification, Transesterification, Waste cooking oil

1. Introduction

For several decades now, society has been facing major challenges directly related to our way of life. Indeed, the population and the increase in energy demand are constantly growing, while the scarcity of resources, food and water, combined with the depletion of fossil fuel resources, are factors of concern for future generations. In this context, scientists, governments, politicians and also citizens are involved in creating and promoting new practices and building a more sustainable future society. This societal change is not simple and requires major multidisciplinary joint efforts to develop greener technologies and more environmentally friendly methodologies. In this context, the use of renewable resources and its biorefinery concept are among the promising alternatives to meet some of these future challenges [1,2]. The recovery of biomass and biomass waste using processes similar to those used in petrochemicals enables the production of valuable chemicals, materials, fuels and

energy [3-5]. However, the use of biomass raises problems related to competition between food/feed and non-food chemistry. In addition, the increased use of biomass also has effects on land use and water availability. On the other hand, the use of biomass waste such as waste cooking oil (WCO) does not create competition between sectors and is therefore a preferred source since it allows for a second cycle (**Fig. 1**). WCO is an oil obtained after any frying process from kitchens and catering industries [6] and is produced at about 16.5 million tons per year [7].

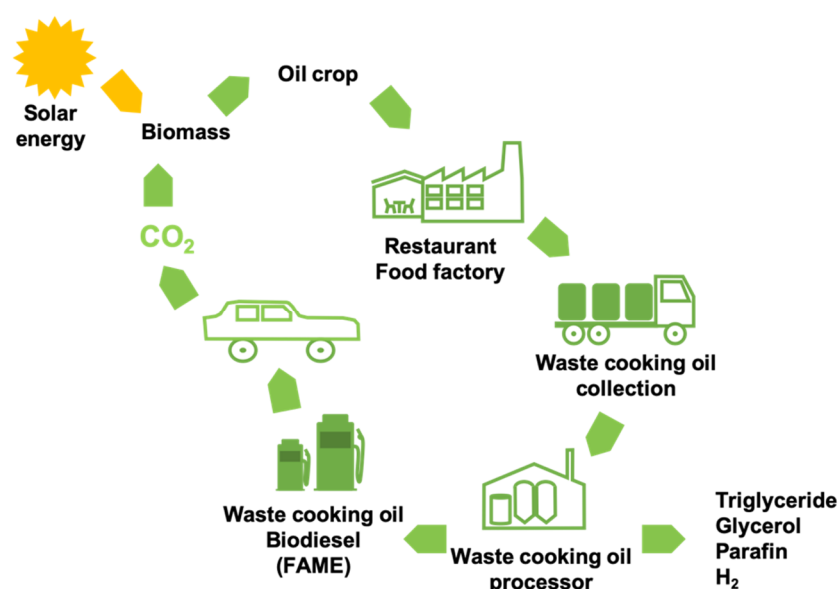


Fig. 1. A generalized map of WCO value chain.

WCOs are basically a mixture of triglycerides and fatty acids, contaminated by some derivatives during the frying process, as free fatty acids (FFA), heterocycles, Maillard reaction products, and metal traces originated from pads and food leaching [8,9]. The composition of WCO is different from that of refined and crude oils (**Table 1**). As the result of the high temperature during cooking, the exposure to air and the water from the food, oil undergoes many chemical and physical changes [10]. For example, triglycerides in the oil are hydrolyzed and this gives rise to an increase in free fatty acids (FFA).

Table 1

Observed chemical changes in oils after use in the frying and cooking processes.

Chemical reactions	Reaction cause	Change in chemical composition
Hydrolysis	Water contained in the food and atmospheric humidity interact with frying oil at high temperature	Production of free fatty acids and glycerol increasing the concentration of total polar molecules
Thermal degradation	Anaerobic degradation of triglycerides at high temperature	Production of alkanes, alkenes, symmetric ketones, oxopropyl esters, CO and CO ₂ , dimeric compounds
Oxidation	Reaction with surrounding atmospheric air/oxygen	Formation of hydroperoxide, change in the composition of conjugated dienes and trienes
Polymerisation	Reactions with in unsaturated fatty acyl groups at high temperature	Formation of polymerized triacylglycerides including dimers and oligomers

Valorization of WCO is of particular interest for two main reasons. First, WCOs are two to three times cheaper than virgin oils. Second, reusing and processing WCO instead of disposing of it down the drain, significantly reduces water treatment costs. It is noteworthy that disposal of WCO in nature affects flora and fauna due to its lower water solubility [11]. WCO can be used without special treatment as main raw materials in many industrial processes, such as bio-lubricant [12] or fuel [13,14] production, or as additives for asphalts [15] and animal feed [16]. WCO can be transformed chemically or biochemically to produce bio-plasticizers, syngas and sorbents for volatile organic compounds (VOCs) [17].

For the sake of clarity, this review focuses on the chemical and biochemical transformations of WCO in the past decade (i.e. from 2010 to 2020), which includes transesterification, interesterification, hydrolysis, hydrodeoxygenation, hydrocracking and hydrogenation using conventional sources of activation and alternative technologies. Transesterification of waste cooking oil is the most highly developed main topic on an academic and industrial scale due to its immediate potential economic impact. Selective reactions on the unsaturated bond of WCO such as epoxidation, dihydroxylation, carbonation and others were not included in this review.

2. Transesterification of waste cooking oil

Catalytic transesterification as main reaction is used for the valorization of WCO and permits the production of biodiesel and biolubricants using various types of catalysts such as heterogeneous and homogeneous catalysts, and enzymes [18].

2.1. Biodiesel production with catalyzed transesterification

Starting from WCO or pure oil, the produced biodiesel needs to match the standard of biodiesel according to ASTM D-6571 and EN 14214 international biodiesel standards. During the last decade, significant researches have been conducted in order to explore intensified technologies using innovative way such as catalysis, dedicated equipment [19-22].

