



Review Paper

A comprehensive review on biodiesel purification and upgrading

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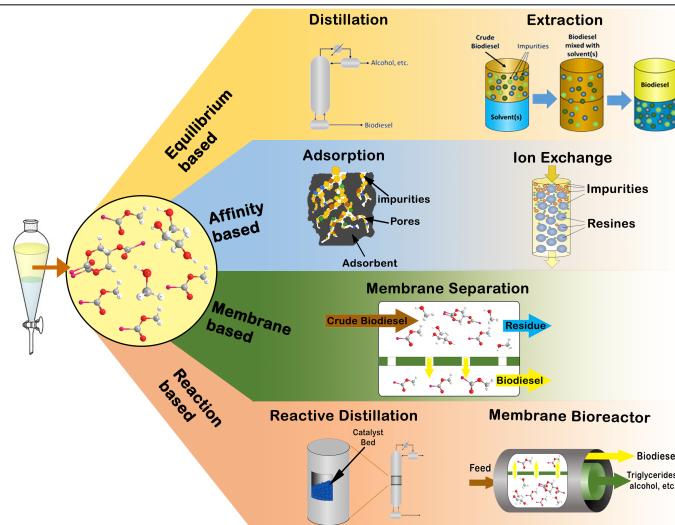
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HIGHLIGHTS

- Various biodiesel purification methods, i.e., equilibrium-based, affinity-based, and reaction-based separation techniques along with membrane technology and solid-liquid separation processes were reviewed.
- Deoxygenating process via hydrodeoxygenation and decarboxylation/decarbonylation pathways is a common way to upgrade bio-based oils to produce biorenewable diesel with excellent fuel properties.
- Catalysts and operating conditions, i.e., pressure, temperature, and contact time, are the most important variables in biodiesel upgrading discussed herein.

GRAPHICAL ABSTRACT



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ABSTRACT

Serious environmental concerns regarding the use of fossil-based fuels have raised awareness regarding the necessity of alternative clean fuels and energy carriers. Biodiesel is considered a clean, biodegradable, and non-toxic diesel substitute produced via the transesterification of triglycerides with an alcohol in the presence of a proper catalyst. After initial separation of the by-product (glycerol), the crude biodiesel needs to be purified to meet the standard specifications prior to marketing. The presence of impurities in the biodiesel not only significantly affects its engine performance but also complicates its handling and storage. Therefore, biodiesel purification is an essential step prior to marketing. Biodiesel purification methods can be classified based on the nature of the process into equilibrium-based, affinity-based, membrane-based, reaction-based, and solid-liquid separation processes. The main adverse properties of biodiesel – namely moisture absorption, corrosiveness, and high viscosity – primarily arise from the presence of oxygen. To address these issues, several upgrading techniques have been proposed, among which catalytic (hydro)deoxygenation using conventional hydrotreating catalysts, supported metallic materials, and most recently transition metals in various forms appear promising. Nevertheless, catalyst deactivation (*via* coking) and/or inadequacy of product yields necessitate further research. This paper provides a comprehensive overview on the techniques and methods used for biodiesel purification and upgrading.

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Abbreviations

AC	Activated carbon
alc.	Alcohol
cra.	cracking/hydrocracking
DCO	Decarbonylation
DCO ₂	Decarboxylation
DES	Deep Eutectic Solvents
dim.	Dimerization
est.	Esterification
FA	Fatty acid
FAAEs	Fatty acid alkyl esters
FAME	Fatty acid methyl ester
FFAs	Free fatty acids
HDO	Hydrodeoxygenation
IL	Ionic liquid
iso.	Isomerization
ket.	Ketonization
LLE	Liquid-Liquid Extraction
MD	Molecular distillation
MeOH	Methanol
met.	Methanation
NMWCO	Nominal molecular weight cutoff
olf.	Olefin
PVDF	Polyvinylidenefluoride
RHA	Rice husk ash
SA	Stearic acid
SCO	Spent cooking oil
SFE	Supercritical fluid extraction
SFFO	Spent fish frying oil
THF	Tetra hydrofuran

1. Introduction

Biofuels have received a great deal of attention due to the increase in global energy demands and the necessity of alternative clean fuels and energy (Bateni et al., 2016; Samadi et al., 2017). Biodiesel is a petroleum diesel substitute and one of the most promising biofuels due to its environmental compatibility and biodegradability (Bateni and Karimi, 2016a and b; Tremblay and Montpetit, 2017). Non-edible vegetable oils as well as algae and waste oils, consisting mainly of triglycerides and free fatty acids (FFAs), are potential biorenewable feedstocks for producing biodiesel since they have hydrocarbon chains in the range of diesel fuel (C₁₂-C₁₈) and do not raise the “food vs. fuel” conflict (Chhetri et al., 2008; Escobar et al., 2009; Greenwell et al., 2009; Srinivasan, 2009; Zhao et al., 2013). In line with that, many researchers have attempted to produce transportation fuels from these feedstocks *via* various methods. Thermal cracking (pyrolysis), catalytic cracking, and catalytic hydrocracking have been tested on these feedstocks (Stumborg et al., 1993; Twaiq et al., 1999; Parvizsedghy et al., 2015). The problem with these processes is the overall low energy efficiency due to considerable formation of C₁-C₄ hydrocarbons (Twaiq et al., 1999). Microemulsions of oil with solvents (and/or surfactants) such as water, methanol, ethanol, and 1-butanol have also been proposed to reduce the viscosity of bio-oils (Bora et al., 2016). However, several issues like unstable fuel properties, miscibility limitations, and heavy carbon residues during combustion have not been addressed (Ma and Hanna, 1999; Snåre et al., 2009).

Transesterification of triglycerides with short-chain alcohols (i.e., methanol or ethanol) in the presence of an alkali catalyst has been most widely used to obtain “biodiesel” or essentially fatty acid alkyl esters (FAAEs) (Ma and Hanna, 1999; Bateni and Karimi, 2016a; Bateni et al., 2017; Tremblay and Montpetit, 2017). Glycerol is an important by-product of the transesterification reaction, which needs to be separated from the biodiesel phase (Atadashi et al., 2011a; Shafiei et al., 2017). Depending on regional regulations, biodiesel needs to meet certain characterizations prior to reaching the market. Even though the densities of biodiesel and glycerol

are distinct enough from one another to be separated *via* gravitational settling and centrifugation (Van Gerpen et al., 2004; Atadashi et al., 2011b), further purification is required to remove impurities (i.e., remaining vegetable oil, alcohol, catalyst, soap, and FFAs) and meet the standard specifications introduced in ASTM D6571 or EN14214. Low-quality biodiesel due to impurities can not only compromise the engine performance but also complicate the storage and transportation of the fuel (Berrios and Skelton, 2008; Demirbas, 2009). Biodiesel purification techniques include wet washing using water, acidified water, organic solvents, or ionic liquids, dry washing *via* adsorption and ion-exchange, and membrane separation (Jaber et al., 2015). Nevertheless, this review categorizes the biodiesel purification methods based on the nature of the process, such as equilibrium-based, affinity-based, membrane-based, solid-liquid, and reaction-based separation processes (Dechow, 1989; Huang and Ramaswamy, 2013) as shown in **Figure 1**. It should be noted that a proper combination of the purification methods is usually required to obtain a robust biodiesel purification technology (Venkatesan, 2013).

2. Biodiesel Purification

2.1. Equilibrium-based separation processes

Absorption and distillation, as well as supercritical fluid extraction and liquid-liquid extraction (LLE), are some of the most common equilibrium-

based separation processes (Huang and Ramaswamy, 2013; Lei and Chen, 2013). Absorption is commonly utilized for separating particles and impurities from a gaseous mixture (Treybal, 1980; De Haan and Bosch, 2013; Huang and Ramaswamy, 2013); therefore, it does not have a major application in biodiesel separation.