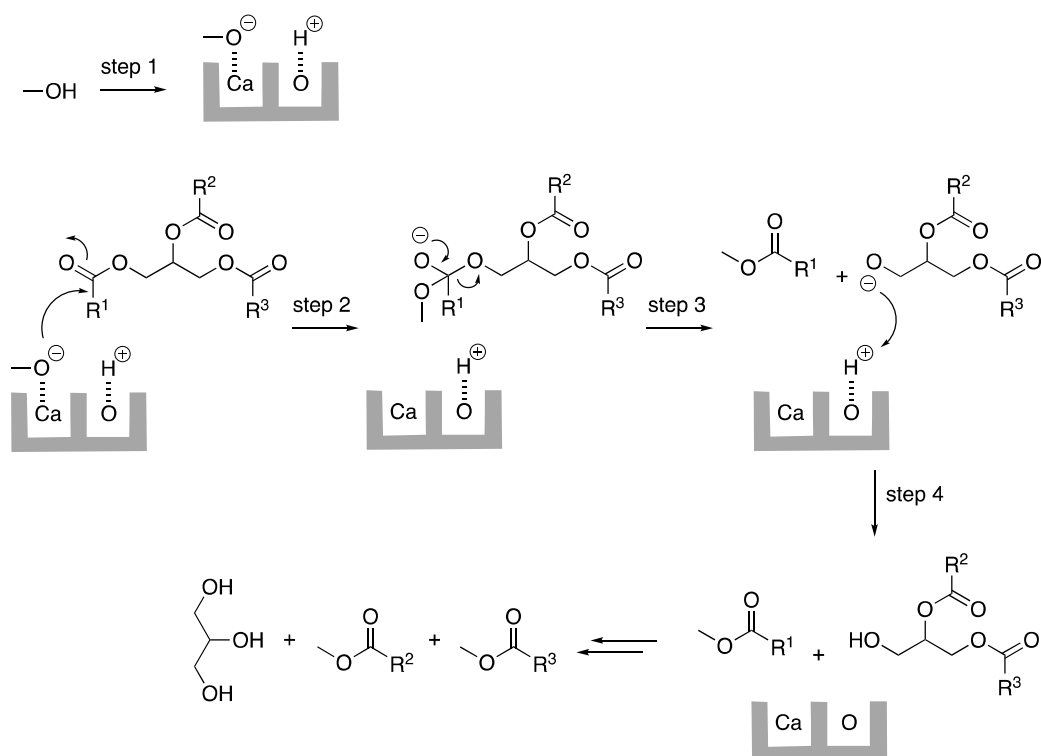
2.1.1. Heterogeneous base catalysis

Heterogeneous base catalysis for the production of biodiesel was well reported [23-30]. Among these catalysts, CaO is the most widely used especially because of its high availability and low cost [31]. General manner of converting eggshell to catalyst contain washing and removing the inner white membrane of the eggshell, drying at 100 °C, manually grinding and finally calcinations at 1,000 °C. Experimental results showed that 1.5 wt% of the catalyst in methanol-oil molar ratio of 12:1 reacting at 65 °C for 2 h are the optimal conditions to obtain approximately 98% of fatty acid methyl ester (FAME) [32]. Ostrich-eggshell and chicken-eggshell gave similar results although the CaO catalyst obtained from Ostrich-eggshell have higher surface area, higher basicity and smaller particle size.

Different ion metals such as lithium [33] and potassium [34] ions with CaO were investigated on the transesterification of WCO in order to introduce stronger heterogeneous base catalyst for the purpose of industrial scale up. Whatever the metal ion was used, maximum conversion of WCO was obtained at 65 °C for 2.5 h with methanol-oil molar ratio of 12-18:1. In addition, other types of metal such as metal salt (KBr) or metal oxide (MgO) are used with CaO to introduce more effective transesterification process and production of biodiesel on larger scales. In this context, diatomite impregnated MgO/CaO can be a competitive base catalyst with high conversion of WCO [35]. The maximum conversion of WCO was carried out at 90 °C for 2 h with methanol-oil molar ratio of 15:1, catalyst concentration of 6 wt% giving FAME in 96% yield. The reactivity of heterogeneous base

catalyst is explained by the presence of highly active alkoxide ions (MgO, CaO) when the alcohol reacted with base catalyst and their role in cleavage of triglycerides.

General mechanism for the production of biodiesel *via* transesterification in the presence of CaO starts with the formation of methoxide anion obtained after reaction between methanol and CaO (Step 1) (**Scheme 1**). The methoxide anion which is binded to the heterogeneous catalyst surface attacks carbon atom of the the carbonyl group at the primary position (Step 2) generating a tetrahedral intermediate. After rearrangement to form a diglyceride anion and a mole of methyl ester (Step 3), the resulting anion is then stabilized by a proton from the catalyst surface to form the diglyceride and regenerate the catalyst (step 4). Repeating the process two times would result in production of three moles of methyl esters and one mole of glycerol. In this case, calcium diglyceroxide can also participate as a catalyst of the process.



Scheme 1. Mechanism pathway for transesterification of triglyceride with methanol in the presence of CaO.

In general, heterogeneous base catalysts allow relatively fast reaction at mild condition with less energy requirement. As one main heterogeneous catalyst, recovery of catalysts via separation are easy and the recyclability is possible. Nevertheless, there are disadvantages. These catalysts are sensitive to FFA content and soap is formed when FFA content in WCO is higher than 2 wt%. Moreover, the formation of soap decreases the FAME yield and cause problem during the extraction. Common with a lot other heterogeneous catalyst, leaching of the active site may result product contamination of the target.

2.1.2. Heterogeneous acid catalysis

Number of heterogeneous acid catalysis is steadily growing and shows high activity and good tolerance to water and free fatty acids, and they do not corrode the equipment. The commonly used materials that are used in this process can be categorized into solid acid catalyst using sulfate or sulfuric acid [36,37], heteropolyacid [38], acidic ionic liquid [39], oxide supported catalyst [40] such as titanium oxide [41], alumina oxide [42,43], niobium oxide [44,45] and using modified resins [46]. Heterogeneous acid catalysts can be reused for several reactions cycle and the mass diffusion limitation can be overcome with providing more active reaction site in comparison of heterogeneous base catalyst. Niobium compounds have been found as very efficient catalysts and supports in several heterogeneous catalysis reactions. Niobium oxides have a tendency to form structural defects and to present acid properties and have the potential to exhibit strong metal-support interactions. It was found that 25 wt% of 12-tungstophosphoric acid (TPA) impregnated on Nb_2O_5 catalyze transesterification and esterification of WCO simultaneously. It was found that, at 200 °C, alcohol-oil molar ratio of 18:1 and 3 wt % catalyst loading, a maximum ester yield of 92 % could be obtained [47]. Production of biofuel from WCO was realized through reaction with sulfonated carbon microsphere (CM-SO₃H) catalyst [48]. It is a type of sugar-based catalyst,

in which xylose is carbonized incompletely in presence of sulfonate ion. Modifying carbon sphere needs immersing of incomplete carbonized carbon in H_2SO_4 at $190\text{ }^\circ\text{C}$ for 24 h. In this step, xylose is dehydrated to furan as an important intermediate for carbonization and the carbon-based catalyst has a high acidity and acid strength with total acid sites of 1.38 mmol g^{-1} . The result of catalyst characterization using Fourier transform infrared spectroscopy showed that catalyst comprises of sulfonic group (SO_3H) and carboxyl (COOH) functional group. The strength of acid functional groups was confirmed with NH_3 -TPD (temperature programmed desorption) and are 0.31 mmol g^{-1} and 1.07 mmol g^{-1} , respectively. One of the benefits of this type of catalyst is the opening up of a new route to the use of H_2SO_4 in industries and introducing a greener process for biodiesel production. Catalytic testing during biodiesel production showed high FAME yield (90%) from transesterification of WCO at $110\text{ }^\circ\text{C}$ for 2 h with methanol-oil molar ratio of 10:1, in the presence of 10 wt% of catalyst. Furthermore, the catalyst can be reused for 3 cycles of repeated reaction. However, it should be noted that an overloading of catalyst for more than 10 wt% can induce soap formation and the stability of this type of catalyst needs to be improved due to leaching of sulfuric acid and acidity of the catalyst. This work is interesting since both the catalyst and the oil were obtained from biomass (**Fig. 2**). It is noteworthy that this concept to use biomass as support for catalyst was demonstrated by Len for furfural production in valorization of Sporopollenin [49].

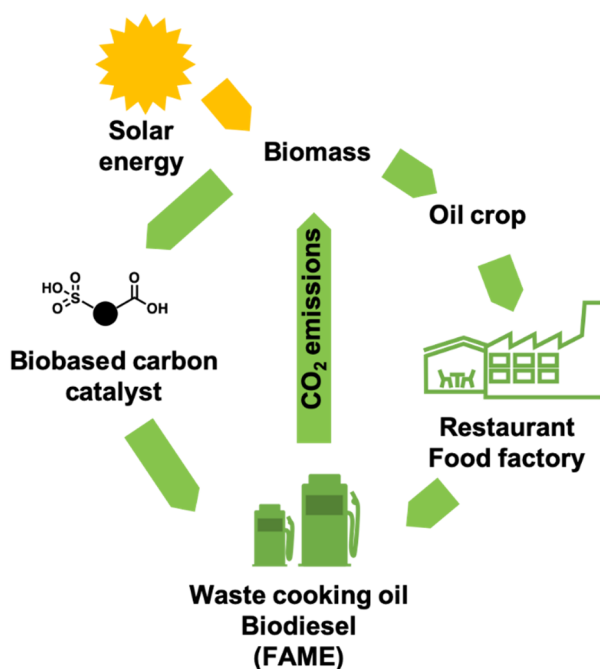


Fig. 2. Integrated biomass valorization for production of waste cooking oil.

Preparing heterogeneous catalyst using sulfate or sulfuric acid with immobilizing the ionic liquid on silica-gel is another route for developing novel heterogeneous catalyst. A silica-gel with 1,3-propyl sulfonic acid lactone and H_2SO_4 was produced and applied to conversion of WCO [39]. The acid liquid having propyl chain as linker could be immobilized on silica gel with a high specific surface area and a pore size of $523.7 \text{ (m}^2 \text{ g}^{-1}\text{)}$ and 1.144 (nm) , respectively. This formed ionic liquid on silica gel could behave as a reusable solid catalyst for 5 times. This result is proved with thermal stability analysis of the catalyst that showed ionic liquid is well immobilized on the silica gel and it could maintain stable below $250 \text{ }^\circ\text{C}$. Even if the structure and nature of the ionic liquid is different, this result is interesting since our group reported the instability of ionic liquid under different drastic conditions [50-53]. The authors reported that the four factors: methanol-oil molar ratio, catalyst amount, reaction time and temperature play important role on the yield of biodiesel. The optimized conditions

requested methanol-oil molar ratio of 25:1, 5 wt% of catalyst at 60 °C for 20 h and led to production of FAME in 88% yield.

Recently, the catalytic activity of metal solid acid TiO_2 supported on mesoporous silica for esterification of WCO to FAME was reported [54]. The catalyst is synthesized with wet chemical method in two steps. The first step was impregnation of SBA-15 with $\text{Ti}(\text{SO}_4)_4$ followed by calcinations at 540 °C. It was interesting to find that the activity of this catalyst is proportional to the acid density of the catalyst surface. The sample catalyst with a good specific surface area of $733.98 \text{ (m}^2 \text{ g}^{-1}\text{)}$ can result a high biodiesel yield 95%. The optimum FAME yield obtained was at reaction temperature of 200 °C, methanol-oil molar ratio of 15:1, catalyst loading of 1 wt% and a short reaction time of 30 min. Under this condition, reusability of catalyst was examined for three times with 90% efficiency and good stability. However, this catalyst requires a high reaction temperature in comparison to homogeneous catalyst which is a negative factor for industrial application.

In general, heterogeneous acid catalysts is insensitive to FFA and water content in WCO. Heterogeneous base catalysts allow relatively fast reaction under mild condition with less energy consumption. Separation of heterogeneous acid catalysts is easy and the recyclability is high. Nevertheless, disadvantages are observed: preparation of the catalyst is difficult and consequently expensive; the experimental parameters with high temperature, long reaction times are energy intensive; leaching of the active site may result to product contamination.

2.1.3. Heterogeneous acid and base catalysis

Since applications of heterogeneous acid and base catalysts have their own limitations, therefore combination of acid and base catalysts is a way for improving catalytic properties to synthesis biodiesel. Acid/base catalysts are a two-step process. First, FFAs of the WCO are

converted to the corresponding esters through esterification and then transesterification of the oil can then be performed when the FFAs content in the oil drops to lower than 0.5–1 wt%. Different mixed catalysts were tested: Mn/ γ -Al₂O₃-15 [55], Zn/CaO [56], S-ZrO₂/SBA-15 [57] were tested. Among them, sulfated zirconium oxide supported on Santa Barbara Amorphous silica (S-ZrO₂/SBA-15) was developed [57]. SBA-15 support itself did not have acidity and the conversion of the WCO with SBA-15 is less than S-ZrO₂/SBA-15. Incorporating ZrO₂ into support SBA-15 caused an increase in the concentration of acidic sites of the catalyst which plays a key role in esterification of the waste cooking oil. After optimization, the biodiesel was obtained in 96% yield at 140 °C within 10 min in methanol-oil molar ratio of 10:1 when 2 wt% of catalyst was used. It is noteworthy that less amount of methanol is required as compared with previous works.

2.1.4. Magnetic heterogeneous catalysis

Numerous researches have been conducted to introduce a suitable heterogeneous catalyst with easy separation process for transesterification of WCO. To overcome these issues, use of magnetic nanoparticles (MNPs) appears to be a logical solution [58]. Magnetic nanoparticles can be simply and efficiently removed from reaction mixtures with an external magnet (**Fig. 3**). MNPs can be used directly or can be modified to support active molecules or transition metals for transesterification reaction. The high catalytic activities, high stability, simple preparation, and magnetism are the key properties of the magnetic solid acid catalyst which could be a potential catalyst in the large-scale biodiesel production [59-61]. Magnetic nano particles as catalyst for transesterification of WCO were investigated with Mn²⁺ doped ZnFe₂O₄ [62]. The nature of ZnFe₂O₄ is a n-type semiconductor with good chemical and thermal stability with a better magnetic performance, superior electrical and magnetic properties. Moreover, ZnFe₂O₄ catalysts are inexpensive, easy handling and highly recyclable.

According to the literature, the catalyst has high magnetization (51.73 emu g^{-1}) and high magnetic moment (2.0837 mB), and hence it could be easily separated by magnetic separation from the reaction mixture. The study concluded that the catalyst possessed a cubic spinel structure with an average crystalline size in the range from 7.49 nm to 9.65 nm . The maximum biodiesel yield of 98% was obtained under the optimized conditions of 65°C for 50 min with methanol-oil molar ratio of $21:1$ when 4 wt\% of catalyst was used. Furthermore, reusability of manganese doped zinc ferrite nanocatalyst is performed for 10 consecutive cycles at optimized reaction condition. The biodiesel yield after 10th cycle was 94% yield which showed high stability of the catalyst (**Fig. 3**).