2.1.1. Distillation

Distillation is the most common method for separation of more volatile compounds from heavier substances in a liquid mixture (Kockmann, 2014; Nag, 2015). There are different distillation techniques including conventional distillation (ordinary, vacuum, and steam distillation), azeotropic distillation, extractive distillation, and molecular distillation (MD) (Doherty et al., 2008). Conventional distillation and evaporation are perhaps by far the most common methods used in biodiesel purification to remove remaining alcohol or water from the crude biodiesel (Atadashi et al., 2011a and b; Stojković et al., 2014). Typically, the unreacted alcohol is separated from biodiesel prior to further purification (Gomes et al., 2011; Moser, 2012; Bateni et al., 2014; Bateni and Karimi, 2016b). In molecular distillation, carried out under high-vacuum, the molecules' free path is longer than the evaporation and condenser surface distance; therefore, most of the evaporated molecules reach the condensing surface without being deflected on collision with foreign gas molecules, resulting in a higher separation yield (Erich, 1982). Wang et al. (2010) used molecular

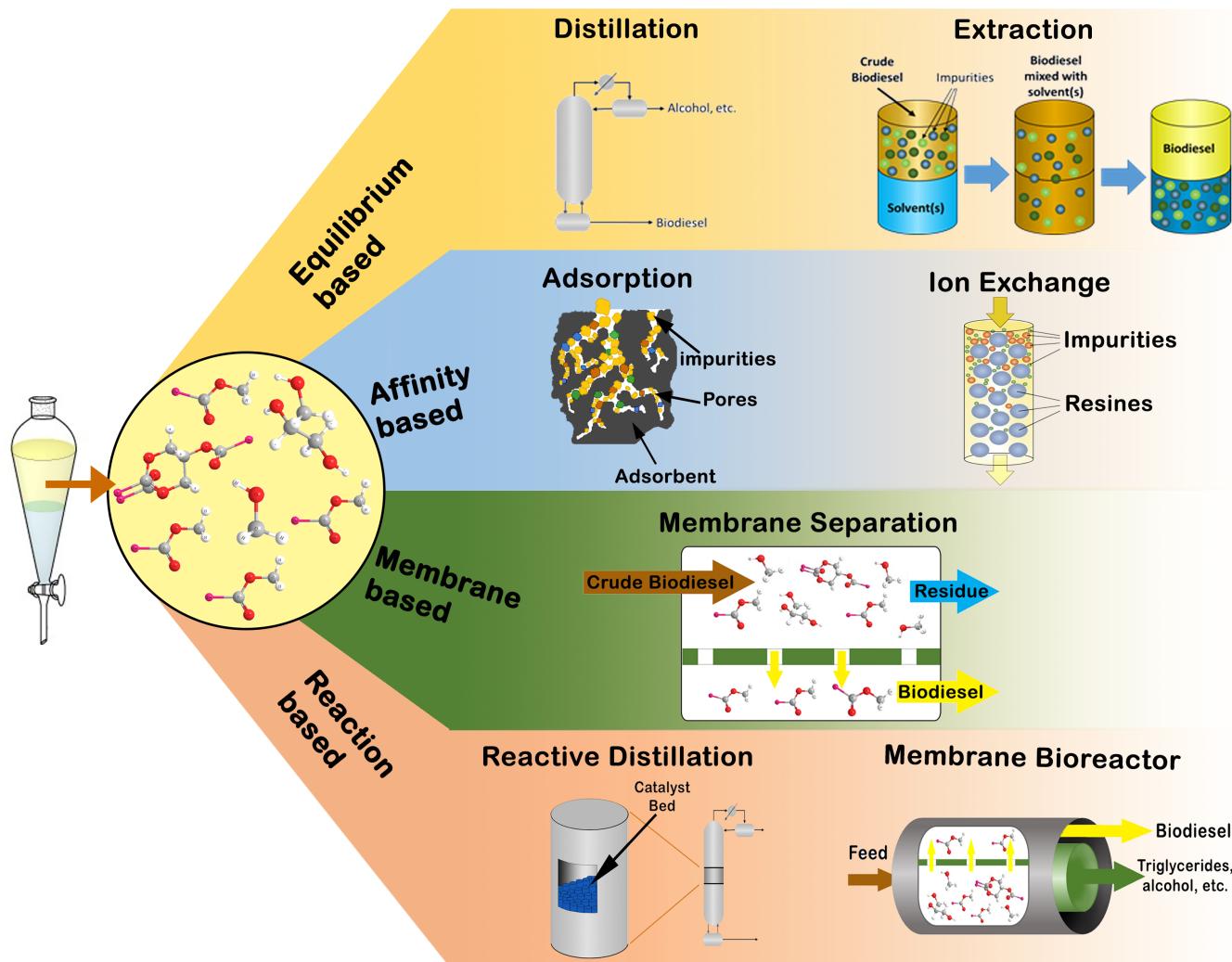


Fig.1. Biodiesel purification techniques classified based on the nature of the processes.

distillation to purify biodiesel obtained from waste cooking oil to achieve a 98% separation yield at the evaporator temperature of 120 °C.

2.1.2. Liquid-liquid extraction

Liquid-liquid extraction (LLE), otherwise known as solvent extraction, is a well-established separation technique to extract desirable component(s) from a liquid feed to a specific solvent (Hanson, 1971; Kertes, 1971; Dechow, 1989; Huang and Ramaswamy, 2013). This process is the most common method used for biodiesel purification that encompasses all the techniques developed for wet washing (Berrios and Skelton, 2008; Veljković et al., 2015). The use of deionized water to remove soap, catalyst, alcohol, and other contaminants of biodiesel is one of the most common biodiesel purification methods (Atadashi et al., 2011a; Serrano et al., 2013). Water temperature and volume are the key factors in improving purification of the biodiesel phase. Higher water temperature results in higher glycerol diffusivity from biodiesel to water and higher water volume provides higher mass transfer area, leading to an elevated volumetric mass transfer coefficient. Therefore, higher glycerol mass transfer to water and consequently a superior purification is expected using higher water volume at an elevated temperature (Muniyappa et al., 1996; Atadashi et al., 2011b). It was reported that water washing using a 1:2 water/biodiesel volume ratio for 20 min decreased the glycerol content from 0.09331% to 0.09% while the use of 3:1 water/biodiesel volume ratio resulted in 0.05% glycerol (Atadashi et al., 2011b). It was also reported that the standard specification (less than 0.02% glycerol) is achieved using a multistage washing process (Ma et al., 1998; Canakci and Van Gerpen, 2003; Rahayu and Mindaryani, 2007; Atadashi et al., 2011a and b). However, increasing the water temperature can result in higher water content in the final biodiesel (Stojković et al., 2014). A gentle mixing during the water washing increases the mass transfer coefficient; however, it may result in the formation of emulsions and biodiesel losses (Atadashi et al., 2011a). An alternative method of purification via spraying water on the ester phase at low velocities was proposed to decline such a concern. Saifuddin and Chua (2004) used this technique in addition to microwave heating to accelerate the process. It is noteworthy that the use of refined vegetable oil, moderate catalyst content, and low alcohol content in transesterification could minimize the amount of required water during wet washing (Saifuddin and Chua, 2004).