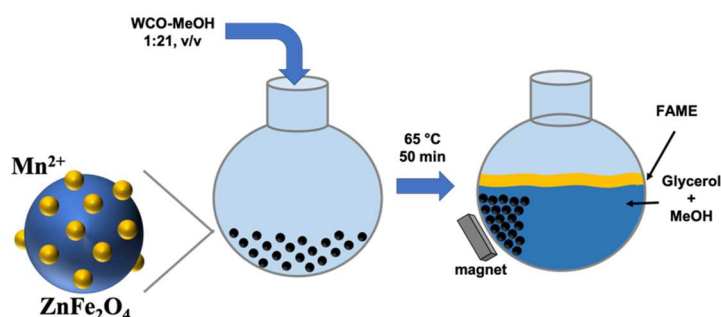
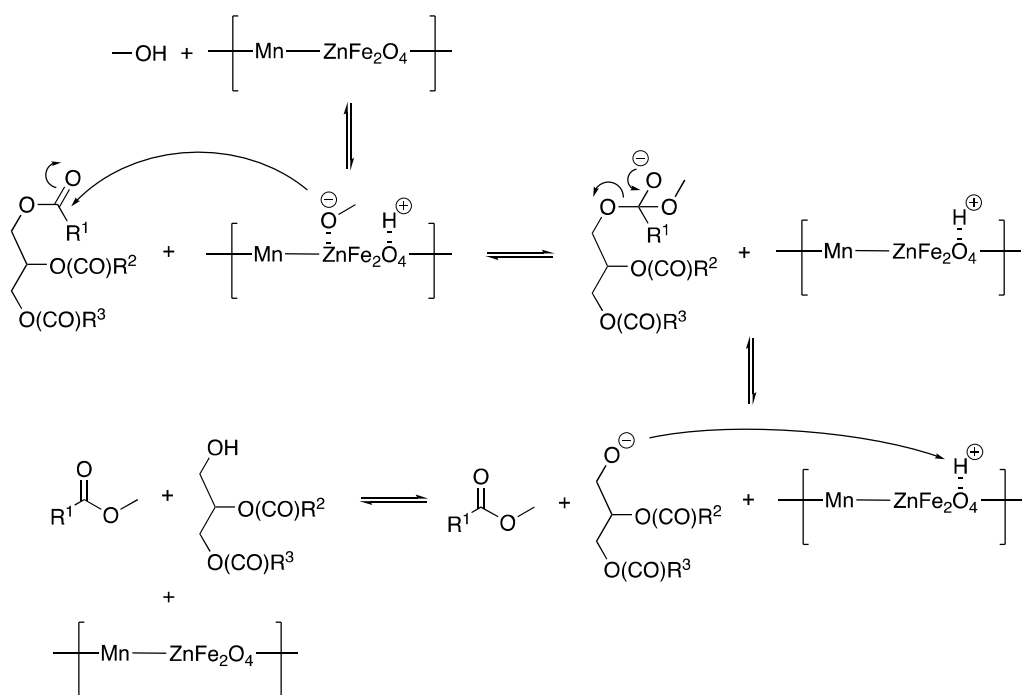


Fig. 3. Catalytic transesterification of WCO to biodiesel using Mn^{2+} doped ZnFe_2O_4 magnetic nanoparticles.

The authors proposed a plausible four steps reaction mechanism (**Scheme 2**). In the first step, O^{2-} of the catalyst removes H^+ of the methanol to form CH_3O^- . Methoxide is a strong base that causes transesterification reaction. In the second step, a tetrahedral intermediate is formed with nucleophilic attack of methoxide anion to the carbonyl triglyceride molecule. The instability of tetrahedral intermediate causes glyceride anion and fatty acid methyl ester. In the third step, intermediate picks up the H^+ from the surface of magnetic nano catalyst and finally rearrangement results in the formation of biodiesel.



Scheme 2. Mechanism pathway for the transesterification of triglyceride with methanol in the presence of Mn^{2+} doped ZnFe_2O_4 magnetic nano particle.

Production of biodiesel from WCO was studied using sulfonic acid group-functionalized ionic liquids immobilized onto magnetic nano particles [63]. A 99% yield was attained with 9 h at 70 °C in the presence of 5 wt% catalyst loading and methanol-oil molar ratio of 15:1. The magnetic nano catalyst illustrated an improved performance for biodiesel production compared to conventional homogeneous and heterogeneous catalysts (**Table 2**). The experimental conditions were identical excepted for the nature of the catalyst and the time of reaction which was optimized for each catalyst.

Table 2

Comparative study of different catalyst [63].

Catalyst	Catalyst Amount (mg)	Reaction time (h)	FFA conversion (%)	Yield (%) ^{a,b}
MNP	50	9	97	99
IL precursor	50	10	85	89
[Et ₃ NH]ClAlCl ₃	60	24	86	79
H ₂ SO ₄	70	18	88	90

^a Reaction conditions: WCO 5 g, methanol 2.91 g, 70 °C.^b The yield was calculated on GC using methyl laurate as an internal standard.

One another breakthrough using magnetic nano particles is the immobilizing enzyme and its use in transesterification of WCO. Also, lipase immobilized on Fe₃O₄ was used as a catalyst for transesterification of WCO. Lipase Km12 and *Fusarium Incarnatum* KU377454 derived lipase with magnetic nano particles permitted a quantitative conversion of WCO [64,65]. The catalysts showed high operational stability and could be separated easily by an external magnetic field. The effect of reaction temperature was investigated in both catalysts. The maximum conversion was obtained at less than 40 °C by both catalysts and the catalyst reusability can be maintained up to 5 cycles.

2.1.5. Homogeneous catalysis

Transesterification of WCO into FAME using homogeneous base-catalysts such as alkali metal hydroxides and methoxides (NaOH, KOH, NaOCH₃) has been extensively

studied in many literatures [66]. The process include investigation for the effects of several parameters such as the amount and type of catalyst, ratio of methanol to oil, the reaction time and the reaction temperature on the yield and quality of biodiesel. Among all the homogeneous base catalysts, KOH is the most commonly used for biodiesel production. In 2014, WCO conversion can be obtained at 50 °C for 40 min with methanol-oil molar ratio of 10:1 in the presence of KOH (0.83 wt%) giving biodiesel in 98% yield [67]. Using similar strategies, co-solvent technology was developed [68] and acetone was applied to increase the solubility of methanol and WCO. The mixture of acetone (20 wt%) and methanol permitted to reduce methanol to oil ratio (5:1) at 40 °C for 30 min and to furnish biodiesel in 96% yield. The use of homogeneous strong base such as NaOCH₃ which acts as base and nucleophilic agent permitted to reduce the time of reaction to 5 min [69]. Catalyzed process based on experimental and numerical simulation of kinetic model and effective condition was found to be 3% of NaOCH₃ with methanol-oil molar ratio of 18:1 at 60 °C. The authors reported that high molar ratios of methanol to oil (>6:1) could prevent saponification. Moreover, other researchers studied physicochemical properties of biodiesel such as oxidation stability and cold flow properties for improving the quality of biodiesel [70-72]. One way to improve the physicochemical properties of biodiesel is to blend WCO with non-edible vegetable oils such as *Calophyllum inophyllum* (CI), *Jatropha curcas* (JC), *Ceiba pentandra* (CP), and *Sterculia foetida* (SF) oils [70]. Some pretreatment processes need to reduce the content of water and impurity. Under these conditions, the optimized transesterification parameters: methanol-oil molar ratio of 50:1, 1 wt% of catalyst amount at 55 °C for 90 min were obtained. It is notable that the volume of methanol is higher than conventional process. The use of alkaline catalysts is preferred because of the higher reaction rate of these catalysts, typically about 4,000 times faster than acid catalysts at moderate temperatures. A major disadvantage of base catalysts for biodiesel production is the requirement of pre-treatment steps if low quality feedstock, such as

WCO which may contain high FFAs ≥ 0.5 wt% and water ≥ 0.3 wt% is used. This is due to the saponification of triglycerides and FAME, leading to emulsification and difficulties in the products separation. Therefore, combining different process seems necessary when homogeneous base catalysts are used for biodiesel production.