More effective purification can be achieved using acidified water followed by water wash (Abbaszadeh et al., 2014; Veljković et al., 2015). According to the results presented by Coelho et al. (2011) for purification of ethyl esters of castor oil, decreasing the pH of water used in the washing step decreased the amount of water required for neutralization (reach pH 7). The most common acids used to neutralize the homogeneous alkali catalyst prior to water washing are phosphoric acid, sulfuric acid, and hydrochloric acid (Atadashi et al., 2011a). It was reported that the use of acidified water results in the hydrolysis of soap to FFAs and subsequently decreases the tendency of emulsification (Atadashi et al., 2011a). However, Huerga et al. (2014) mentioned that this phenomenon can increase the acidity of the final product. Therefore, they used acid washing between two water washing steps to avoid soap hydrolysis (Huerga et al., 2014). Water washing does not show a promising result for the purification of biodiesel from heterogeneous processes, especially in the case of calcium-based catalysts. It was suggested that the formation of very stable calcium soaps dissolved in biodiesel can be the main reason for this deficiency (Alba-Rubio et al., 2012; Veljković et al., 2015). Organic solvents, e.g., petroleum ether and n-hexane, were also evaluated for biodiesel purification where the crude biodiesel is dissolved in the solvent prior to further water washing (Karaosmanoğlu et al., 1996; Atadashi et al., 2011a).

It should be noted that the purified biodiesel produced using wet washing needs to be dehydrated to decrease the water content to an acceptable range (Predojević, 2008; Atadashi et al., 2011a; Serrano et al., 2013). The dehydration process (drying) can be performed via different processes, including vacuum flash evaporation, convective heat drying, anhydrous salts, hot air bubbling, and other water absorbents (Serrano et al., 2013; Stojković et al., 2014; Veljković et al., 2015).

The water washing techniques usually suffer from high water consumption, large quantity of wastewater production, and high production cost (Serrano et al., 2013; Jaber et al., 2015; Veljković et al., 2015). In fact, for each liter of biodiesel, 3–10 L of water is used resulting in an equivalent volume of wastewater that needs to be treated (Jaber et al., 2015; Veljković et al., 2015). Jaber et al. (2015) proposed a novel method to decrease the required water for

biodiesel purification. The authors used microfiltration accompanied by separation with sand filtration/activated carbon (AC). They also used 70% dilution rate with make-up water to purify the biodiesel with up to 15% lower water consumption (Jaber et al., 2015). Overall, it should be noted that the water content of biodiesel purified via a wet washing method is usually above 1000 ppm and further reduction of water content to meet the standard specification is difficult, time-consuming, and costly (Dugan, 2007). These challenges motivated the scientists to seek out waterless methods for biodiesel purification.

Ionic liquids (ILs) have attracted a great deal of attention as green solvents owing to their non-flammable, non-volatile, and reusable properties making them excellent and safer choices for the extraction processes (Han and Row, 2010; Zhao and Baker, 2013). Many different organic, inorganic, and organometallic materials can be easily and efficiently dissolved in ILs; however, their high costs often limit their applications (Shahbaz et al., 2010). The low cost of the Deep Eutectic Solvents (DES) along with their great solvent characterizations, including biodegradability, non-toxicity, and non-reactivity with water, make them promising solvents for biodiesel purification (glycerol removal) (Shahbaz et al., 2010 and 2011). A mixture of quaternary ammonium salt with glycerol (with a 1:1 ratio) was utilized to remove the glycerol from the biodiesel where $[EtNH_4]Cl$, $[ClEtMe_3N]Cl$, and choline chloride were the most effective salts for glycerol removal. It was reported that 51% glycerol removal was obtained when an eutectic mixture/biodiesel ratio of 1:1 was used for the eutectic mixture of choline chloride/glycerol (1:1) (Hayyan et al., 2010). Shahbaz et al. (2010) combined choline chloride with either ethylene glycol or 2,2,2-trifluoroacetamide to prepare two series of DESs for biodiesel purification. Choline chloride/ethylene glycol (1:2.5 molar ratio) and choline chloride/2,2,2-trifluoroacetamide (1:1.75 molar ratio) with a corresponding DES/biodiesel ratio of 2.5:1 and 3:1 showed effective glycerol removal from palm oil based biodiesel (Shahbaz et al., 2010). Shahbaz et al. (2011) also reported that glycerol, KOH, mono- and diglycerides from the biodiesel could be effectively removed with the DES formed using methyltriphenylphosphonium bromide and ethylene glycol.

2.1.3. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is a mass transfer process at the operating conditions (i.e., temperature and pressure) above the critical point of the solvent. Supercritical carbon dioxide is considered a safe and green solvent in biomass processing (Steytler, 1996; Mantell et al., 2013). Wei et al. (2014) used supercritical carbon dioxide for biodiesel fractionation. A biodiesel separation yield of 99.94% was obtained at the temperature of 40 °C, pressure of 30 MPa, and flow rate of 7 mL/min CO_2 with a retention time of 90 min (Wei et al., 2014).

2.2. Affinity-based separation processes

Adsorption and ion exchange are the most common affinity-based separation processes, also known as dry washing methods, for biodiesel purification. In these processes, an appropriate adsorbent is used to selectively adsorb certain impurities from the liquid phase onto its surface (Huang and Ramaswamy, 2013; Atadashi, 2015).

Dry washing offers several advantages over wet washing, including ease of integration into an existing plant, shorter purification time, no water consumption and wastewater production, and smaller unit sizes (Atadashi et al., 2011a). The absence of water in purification of biodiesel during dry washing results in biodiesel with acceptable water content (less than 500 ppm) based on ASTM D6751 (Dugan, 2007).

2.2.1. Adsorption

Adsorption is the process by which atoms, ions, or molecules, known as adsorbates, from a substance (mostly liquid or gas) adhere to a solid surface, called the adsorbent (Dechow, 1989; Venkatesan, 2013). Adsorption is not interchangeable with absorption; however, the term “sorption” refers to both processes. In the absorption process, the component penetrates or dissolves in the bulk of adsorbent while surface adhesion occurs during adsorption (Venkatesan, 2013).

Adsorbents are natural or synthetic materials of amorphous or microcrystalline structures owning basic and acidic adsorption sites (LeVan and Carta, 2008), where polar substances such as glycerol and methanol can be adsorbed and filtered out of biodiesel (Atadashi, 2015). Adsorption loading, selectivity, regenerability, kinetics, compatibility, and cost are the most important criteria that need to be considered for adsorbent selection (Dechow, 1989; Venkatesan, 2013). A proper selection of an adsorbent can positively impact the process economy (Venkatesan, 2013).

The adsorption process for biodiesel purification can be also classified based on the type of adsorbent. Silica-based adsorbents (e.g., Magnesol and Trisyl), bio-based adsorbents such as (ligno)cellulosic substrates and activated compounds, including AC, activated fiber, and activated clay are among the most common adsorbents for this process (Atadashi et al., 2011a and Atadashi, 2015).