All things being equal, homogeneous base catalysts allow relatively fast reaction under mild condition with less energy intensity. The preferred catalysts such as KOH and NaOH are inexpensive. Nevertheless, the following disadvantages are observed: sensitive to FFA content and soap is formed when FFA content in WCO is higher than 2 wt%. Moreover, the formation of soap decreases the FAME yield and cause problem during the extraction. Homogeneous acid catalysts are insensitive to FFA and water content in WCO, but some disadvantages are observed: the rate of reaction is slow; the catalysts are sometimes corrosive and separation of the catalyst is difficult.

2.1.6. Bio-catalysis

Enzymatic biodiesel production especially those using lipase has attracted much attention in recent decade. Less amount of wastewater production, better recovery of glycerol and being environmentally friendly are the advantage of using biocatalysts. The following section reviews some of the enzymatic transesterification of WCO to biodiesel with an emphasis on given the optimum experimental conditions using biocatalyst [73]. *Yarrowia lipolytica* NCIM 3589 was found to provide a high potential applicability *in situ* transesterification and producing high yield of biodiesel [74]. Indeed, *Yarrowia lipolytica* was able to convert 88% of WCO to biodiesel at 50 °C with an oil-methanol molar ratio of 1:10, 4 g of bio catalyst and reaction time of 15 h. In addition, a key challenge in this study was one step process instead of three steps conventional method. To overcome the difficulties of conventional method all three steps of cell lysis, extraction of lipid and transesterification

directly done with *Yarrowia lipolytica*. On the other hand, lower amount of solvent and energy are consumed to achieve the maximum yield of FAME. Immobilized steps in lipase on Sc-CO₂ led to high enzymatic activity in transesterification of WCO to biodiesel [75]. It was observed that Cs-CO₂ is efficient in mass transfer and its combination with immobilized steps due to green and sustainable catalyst for biodiesel production. Biodiesel yield of 94% was obtained under the following reaction conditions: 14 wt% of catalyst, reaction temperature at 50 °C, methanol-oil molar ratio of 28:4, pressure of 10 MPa and reaction time of 14 h. Besides, reusability of the catalyst was studied and it can be reused for more than 5 times which indicated a well operational stability of the catalyst. However, it is noteworthy that enzymatic reaction still needs to progress especially for the need of industrial scale up, the cost of enzyme, and slow reaction rate.

All thing being equal, enzymes are insensitive to FFA and water content in WCO. The temperature of reaction is low to respect the enzyme and the separation of the catalyst is quite simple. Unfortunately, the reaction time is slow and the catalyst is expensive. In the presence of alcohol such as methanol, enzymes can be deactivated.

2.1.7. Alternative technologies

Due to current impetus in promoting green chemistry for sustainable development, chemists have recently established catalytic reactions using alternative technologies such as electrolysis, continuous flow, microwave irradiation, ultrasound irradiation [76-84]. Electrolysis process for producing biodiesel from WCO is one of the latest methods used. This process has some advantages such as lower energy consumption. The reaction can be carried out at room temperature and shorter reaction time was needed using a co-solvent. The application of zeolite/chitasan-KOH catalysts with electrolysis method in transesterification of waste cooking oil was demonstrated [85]. Several electrolysis voltages were examined and

result showed that by increasing voltage, formation of hydroxide ion on the cathode increased that caused a significant enhancement in production of FAME. The highest biodiesel yield of 93% was obtained at room temperature, methanol-oil molar ratio of 1:7 in presence of 1 wt% of catalyst and 10 wt% acetone as a co-solvent, and reaction time of 3 h at 40 V and with a stirring rate of 100 rpm. It is clear that the use of a co-solvent permitted to have a lower amount of methanol production. These overall results from the researchers deliver a promising concept for using electrolysis process in transesterification of WCO through the enhancement of catalytic reaction. Transesterification reaction by electrolysis process happens in electrolysis cell consist of DC current source, with a cathode and an anode (**Fig. 4**). Cathode produces OH^- ions that cause nucleophilic attack to carbonyl moiety of the triglyceride to form methyl ester and glycerol. Liquid electrolytes contain a catalyst and methanol, and are charged with an electrical DC current. Methoxide ions form in the solution and move to the electrode that cause chemical reaction occur through electrolyte solution [86].

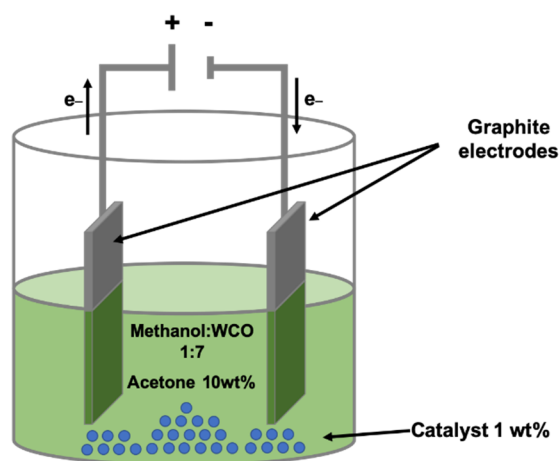


Fig. 4. Production of biodiesel using WCO in an electrolysis system.

Combination of electrolysis process at a voltage of 50V with a graphite electrode in the presence of MgO-NaOH nano-catalyst permitted to have an optimum WCO conversion [87].

The authors reported the production of biodiesel in 98% yield using an alcohol-to-oil ratio of 6:1 in the presence of 3-5 wt% catalyst and 10 wt% of THF as a co-solvent at room temperature for 6 h.

Among the latest invention for biodiesel synthesis from WCO, ultrasonic technology has been recognized as an effective method for improving the yield within a shorter reaction time [88-90]. Through ultrasonic process, molecular spacing in the medium will continuously compress and stretched with high frequency sound thus molecules will continuously vibrate and cavitate. The main advantage of ultrasound field concerned the efficiency of mass transfer generated by mechanochemical energy. Application of ultrasound in heterogeneous transesterification of waste cooking oil using MgMoO₄-supported TiO₂ was reported [91]. A good triglyceride conversion and high biodiesel yield of 97% can be achieved with methanol-to-oil ratio of 9:1 at 65 °C in 30 min in the presence of 0.5 wt% of MgMoO₄/TiO₂. The result also proved a positive effect of ultrasound method in catalytic transesterification of WCO and a high potential of ultrasonic process for industrial biodiesel production. The potential of ultrasonic system for enzymatic transesterification of WCO in the presence of immobilized enzyme (Novozym 435) [92] and *Combi-lipases* were utilized as a biocatalyst in this system [93]. Under the optimal reaction conditions, such as molar ratio of ethanol-oil of 6:1, 15 wt% of catalyst, reaction temperature at 40 °C, the frequency of ultrasonication (40 kHz) which was occupied at a power of 100 W, an overall biodiesel production of 96% was achieved in 18 h. It was found that the yield of biodiesel can be enhanced with an optimization of the amount of combined-lipase, added water, and substrate molar ratio (ethanol-oil) which is an essential strategy for industrial scale production. This optimization can reduce the overall cost of enzyme and better feasibility of ultrasonic - enzymatic synthesis of biodiesel.