- Silica-based adsorbents

Silica is one of the key elements in different types of industrially available adsorbents, including silica-gel, zeolites, and molecular sieves (Dechow, 1989; Venkatesan, 2013). Silica-gel is an amorphous inorganic mesoporous adsorbent produced via polymerization of silicic acid (Venkatesan, 2013). Silica-gel owns a hydrophilic surface due to the presence of hydroxyl groups which makes it a proper adsorbent for water, alcohol, and other polar molecules (Ruthven, 1984). Silica-gel showed promising potential for biodiesel purification at room temperature (Yori et al., 2007; Mazzieri et al., 2008; Manuale et al., 2011). Silica showed great potential for removal of glycerol from biodiesel synthesized from waste cooking oil (Yori et al., 2007; Predojević, 2008; Faccini et al., 2011). Yori et al. (2007) used a silica-gel bed crushed and sieved to 10-40 mesh to purify biodiesel samples with 0.1-0.2% glycerol at a space velocity of 3-11 cm/min. The full capacity of the bed (0.13 g of glycerol per g of silica) was used in case of using adsorbent with particle size of 1-1.5 mm. However, mass transfer limitations in the case of industrial adsorption units (with typical 1/8 in. silica beads) limited the practical capacity of the process (Yori et al., 2007). Mazzieri et al. (2008) reported that silica-gel could effectively remove glycerol and monoglycerides from biodiesel and the presence of small amounts of water and soaps did not influence the adsorption of glycerol. However, the presence of alcohol (methanol) negatively affected glycerol adsorption and decreased the effective saturation capacity by about half due to the affinity effect of methanol on silica surface and glycerol (in liquid phase) (Mazzieri et al., 2008). The presence of water at severe conditions results in vegetable oil and glycerol hydrolysis to FFAs which need to be separated during the biodiesel refining process. Manuale et al. (2011) showed great potentials of silica-gel for separation of FFAs from the biodiesel produced from non-catalytic biodiesel production using supercritical methanol. The adsorption capacity of silica-gel was as high as 1.35 g per g of adsorbent while that value did not exceed 0.101 g per g of adsorbent for treated AC (Manuale et al., 2011).

Natural low silica content bentonite was also used for biodiesel purification. It was reported that activation of the aforementioned clay with 0.1 M sulfuric acid at 100 °C for an hour increased its adsorption properties. Moreover, the particles within the mesh size of 120-200 had a superior performance due to accessibility of the pores and higher surface area (Leeruang and Pengprecha, 2012). Magnesol is one of the common commercially available silica-based adsorbents used for biodiesel purification (Berrios and Skelton, 2008). Magnesol is in fact an inorganic matrix of magnesium silicate and anhydrous sodium sulfate offering a great potential for selective adsorption of hydrophilic impurities of crude biodiesel (Atadashi et al., 2011a; Faccini et al., 2011). Similar to other adsorbents, biodiesel needs to be thoroughly mixed with the Magnesol powder for a certain period of time. The mixture is then subjected to filtration to separate the Magnesol from the final fuel. Faccini et al. (2011) evaluated different type of adsorbents for biodiesel purification where 1% Magnesol and 2% silica showed promising results. The soap, methanol, and water content of the crude biodiesel were 1670 ppm, 2.13%, and 1300 mg/kg, respectively. Those values correspondingly decreased to 60.85 ppm, 0.19%, and 500 mg/kg after purification by 1% Magnesol. This adsorbent also successfully decreased the free and total glycerol from 0.71 and 0.26 to 0.28 and 0.02, respectively. The effects of Magnesol concentration and humidity of the adsorbent on the purification of biodiesel was evaluated at two different temperatures (room temperature and 60 °C) (Berrios and Skelton, 2008). The increase in Magnesol concentration from 0.25 to 1% improved the glycerol and

soap removal. Surprisingly, drying the adsorbent prior to use did not significantly affect the results. A slightly better methanol removal was observed in the case of purification at 60 °C, which might be due to methanol evaporation instead of a superior adsorption process (Berrios and Skelton, 2008).

- Biomass-based adsorbent

Cellulosic and lignocellulosic substrates were also found to be effective adsorbents for biodiesel purification (Manique et al., 2012; Gomes et al., 2015). These materials are abundant and inexpensive in addition to their advantages as renewable, biocompatible, and non-toxic materials (Gomes et al., 2015; Bateni et al., 2016; Noori and Karimi, 2016a and b).

This method is widely and simply used in small scale biodiesel plants and the biomass that absorbed the impurities is burned for heating after saturation and refilled with a fresh biomass.

Gomes et al. (2015) used different types of starch with various morphologies along with cellulose as a natural adsorbent for biodiesel purification. Corn starch and rice starch own a polyhedral structure while potato starch and cassava starch have ellipsoidal and semi-spherical structures, respectively. The eucalyptus bleached kraft cellulose with a tape format was also used for biodiesel purification. The dry washing was performed via admixing 1-10% of adsorbent in biodiesel for 10 min at room temperature and 150 rpm followed by filtration using filter paper. Regardless of adsorbent type and content, the acidity index decreased after purification with the aforementioned biomasses. The free glycerol content of biodiesel was about 0.13%, which was completely removed using the following substrates: 5% potato starch, 1-2% cassava starch, and 1% rice starch. The purified biodiesel with 2% corn starch could also meet the standard specification for free glycerol. Turbidity, showing the presence of impurities in the biodiesel, was also significantly decreased in the case of using 5% potato starch or 1-2% cassava starch (Gomes et al., 2015).

Rice husk ash (RHA) (1-5%) showed a promising performance in biodiesel purification. The adsorption capability of RHA is attributed to its high silica content and the presence of meso- and macropores in its structure. Although the water content of the purified biodiesel with RHA was still above the acceptable value, it was significantly lower than that of the purified biodiesel using acidified water (1% phosphoric acid) and Magnesol 1% (Manique et al., 2012).

- Activated compounds

AC, activated fiber (carbon fiber), and activated alumina are among the most common adsorbents in industrial applications. AC, which owns a large porous volume and high surface area, can be manufactured from any carbonaceous organics, e.g., sawdust, petroleum coke, wood, charcoal, peat, fruit nuts, bituminous coal, lignite, and coconut shells (Venkatesan, 2013). The porous structure is activated through either steam or chemical activation. In the case of steam activation, the substrate is heated at 400-500 °C in an oxygen-free atmosphere to remove the volatile components (carbonization step), followed by oxidization using steam (or carbon dioxide) at 800-1000 °C. The chemical activation is performed via impregnation of the substrate with a strong dehydration agent (e.g., phosphoric acid or zinc chloride), followed by heating to 500-800 °C, washing, drying, and grinding (Yang, 2003).

Thermal dehydration of hydrated alumina and recrystallization is the most common method used to produce activated alumina. The presence of Lewis acid sites on the surface of activated alumina makes it a suitable adsorbent for polar compounds and oxygenates such as alcohols, aldehydes, ketones, and carboxylic acids (Yang, 2003; Venkatesan, 2013).

Fadhil and Dheyab (2015) compared the performance of AC prior to and after acid treatment either with sulfuric acid or hydrochloric acid for purifying biodiesel synthesized from spent cooking oil (SCO) and spent fish frying oil (SFFO). The AC purifications led to a better biodiesel yield (91.50-93.75%) with respect to water washed product (86-89%) on both of the feedstocks. In the case of SFFO, the modification of AC with acids improved its performance, especially in the case of the AC modified by sulfuric acid which resulted in a biodiesel yield of 93.75%. On the other hand, the untreated AC led to the best purification result for SCO biodiesel (93.4% yield) (Fadhil and Dheyab, 2015).