A few reports described the microwave-assisted transesterification for the biodiesel production from WCO [94-98]. One of the recent studies is the utility of microwave radiation

with a calcium diglyceroxide catalyst for the biodiesel production [99]. Predetermined amount of WCO, methanol and catalyst was firstly charged in a batch reactor, and the overall biodiesel conversion achieved was 95% at 65 °C for 15 min with a methanol-to-oil ratio of 7.46:1, and 1.03 wt% calcium diglyceroxide was used as the heterogeneous catalyst. It is noteworthy that calcium diglyceroxide was obtained using conventional preparation method containing CaO, glycerol and methanol at 60 °C for 3 h. The study also reported that microwave irradiation has significant advantage over conventional heating method, since the yield of biodiesel is reduced to half (42% *versus* 95%). The results clearly showed that microwave irradiation is more energy-efficient than conventional heating method. Furthermore, reusability and leaching of the catalyst showed high recovery yield of the catalyst and reusability of 4 times with insignificant leaching of catalyst.

Recently, continuous flow biodiesel production from WCO received considerable attention. Most of the previous studies focused on evaluation of effective catalyst or optimization of the operating conditions of biodiesel on batch mode. However, to realize the scale-up the biodiesel production, it is better to utilize continuous flow process to convert WCO to biodiesel continuously [100,101]. The transesterification reaction of WCO with methanol was carried out in a packed bed reactor with an agglomerated Zr-SBA-15/bentonite catalyst [102]. With a residence time of 30 min (i.e. liquid hourly space velocities, LHSV of 2 h⁻¹) and methanol-oil molar ratio of 50:1 at 210 °C and 70 bars, biodiesel was obtained in 96% yield. Stability of the process was confirmed with a production of biodiesel (96% yield) after 260 h. The typical configuration of the continuous reactor mainly consists of a packed bed reactor with bed length of 120 cm and an inner diameter of 0.9 cm with pressure, and temperature controllers (**Fig. 5**).

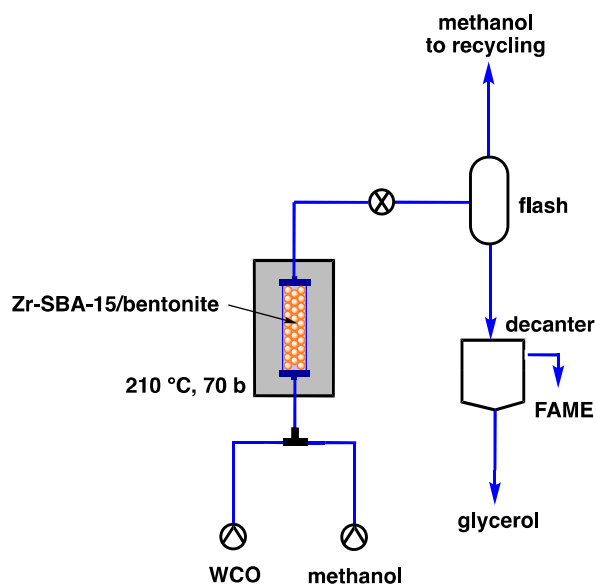


Fig. 5. Schematic diagram of the packed bed reactors for biodiesel production using Zr-SBA15/bentonite.

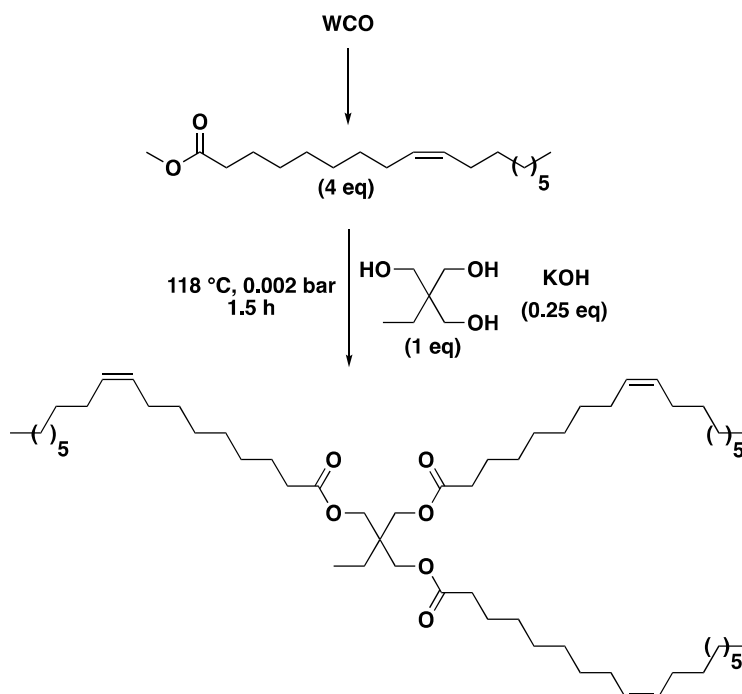
In 2017, a microwave-assisted continuous transesterification for large scale production of biodiesel was reported [103]. The feeding medium consists of WCO and methanol are pumped by a peristaltic pump from the top of the catalyst fixed bed packed in the reactor under microwave heating. After exploring the use of the strong base SrO as a catalyst for production of FAME, the corresponding silica derivatives SrO/SiO₂ was studied. In this context, 15 g of 41 wt% SrO/SiO₂, methanol-oil molar ratio of 12:1 at 200 °C for a residence time of 8 min, WCO was converted to FAME in 99% yield. Combination of microwave and continuous flow technique can provide the opportunity to resolve the physical limitation of microwave reactors. Continuous-flow transesterifications using immobilized enzymes have been receiving considerable attention. In 2017, *Pseudomonas mendocina* cells were covalently immobilized on the surface of Fe₃O₄-sodium alginate microspheres and used for transesterification of WCO with high activity in biodiesel yield with a methanol-oil molar ratio of 3.74:1, a flow rate of 20 mL min⁻¹ at 35 °C. In these conditions, biodiesel was obtained in 92% after 48 h [104].

A very recent work shows the development of a semi-continuous mechanochemical process for biodiesel production [105]. The use of mechanical-assisted energy with beads ($d=1$ mm) in continuous flow allows to overcome the miscibility problems of methanol and oil and the diffusional problems as the rate-controlling process. Thus, a biodiesel yield higher than 90% is reached using a methanol:oil molar ratio close to stoichiometric value (4:1) and 1.5 wt.% catalyst, after passing through the reactor with a flow rate between 4 to 45 L/h and subsequent stirring of 4 h at 50 °C, or 24 h at room temperature. Calcium diglyceroxide is used as catalyst and it is synthesized using the same flow mechanochemical reactor. It is noteworthy that this patented synthesis favours the formation of CaDG with a low glycerol/CaO molar ratio (3:1) at room temperature, without additional solvent and just 30 min of subsequent stirring [106]. This new process for biodiesel production can easily be scaled up and applied to the conversion of used cooking oils, without any significant yield decrease. A cost study was also performed, demonstrating that it is more economical than the conventional batch stirring-based process.