2.2. Ion exchange

Ion exchange is the process of exchanging the ions between the solution and a proper solid phase (exchanger) due to a stronger affinity (electrostatic force) between the target species and the functional groups on the surface (Treybal, 1980; Dechow, 1989; LeVan and Carta, 2008; Berrios et al., 2013). Ion exchangers consist of a matrix with excess charges localized in specific sites of the structure (Grandison, 1996; Berrios et al., 2013). Ion exchangers resins are one of the most common types of exchangers typically produced *via* functionalization of the polymer obtained from copolymerization of styrene cross-linked with divinylbenzene. The ion exchange resins are categorized based on the functionality and yet divided according to their strength (density of the charge) to strongly acidic cation-, weakly acidic cation-, strongly basic anion-, and weakly basic anion-exchange resins (Dechow, 1989; Berrios et al., 2013). The presence of sulfonic acid groups (sulfonated polystyrene, R-SO₃⁻H⁺) in the matrix leads to the formation of strong cation exchange resin as the protons can easily be exchanged with other cations. On the other hand, carboxylic groups (R-CO₂⁻H⁺) are usually incorporated in the exchanger's matrix to produce a weak cation exchange resins (Berrios et al., 2013). The strong anion exchange resins are usually obtained by insertion of the quaternary ammonium species into the matrix structure while the presence of radicals of secondary or tertiary amines leads to the formation of weak anion exchangers (LeVan and Carta, 2008; Berrios et al., 2013). The structural properties (e.g., degree of cross-linking, porosity, and particle size), exchange capacity, stability, type, and density of the charges (strength of the resin) need to be considered in order to choose a proper ion exchange resin (Grandison, 1996; Dechow, 1989; Berrios et al., 2013). The strong acid cation resins are the most common exchange resins used to purify biodiesel (Atadashi et al., 2011a; Faccini et al., 2011; Berrios et al., 2013). Berrios and Skelton (2008) studied the performance of PD206 and BD10 Dry ion-exchange resins (strong acid cation resins) for purification of biodiesel produced from used cooking oil and rapeseed oil. Although the resins showed promising performances for soap and glycerol removal, the methanol removal was not satisfactory (Berrios and Skelton, 2008). Lewatit GF202, on the other hand, showed a great potential for methanol removal along with its capability to decrease the soap and glycerol content in the purified biodiesel. The reusability of this resin was an additional advantage (Berrios et al., 2011). Mata et al. (2011) also used a 15 cm bed of Lewatit GF202 in a column with 5 cm diameter and 30 cm length to purify biodiesel with a constant flow rate of 236 cm³/h. The dry washing showed a positive impact in decreasing the biodiesel acidity and viscosity compared with water washing, although the final product did not meet the specification for metal content (sodium and potassium). Wall et al. (2011) studied the mechanism of biodiesel purification using industrially available ion-exchange resins, i.e., T45BD and T45BDMP (Thermax) along with BD10 Dry (Dow Chemical). They concluded that filtration, physical adsorption, ion exchange, and soap removal by glycerol affinity are the most important factors during this process. It is noteworthy that the resins showed a better performance for sodium soap removal compared with potassium soap and decreasing the particle size further improved the process in the case of sodium soaps (Wall et al., 2011). Chen et al. (2012a) showed the great affinity of the glycerol to sodium form sulfonated resins; however, their hydrogen form owned higher adsorption capacity (Chen et al., 2012b). Dias et al. (2014) investigated the effect of resin (PD206, Purolite) content (2-40%) on the ester and water content of the final biodiesel samples from soybean oil and waste frying oil where the purification was performed at room temperature for 1 h. Purification of the samples using 40% resin provided the best quality products even though the ethyl ester contents were still slightly lower than the standard value reported in EN 14214 (Dias et al., 2014). Comparing the results of soybean oil biodiesel purification using 2% Purolite at room temperature (Dias et al., 2014) and 65 °C (Faccini et al., 2011), it can be concluded that the purification at lower temperature resulted in lower water content in the final biodiesel.

It is noteworthy that the ion exchange resins can also effectively remove the metallic compounds leached out of a solid catalyst to the liquid phase (biodiesel) in the case of heterogeneous catalysis transesterification (Kouzu and Hidaka, 2013).

2.3. Solid-liquid separation processes in biodiesel purification

Biodiesel purification using solid-liquid separation methods is limited to filtration mostly after heterogenous transesterification or biodiesel purification

by a dry washing method. However, filtration is one of the main mechanism for soap removal as mentioned earlier. Methanol acts as the co-solvent of soaps in the biodiesel; therefore, they should precipitate upon methanol removal. Therefore, filtration is considered as an effective method in the case of high concentration of soap and absence of methanol especially in the case of sodium soaps. In fact, contrary to potassium soaps which are considered soft soaps, sodium soaps are hard soaps showing the tendency to solidify and make a gel-like layer at room temperature. Therefore, sodium soaps can be separated from biodiesel more effectively (Wall et al., 2011).

2.4. Membrane-based separation technologies in biodiesel purification

By stark contrast to the high-water content involved in typical water washing methods (Jaber et al., 2015), membrane technology has emerged as a low or no-water alternative in the purification of crude biodiesel. As well as the cost advantages associated with a lack of wastewater, this method avoids potential emulsion in the product, facilitating two-phase separation. Microfiltration (between 0.1 – 10 µm), ultrafiltration (between 1 and 20 nm), and nanofiltration (maximum pore size of 1 nm) membranes are all used depending on the characteristics of the feedstock.

2.4.1. Phase behavior in membrane separation

Generally speaking, the goal of a membrane filtration system is to selectively permeate fatty acid methyl esters (FAMEs) that comprise a typical biodiesel product. Therefore, the phase behavior of other compounds typically present in a crude biodiesel feedstock (unreacted triglycerides, methanol/ethanol, glycerol and soap, among other impurities) becomes paramount in the discussion of filtration.

Glycerol can pose as a challenge in separation, due to its existence as a droplet suspension in the crude biodiesel phase – this is dependent on temperature (Saleh et al., 2011) and composition (Wang et al., 2009; Gomes et al., 2010). Both additional alcohol (Gomes et al., 2010) and saponification products (Saleh et al., 2010a and b) can prevent the glycerol droplets from reaching the necessary size for effective separation – this is due to their role as surfactants in the biodiesel phase, decreasing the surface tension in the droplets which increases overall glycerol permeability. The saponification products, specifically, can form glycerol-alkali bonds which form a “reverse-micelle” structure – this can further complicate both glycerol and saponification product separation (Wang et al., 2009).

Unreacted oils (di- and triglycerides) can also form droplets in membrane reactors – Falahati and Tremblay (2012) found that the droplets comprised a bimodal size distribution whose characteristics depended on the original oil. In their case, waste cooking oil formed larger droplets than unprocessed canola oil, allowing for ease of separation of these unreacted oils due to size exclusion.

This biodiesel phase behavior is additionally dependent on temperature – in a ternary methanol-oil-FAME system, Cheng et al. (2009) tested different distributions of these three components at three temperatures (20, 40, and 60 °C) in facilitating membrane separation. The two-phase region was noticeably narrower at higher temperatures according to experiments. Once the conditions for single-phase flow were met, permeate flux dramatically increased. However, this flow was not functionally different from the crude retentate in terms of composition, implying a total lack of separation beyond the two-phase region. For an initial feed of oil:FAME:MeOH of 26:54:20 wt.%, the permeate had no triglycerides at 20 °C; further increases to 40 and 60 °C produced an oil content of roughly 26%. Given that the two-phase region is crucial to separation, this implies a temperature dependence of separation as well as composition dependence.

Based on the above work, the unreacted oil and methanol are themselves insoluble; however, it is the increases in FAME that can push the two-phase system into the single-phase region. Cao et al. (2007) used octanol-water coefficients to calculate the volume fractions of methanol and biodiesel that would produce heterogeneous two-phase flow. A semi-empirical model (Ho et al., 1990) noted that phase inversion would occur with volume fractions of methanol lower than 0.31 – the experiments conducted by Cao et al. (2007) found a complete lack of permeate flux at a volume fraction of 0.28, implying that the lack of a methanol-rich phase prohibited the separation.