2.2. Biolubricant production with catalyzed transesterification

WCO is an attracting alternative to produce different value-added chemicals such as biolubricants. Besides biodiesel, bio-lubricant is one of the most potential applications of WCO. Bio-lubricants are typically prepared in a multi-steps reaction and researches have been developed to improve the process with a particular focus on heterogeneous, homogeneous and biocatalysis. After formation of FAME starting from WCO, homogeneous base KOH to trimethylolpropane with molar ratio of 0.25:1 and an excess of FAME (4 eq) at 118 °C and 0.002 bar for 1.5 h furnished the desired triester in a yield of 86% [107] (**Scheme 3**). After conventional work-up, the bio-lubricant was purified by MD80 molecular distillation (MD). The authors reported that the properties of the target compounds met the requirements

specified in the ISO standard. The production of identical biolubricant was developed using hydrotalcite loaded with potassium carbonate as a promising heterogeneous solid base catalyst [108].



Scheme 3. Synthesis of trimethylolpropane fatty acid ester from WCO in the presence of KOH as a homogeneous base catalyst.

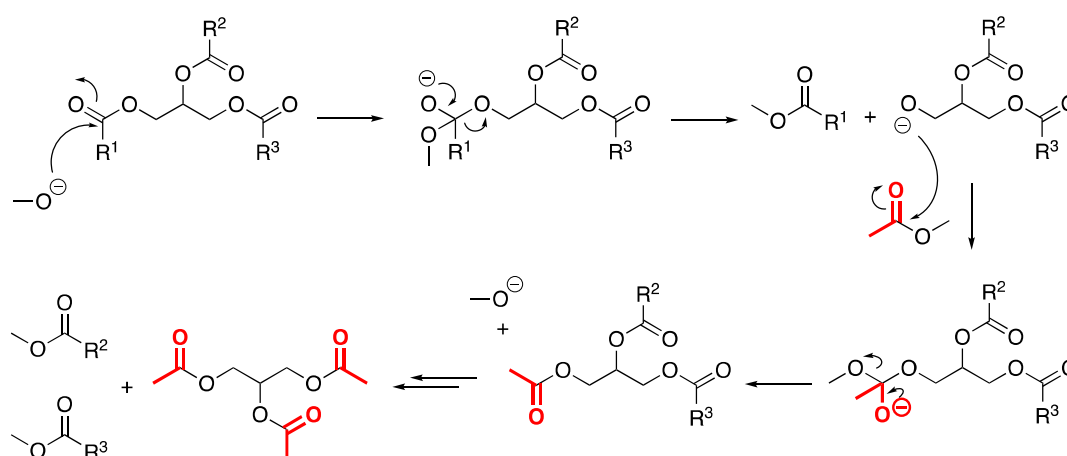
Enzyme catalysis has many advantages such as higher selectivity, and reduced energy demand and different lubricant have been produced from WCO [109,110]. Based on the magnetic nano particle strategy, *Thermomyces lanuginosus* lipase (TL) and immobilized TL on Fe₃O₄ having citric acid moiety (Fe₃O₄-CA) was found to show a promising result in biolubricant production from WCO [111]. In a first step, the saponification of WCO was done in the presence of immobilized TL at 40 °C for 4 h. In the second step, the obtained FFA was mixed with neopentyl glycol in the presence of immobilized TL on Fe₃O₄-CA at 45 °C for 24 h to afford neopentyl glycol fatty acid esters in a yield of 88% in a solvent free system. With the help of the magnetic nano particle, the enzyme catalyst was recycled and permitted

to furnish the biolubricant in a yield of 75% after 10 cycles. More complex biolubricants having glycone moiety were obtained starting from WCO. A new glycolipid mannosylerythritol lipid was produced by biotransformation in the presence of *Pseudozyma aphidis* ZJUDM34 [112]. It was observed that this biocatalyst has high enzymatic activity when used in a solvent-free system. Biolubricant yield of 61.50 g L⁻¹ was obtained at 35 °C for 10 days. Comparing with the fatty acids profiles from soybean oil, waste cooking oil showed the same amount of glycolipids (20 mg L⁻¹) production. However, the low price of WCO in the global market makes it the first choice as compared to soybean in fermentation process and ensures an overall better economic of the final product.

3. Interesterification of waste cooking oil

As an alternative to transesterification, interesterification of oil and fats is a chemical or enzymatic process used for acyl-rearrangement on the glycerol molecule of oils and fats [113-115]. Methyl acetate is mainly used for the interesterification of WCO, but sometimes ethyl acetate is preferred for conducting to the FAEE instead of the FAME. Interesterification of WCO was carried out in a batch reactor using a NaOH and acetic acid as homogeneous catalysts [116]. The interesterification between WCO and ethyl acetate produces one mole of biofuel (in terms of FAEE) with triacetin as a by-product. Using NaOH:WCO of 0.015:1 M ratio and ethyl acetate:WCO of 30:1 M ratio at 80 °C for 3 h, the FAEE was obtained in 92% yield. Potassium methoxide as a catalyst for the interesterification of WCO with ultrasound assistance was evaluated by determining the compositional change of fatty acid into corresponding fatty acid methyl esters [117]. The interesterification process resulted in the formation of new glycerides, mainly triacetin instead of glycerol. This change in process of producing biodiesel resulted in an improvement of the biodiesel properties, particularly in flash point and kinetic viscosity. Maximum biodiesel yield of 90% was attained in steady

state using ultrasonic horn in about 30 min, oil-methyl acetate molar ratio of 1:12, a catalyst concentration of 1.0% and temperature of 40 °C. The same group compared hydrodynamic cavitation strategy instead acoustic cavitation and WCO to methyl acetate molar ratio of 1:12 in the presence of potassium methoxide (1 wt%) using slit venture at the inlet pressure of 3 bars furnished FAME in 90% yield [118]. The mechanism of the transesterification of WCO using methoxide as a catalyst first generated a tetrahedral intermediate as observed during the trans-esterification process (**Scheme 4**). When the diglyceride anion is formed, it attacks the carbon atom of the carbonyl group of methyl acetate and generates a new tetrahedral intermediate which forms monoacetindiglyceride. Repeating the process twice permits the production of three moles of methyl esters and one mole of triacetin.



Scheme 4. Mechanism pathway for the transesterification of WCO and methyl acetate in the presence of methoxide.

4. Hydrolysis of waste cooking oil

Hydrolysis of WCO permits to generate free fatty acids, glycerol and water [119]. After hydrolysis, a subsequent esterification between the resulting free fatty acids and alcohol permits the production of biodiesel [120,121] or biolubricant [122]. Recently, ultrasound was used for hydrolysis of WCO in the presence of enzyme to accelerate the initial rates of

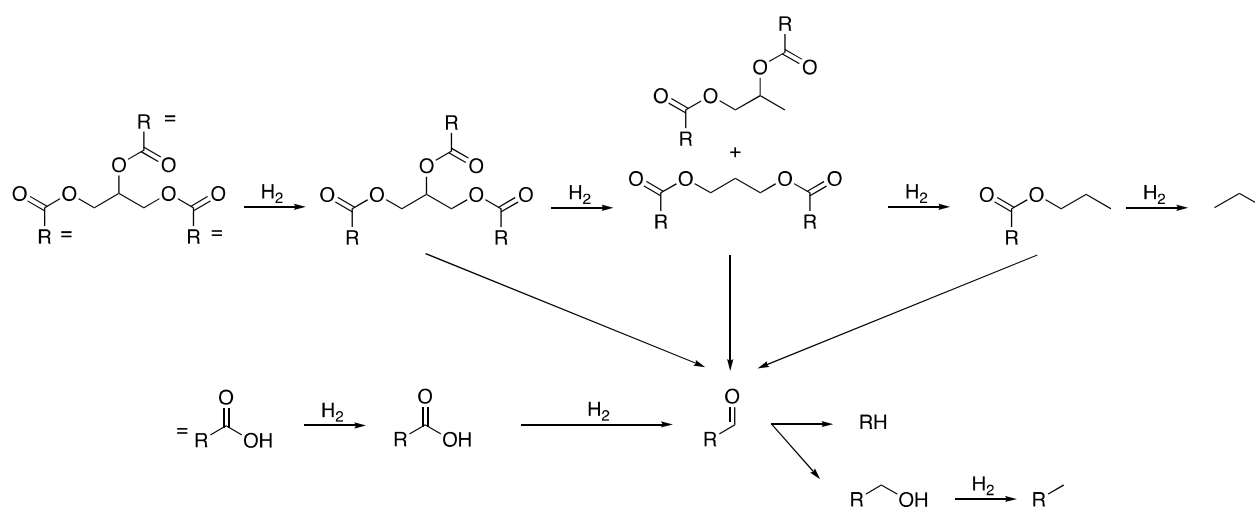
reactions. Using Lipozyme TL IM as an enzyme catalyst (10 wt%) in water under an ultrasound power of 132 W for 2 h at 40 °C, conversion of WCO afforded free fatty acids in a yield of 61% [123]. Moreover, the lipase activity after kinetic evaluation showed that the enzyme catalyst could be reused several times after recovering when isopropanol was used as a solvent for extraction. It is clear that ultrasound as an alternative technology is more effective than conventional activation and no damage of the protein structure was observed. Similar strategy was developed under the solvent free condition [124]. Commercial immobilized lipase (Novozym 435) of 1.25 wt%, molar ratio of oil-water of 3:1 at 50 °C for 2 h, ultrasonication power of 100 W and a frequency of 22 kHz resulted in free fatty acid yield of 75%. The catalyst did not end with good recyclability.

5. Hydrodeoxygenation, hydrocracking and hydrogenation of waste cooking oil

Hydrodeoxygenation (HDO) involves the hydrogenation of oxygenated chemicals to produce a more deoxygenated product and water as by-product [125-130]. During HDO, deoxygenation (C-O cleavage), hydrogenation (saturation of C=O), hydrogenolysis, hydrocracking may occur. HDO of WCO (0.25 g) over Ir-ReOx/SiO₂ (Re/Ir = 3) (0.05 g) in cyclohexane was optimized at 200 °C under 20 bars of hydrogen for 18 h [131]. The total alkanes yield was 82% with octadecane yielded as the main product (i.e. a resultant yield of 69 %). With a shorter reaction time of 3 h versus 18 h, the total alkanes yield was 20%.

A plausible mechanism for HDO of WCO is proposed (**Scheme 5**). After hydrogenation of the unsaturated bond of the triglycerides and free fatty acids, a cascade reaction was realized without any carbon atom loss: (i) hydrogenolysis of the carbonyl bond resulted in an aldehyde; (ii) hydrogenation of aldehyde led to formation of the corresponding alcohol; (iii)

hydrogenolysis of alcohol led to alkane. Concurrently, different 1,2-propane, 1,3-propane diesters and derivatives are formed giving long chain alkanes and propane. Hydrogenation of free fatty acids furnished successively the corresponding aldehyde, the alcohol and the alkane. From the aldehyde, a minor pathway permitted to produce the corresponding alkane with one carbon atom less *via* decarbonylation.



Scheme 5. Mechanism pathway for HDO of WCO.

HDO of WCO in continuous flow in the presence of 5.37-Ni₂P/AC-1.5 (Ni/P molar ratio of 1.5 and Ni loading 5.37 mmol g⁻¹ of AC) at 300 °C and atmospheric pressure for 40 min with a space velocity of 3.33 min⁻¹ permitted the production of a mixture of C₁₅-C₁₉ alkanes in 25.4 % yield, a mixture of C₂₀-C₂₂ alkanes in 27.1 % yield and alkenes in 14.7 % yield as the main chemicals [132]. The authors reported that the results depend on the reaction conditions and on the Ni₂P phase as well.

Hydrocracking is a process involving conversion of heavy oils molecules to lighter products. The main advantage of hydrocracking is the possibility of WCO conversion over conventional catalysts into green product such as green naphtha (C₅-C₉), green gasoline (C₁₀-C₁₂) and green diesel (C₁₃-C₂₀) [133,134]. Bi-functional Ni- Mo/alumina catalyst was

examined for the hydrocracking of WCO [135]. The highest conversion of WCO was performed in a batch reactor in the presence of 5 wt.% nickel as a catalyst at 250 °C and hydrogen pressure of 5 bar for 1 h with a catalyst:oil ratio of 1:75. In these conditions, the main chemical biogasoline (C₆-C₁₂) was obtained in a yield of 59%.

Hydroprocessing of waste cooking oil over NiMo/ γ -Al₂O₃ catalysts involves conversion of the double bond of WCO with hydrogenation and the removal of oxygen through a NiMo/ γ -Al₂O₃ catalyst [136]. Hydrogenation takes place in metal active sites of the catalyst and metal must be carried out on an acid support. In this, the effect of different parameter such as temperature, H₂ to oil ratio, pressure and liquid hourly space velocities (LHSVs) are studied and the recommended conditions were 400 °C, a hydrogen-to-oil ratio of 950, a pressure of 800 Psi, and LHSVs of 0.9 h⁻¹. In general, hydroprocessing can be one of the promising technologies for green fuel production from WCO. One of the benefits of this process is the possibility of using the same catalyst, reactor type and separation equipment used in petroleum refineries. Another perspective is whether the dihydrogen H₂ can be derived from renewable resources, as hydrogenation uses a large amount of H₂ industrially [137,138].

6. Conclusions

For this review, comparison of the results is difficult because no resembling experimental setup was used. Indeed, WCO valorization was reported with parameters that are specific: variation of the starting substrate, ratio of the oil and solvent mixture, nature and loading of the catalysts, temperature and alternative techniques. Moreover, the variability of WCO quality (e.g. free fatty acid and water contents) in addition to its instability under storage conditions pose serious problems to efficient valorization of WCO. Valorization of WCO was realized by the following transformations: transesterification, interesterification,

hydrolysis, hydrodeoxygenation, hydrocracking and hydrogenation. Among them, transesterification is the main process permitting the production of biodiesel and biolubricant. The biodiesel can be obtained by heterogeneous catalysts having basic sites, acidic sites, a mixture of acidic and basic sites or enzymes. Among the heterogeneous catalysts, magnetic catalysts have been developed in order to have an easy separation of the catalysts after each run. Homogeneous catalysts and enzyme as catalysts permit the production of biodiesel as well. Different alternative technologies such as electrolysis, ultrasound, microwave, continuous flow even microwave-assisted continuous flow were studied with success. In comparison with transesterification, interesterification permits the production of biodiesel and triacetin as well instead of glycerol. Hydrolysis of WCO generates free fatty acids, glycerol and water while hydrogenation of WCO permits the production of free fatty acids, free fatty aldehydes, free fatty alcohols and alkanes *via* hydrodeoxygenation, hydrocracking using similar process from petroleum chemistry. The valorization of WCO using green and sustainable process proves its efficiency and may pave the way of a more intensive utilization toward the production of high value-added chemicals.

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**Restaurant
Food factory**

WCO