The addition of water can further alter this two-phase behavior; by introducing small amounts of water between 0.06 and 0.2 wt.%, Saleh et al. (2010b) found that glycerol readily separated from a FAME flow at percentages of water above 0.1% at temperatures of 25 °C. Gomes et al. (2013) provided further insight into the effect of 10, 20, and 30 wt.% acidified water (0.5% HCl) on phase behavior in membrane separation—10 wt.% water was the most effective at retaining glycerol and stabilizing the permeate flux. At 20 wt.%, the authors found that agglomerates tended to form on the membrane pores, introducing a fouling mechanism; further increases to 30 wt.% allowed for phase inversion where glycerol was able to permeate through the membrane.

2.4.2. Organic/Polymeric membranes

The organic membranes employed in biodiesel purification include polysulfone (Alicieo et al., 2002; He et al., 2006; Alves et al., 2013; Giorno et al., 2013), polyamide (Jiang et al., 2009), and polycarbonate (Cao et al., 2007), regenerated celluloses and polyvinylidenefluoride (Mah et al., 2012; Giorno et al., 2013), and polyacrylonitrile (He et al., 2006; Saleh et al., 2010b) with varying success. These organic membranes can be sorted according to their hydrophilicity or corresponding hydrophobicity. A hydrophilic membrane is less susceptible to fouling from a variety of biorefinery feeds due to the water content, but is more susceptible to deformation due to pH and temperature swings; a hydrophobic material is more useful for the separation of oils (Mänttäri et al., 2013).

He et al. (2006) directly compared polysulfone and polyacrylonitrile membranes in obtaining high purity biodiesel, as well as using water and acid washing for comparison. While all methods were able to produce high purity (97.5%) biodiesel, only the membrane extraction method was successful in decreasing ester losses endemic to water- and acid washing methods; 10.1 wt.% esters were lost even at the optimum temperature of 50 °C with distilled water due to emulsification. The polysulfone and polyacrylonitrile membranes, by contrast, were able to purify biodiesel with only 8.1 wt.% and 10.3 wt.% ester losses. However, the polyacrylonitrile membrane allowed for higher water content in the final biodiesel product than any other methods, making it perhaps unsuitable for biodiesel refining. The polysulfone membrane additionally led to the highest purity of biodiesel at roughly 99% without additional steps. Later comparisons conducted between ultrafiltration poly(ether-sulfone) and microfiltration cellulose ester membranes (Alves et al., 2013) demonstrated successful separation of glycerol from the final biodiesel product; with a nominal molecular weight cutoff (NMWCO) of 10 kDa, the ultrafiltration poly(ether-sulfone) membrane alone could reach 0.02 wt.% glycerol in the permeate, meeting international standards. Additional successes with ultrafiltration polyacrylonitrile membranes have been experienced for glycerol separation from a biodiesel product – Saleh et al. (2010b) found a 63% reduction in glycerol content for the permeate upon adding 1 wt.% water by mass, reaching a level of 0.013 wt.% glycerol in the permeate. There are other membranes being considered for biodiesel purification, including polyimides which have been studied recently (Jiang et al., 2009) and as a membrane precursor for pervaporation (Freeman et al., 2012). However, these membranes have not been studied for the purposes of biodiesel purification. Additionally, their hydrophobicity would prove challenging to implement due to fouling from agglomeration mechanisms (Mänttäri et al., 2013).

Glycerol is difficult to separate from the final biodiesel product, but this separation is key in meeting international standards; thus, there have been extensive studies on the use of organic membranes for this very purpose (Saleh et al., 2010b). Depending on the composition, glycerol will form droplets of various sizes; Saleh et al. (2010b) found these droplets varied from 250 nm in pure FAME to more than 2500 nm in 0.06 wt.% water. Thus, an organic membrane chosen for glycerol separation should generally have smaller pores than this to facilitate the separation of these droplets. In tests for glycerol separation, a modified hydrophilic polyacrylonitrile membrane at 100 kDa NMWCO was able to separate glycerol more easily with higher water contents – from 3% in pure FAME to 63% in 0.2 wt.% water after 180 min of time on stream (Saleh et al., 2010b). For a poly(ether-sulfone) membrane at 10 kDa NMWCO, small additions of water (up to 0.2 wt.% by mass) drastically improved glycerol removal, from 0.02% to 0.009% glycerol in the permeate (Alves et al., 2013). This glycerol/water miscibility directly contributes to a two-phase flow that is crucial for separation (Wang et al., 2009; Gomes et al., 2010; Saleh et al., 2011; Alves et al., 2013). However, soap and methanol tend to complicate the mechanism of separation due to their role in increasing

glycerol solubility (Saleh et al., 2010a and b). Saleh et al. (2010b) found negligible separation of glycerol in the presence of 1 wt.% methanol and soap and 0.06 wt.% water for the aforementioned polyacrylonitrile membrane at 100 kDa. These authors (Saleh et al., 2010a) later employed dispersive light scattering to determine glycerol particle sizes in various concentration profiles of glycerol, soap, and methanol – they found that separation increased as particle size increased, even in homogeneous flow regimes where glycerol was unable to form said droplets.

Organic membranes could find some use in the filtration of biodiesel produced from microalgae cells (Giorno et al., 2013), whose production is traditionally limited by harvesting efficiency and triglyceride recovery from the cells themselves (Wijffels et al., 2010). Organic membranes have been employed in algal cell separation (Rossi et al., 2008) as well as protein and lipid separation from wastewater (Dumay et al., 2008). Giorno et al. (2013) utilized tested the fouling mechanisms for various organic membranes including regenerated cellulose, polysulfone and polyvinylidenefluoride (PVDF). The membranes tested were between 100 and 150 kDa NMWCO in 20 min runs with 40 mL of the microalgae *Nannochloropsis* sp., and the flux was measured with water both before and after contact between the membrane and the fresh algal cells. Only the PVDF membrane lost flux after contact with the microalgae; this membrane is highly susceptible to fouling in fluctuations of pH and oil concentrations (Mah et al., 2012). The regenerated cellulose membrane outperformed the polysulfone membrane at similar kDa cutoffs; thus, a smaller 30 kDa regenerated cellulose membrane was employed to heighten purification. The authors found that a 30 kDa regenerated cellulose membrane could remove 89% of proteins vs. only 61% of proteins at 100 kDa; further sonication of the algal cells provided both higher fluxes and purities.

2.4.3. Inorganic/Ceramic membranes

There is a substantially less variety in inorganic membranes vs. their organic counterparts; they are generally focused on an alpha-alumina support structure with titanium oxide (Alicieo et al., 2002; Basso et al., 2006; Cao et al., 2008a and b; Gomes et al., 2010; Baroutian et al., 2011; Gomes et al., 2011; Gomes et al., 2013) or zirconium oxide (Cheng et al., 2009). These membranes have numerous positive qualities over organic membranes, such as increased fouling, temperature and pH fluctuation resistance, and a longer time-on-stream – this allows inorganic membranes to deal more effectively with the base catalysts used in transesterification reactions endemic to biodiesel production (Barredo-Damas et al., 2010; Atadashi, 2015). These increased resistances additionally lend to usefulness in a continuous process in which a FAME-rich permeate flow is separated from an unreacted retentate as transesterification occurs down the length of a membrane bioreactor (Cao et al., 2008a; Baroutian et al., 2011).

When discussing the separation of biodiesel from unwanted components, glycerol separation again becomes paramount. Thus, glycerol separation has been studied in literature from both palm and canola oil (Wang et al., 2009; Saleh et al., 2011) in pore sizes in the ultrafiltration to microfiltration range (Wang et al., 2009; Saleh et al., 2011; Atadashi et al., 2012). In these pore sizes, increases in transmembrane pressure and pore size increase the permeate flux while potentially decreasing the ability to filtrate glycerol at higher pressures (Hua et al., 2007; Gomes et al., 2010; Atadashi et al., 2012). Even though glycerol and soap will form agglomerates with rough sizes of 2.21 μm, increases in pore size to 0.6 μm will still yield increases in glycerol permeate concentration, implying that some free glycerol still exists (Wang et al., 2009). Additionally, in time-on-stream tests, larger pores and higher membrane pressures lead to fouling due to these glycerol agglomerates (Hua et al., 2007; Gomes et al., 2010). With a 0.05 μm ceramic membrane at 25 °C, Saleh et al. (2011) successfully met ASTM standards for glycerol in the final biodiesel product (less than 0.02 wt.%). Increases in temperature seem to correlate positively with both permeate flux and separation – Atadashi et al. (2012) increased glycerol retention to 99.2% at temperatures up to 40 °C. Additional increases have been noted at temperatures up to 60 °C in systems lacking methanol as a component (Wang et al., 2009) – this may not be noted in systems where phase inversion can occur (Cheng et al., 2009; Saleh et al., 2011).

Cation removal is more complex and is dependent on the cation being discussed – namely, the “reverse micelle” particles formed between

glycerol and soap are dependent on the cation in question (Wang et al., 2009). In a study by Wang et al. (2009), the authors were able to decrease the potassium and magnesium content of the permeate flow by decreasing the pore size from 0.6 to 0.1 μm , decreasing potassium and magnesium by 60% and 40%, respectively. Sodium and calcium retention was unaffected by this decrease – leading the authors to conclude: “no trend of retention of cation with pore size was observed in this work” (Wang et al., 2009). Further work with calcium removal reflected this conclusion – however, the addition of sodium carbonate allowed for much greater calcium retention, reducing the calcium concentration in the permeate from 305 ppm to 1.9 ppm for a 0.1 μm pore size (Ferrero et al., 2014). Given that sodium is more readily removed by a membrane than calcium, the exchange of these cations allowed for calcium to be more easily removed as calcium carbonate (Ferrero et al., 2014). If these soaps are not handled properly, they can easily foul the membrane – Gomes et al. (2011) found that a crude biodiesel product had roughly a fifth of the permeate flux of a synthetic biodiesel-glycerol-ethanol mixture (12.9 kg/h/m² vs. 78.4 kg/h/m²). This mimics behavior as seen above with organic membranes (Saleh et al., 2010b) – however, agglomerates can be more easily removed in ceramic membranes with hexane at high flow velocities and low transmembrane pressures (Basso et al., 2006). Alcohols such as ethanol further complicate separation mechanics in ceramic membranes as well as their organic counterparts, as glycerol droplet size is modified by hydrophilic surfactants (van der Graaf et al., 2005) which decrease interfacial tension in the agglomerated particles (Yilmaz et al., 1999; Pittia et al., 2005). With an α -Al₂O₃/TiO₂ membrane, Gomes et al. (2010 and 2011) found complex effects on the permeate flux, increasing from 63.1 kg/h/m² at 5 wt.% ethanol to 78.4 kg/h/m² at 10 wt.% ethanol, and decreasing to 59.5 kg/h/m² at 20 wt.% ethanol. However, the effects on glycerol retention were less complex, with direct decreases as ethanol concentration increased (99.6% at 5 wt.% to 98.1% at 20 wt.%, respectively) (Gomes et al., 2010).

Water has complex effects on phase behavior (Gomes et al., 2011; Gomes et al., 2013) as previously described in organic membranes (Saleh et al., 2010b). For an α -Al₂O₃/TiO₂ membrane, Gomes et al. (2011) facilitated glycerol separation with the addition of 20 wt.% acidified water (0.5% HCl), decreasing glycerol concentration in the permeate flow from 0.1 wt.% to less than 0.02 wt.% glycerol in the permeate for transmembrane pressures between 1-3 bar (from 0.005 wt.% glycerol to 0.014 wt.% glycerol from 1 bar to 3 bar, respectively). These concentrations, however, produced much smaller steady-state permeate fluxes, reaching no higher than 10.3 kg/h/m² at 3 bar transmembrane pressure, a stark decrease from 78.4 kg/h/m² at 2 bar transmembrane pressure without added water (Gomes et al., 2011). Later work from these authors increased acidified water concentration to around 30 wt.% for the same α -Al₂O₃/TiO₂ membrane (Gomes et al., 2013). While the permeate flux increased (up to 57.6 kg/h/m²), the glycerol retention was unstable, with permeate concentrations as high as 40 wt.% glycerol in some cases implying little retention occurred. This behavior is identical to that seen above with organic membranes (Saleh et al., 2010b) – increasing water content can allow the emulsion of droplets to coalesce in the bulk phase (Groeneweg et al., 1998). Reiterating as seen above, separation of glycerol and unreacted triglycerides from the final biodiesel product relies on a two-phase system (Cao et al., 2007; Dubé et al., 2007; Cheng et al., 2009), which is both composition and temperature dependent (Cheng et al., 2009).

2.5. Reaction-based separation processes in biodiesel purification

In the case of reversible reactions, the process yield is limited by the equilibrium. To overcome this limitation, a separation process should be integrated with the reaction to separate the substance (product) and keep its concentration from the equilibrium concentration. Hybrid reaction-membrane separation (e.g., membrane bioreactor), reactive distillation, and adsorptive distillation system are some of the common reaction-based separation methods (Huang and Ramaswamy, 2013).

2.5.1 Reactive distillation

The integration of chemical reaction and product separation (purification) in a single multifunctional process is known as reactive distillation. This integration declines the chemical equilibrium limitations, avoids the potential necessity of auxiliary solvent, and increases the selectivity (Lei et al., 2005; Kiss, 2013; Kolah et al., 2013). Therefore, reactive distillation has the potential

to improve the efficiency of the process while it needs a lower capital investment, operation cost, and energy consumption (Sundmacher and Kienle, 2002). However, this process also has its own operation challenges and economic limitations especially in case of gas-liquid reactions at severe operating conditions of very slow reactions. In fact, a large column is required to provide a reasonable residence time in the case of very slow reactions which compromises the feasibility of the process (Kiss et al., 2006a and b; Kiss et al., 2007; Dimian et al., 2009; Kiss, 2010; da Silva et al., 2010; Gomez-Castro et al., 2010; Mueanmas et al., 2010; Qiu et al., 2010; Machado et al., 2011; Kolah et al., 2013; Poddar et al., 2015; Pérez-Cisneros et al., 2016).

Wang et al. (2001) reported 10% saving in energy consumption along with 50% higher productivity for methyl acetate hydrolysis using reactive distillation compared with the conventional process using fixed-bed reactor followed by a distillation process. Reactive distillation using acid catalysts has a potential to be used for biodiesel production or pretreatment of feedstock with high FFAs contents (Russbueldt and Hoelderich, 2009; Simasatikul et al., 2011; Kolah et al., 2013). Therefore, various designs have been studied to maximize the reaction rate and biodiesel yield (Kolah et al., 2013). It is noteworthy that the downstream alcohol recovery step can be avoided in the case of biodiesel production using reactive distillation (Qiu et al., 2010).

2.5.2. Membrane bioreactors for biodiesel processing

Of the organic membranes noted above, polysulfone has alone received attention in biodiesel production and refining (Shi et al., 2016a and b) due to its temperature resistance and relative inert behavior to other organic membranes (Hao et al., 2000; Li and Wang, 2005; Li et al., 2006; Slade et al., 2012). Quaternized ammonium was grafted to polysulfone to act as a catalyst in anion exchange membrane fuel cells (Slade et al., 2012); Shi et al. (2016a) applied this concept to biodiesel production via a chloromethylated polysulfone membrane. After alkalization at an optimum synthesis time of 24 h and an optimum ratio of chloromethyl ether:polysulfone of 10:1 (Hao et al., 2000), the biodiesel synthesis was performed with methanol and co-solvents (Shi et al., 2016b). Tetrahydrofuran (THF) and n-hexane both performed well as co-solvents for the reaction – the authors (Shi et al., 2016a and b) proceeded with n-hexane due to lower toxicities. The conversion increased with increasing amounts of n-hexane as a co-solvent, from 65.7% at 30 wt.% n-hexane to 95.8% at 60 wt.% n-hexane (Shi et al., 2016b). Small amounts of water in the reaction mixture had only a small negative effect – at 5 wt.% water, the conversion was 87.0% vs. 95.3% with no water in the mixture. Further increases in water content had sharper negative effects, decreasing to 73.9% at 6 wt.% water and 65.4% at 7 wt.% water. Small amounts of FFAs in the reaction mixture had limited effect, decreasing conversion to 91.3% at 2.5 wt.% FFA vs. the aforementioned 95.3% with no FFA content. After 5 runs with 4 h reaction times each, the catalyst only experienced a loss of 2.1% conversion, owing to its overall stability on the polysulfone surface (Shi et al., 2016b).

Inorganic membranes have seen a larger amount of focus due to their relative stability and narrow pore distribution as noted above compared with organic membranes (Cao et al., 2007; Dubé et al., 2007; Cao et al., 2008a and b; Tremblay et al., 2008; Baroutian et al., 2011; Falahati and Tremblay, 2012). Dubé et al. (2007) employed membrane reactor technology using an inorganic carbon membrane in biodiesel production and subsequent purification. At temperatures of 65 °C and 2 wt.% sulfuric acid, the authors were able to achieve up to 64% conversion; this conversion increased with increasing flow rates. A base catalyst (1 wt.% NaOH) was able to achieve 96% conversion at the same flow rate of 6.1 mL/min; however, this also allowed the saponification reaction to take place (Dubé et al., 2007).

As previously discussed, two-phase behavior is paramount in effective separation via membrane technologies; this is no less important when considering a membrane bioreactor (Cao et al., 2007; Cao et al., 2008a and b). Using a model for calculating droplet sizes based on interfacial tension for liquids of very different viscosities (DeRoussel et al., 2001), Cao et al. (2007) found a minimum droplet size of 12 μm for a suspension of oil droplets – thus, the authors employed no larger than 1.4 μm pore sizes in their work. Additionally, at methanol volume fractions below 0.31 (Ho et

al., 1990), phase inversion occurs – demonstrating this, the authors found a complete lack of separation at volume fractions of 0.28 for methanol (Cao et al., 2007).

In optimizing the inorganic membrane for bioreactor technology, three factors have thus far been studied – amount of catalyst (Tremblay et al., 2008; Baroutian et al., 2011), appropriate residence times for complete conversion (Tremblay et al., 2008; Falahati and Tremblay, 2012), and methanol-to-oil ratio (Cao et al., 2008a and b). Maximizing conversion is imperative for reducing the buildup of unreacted oil inside the reactor (Tremblay et al., 2008; Baroutian et al., 2011). Baroutian et al. (2011) tested potassium hydroxide catalyst loadings up to 250 mg/cm³ at temperatures of 50 and 70 °C in a packed bed reactor on activated carbon. For loadings of 37.5 mg/cm³, the conversion reached no higher than 89.3% at 70 °C - further increases to 143.75 mg/cm³ yielded conversions up to 93.5% at 70 °C. Beyond this, the conversion dropped slightly to, at maximum, 91.5% at 250 mg/cm³ and 70 °C due to soap formation. The authors concluded that an optimum catalyst loading for maximum conversion was 157.04 mg/cm³ based on numerical optimization. For a TiO₂ membrane, Tremblay et al. (2008) tested external loadings of a base catalyst (NaOH) in a methanol/oil mixture. With a 2 h residence time, complete conversion could be achieved with loadings as low as 0.03 wt.%; halving the residence time to 1 h required higher loadings of 0.05 wt.% for complete conversion. Further increases of catalyst (up to 1 wt.%) did little to the conversion of oil fed to the reactor; however, this was useful in converting the oil already present inside the reactor, achieving 98.2 % conversion of the initial oil at 1 wt.% NaOH (the conversion of the oil fed alongside the NaOH remained at 100%). At 0.03 wt.% NaOH and a 1 h residence time, transmembrane pressure continued to increase without reaching steady state – by contrast, increasing the residence time to 2 h for complete conversion allowed the transmembrane pressure to stabilize at 30.2 kPa (Tremblay et al., 2008). At their limit, uncontrollable increases in transmembrane pressure will foul the reactor due to the accumulation of oil droplets on the membrane pores (Hua et al., 2007). Using a TiO₂ ultrafiltration membrane with a 30 nm pore size, Falahati and Tremblay (2012) tested residence times for canola oil conversion as low as 35 min for a membrane bioreactor – this work employed catalyst loadings of 0.5 and 1.4 wt.% and a reaction temperature of 65 °C. A steady state transmembrane pressure could not be obtained for residence times of 35 min, dramatically increasing to over 350 kPa in less than 20 min. By increasing residence time to 60 min, the transmembrane pressure could then stabilize for canola oil – the authors tested a variety of feedstocks at this minimum residence time, determining that higher residence times were needed for certain feedstocks to stabilize the pressure at manageable levels (65 min for corn oil and 80 min for waste cooking oil) (Falahati and Tremblay, 2012).

In the earlier work discussed above, Cao et al. (2007) employed different methanol/oil molar ratios from 11:1 to 46:1. The authors (Cao et al., 2008a and b) posited that a lower molar ratio (6:1) could be reached by recycling the methanol-rich phase. With a TiO₂ membrane with a nominal molecular weight cutoff of 300 kDa, Cao et al. (2008a) tested the use of cooling for the retentate phase in order to separate methanol from biodiesel for the purposes of recycling. Even with complete recycling (100% without purge), the FAME production was unhindered and remained between 0.0355 and 0.0423 kg/min with no correlation with recycle amounts. However, transmembrane pressure and glycerol concentration experienced a slow buildup at recycle amounts of 100% and 75%; thus, the authors (Cao et al., 2008a) recommend a 50% recycle for the methanol-rich phase to avoid unwanted fouling of the bioreactor via glycerol agglomeration (Saleh et al., 2010b; Gomes et al., 2011). To test this concept with high FFA feedstocks, later work (Cao et al., 2008a) utilized methanol recycling to reach a 10:1 molar ratio for a variety of feedstocks, including soybean, palm and canola oil as well as yellow and brown grease. All of these runs were conducted at a reaction temperature of 65 °C and a 0.5 wt.% loading of NaOH as a catalyst. This reaction system was able to outperform a batch reactor at similar conditions for glycerol content with water washing for both reactors, meeting ASTM standards (less than 0.24 wt.%) – additionally, the soybean and canola products met this standard in the absence of any water washing whatsoever.

3. Biodiesel upgrading

Biodiesel has been blended with petroleum diesel and used successfully as transportation fuels in modified engines (Schuchardt et al., 1998; Kim et al., 2004; Demirbas, 2008). However, it still suffers from moisture absorption,

corrosiveness, high viscosity, poor cold-flow properties, and low power density mainly due to high oxygen content (Srifa et al., 2015).

To address the issues associated with biodiesel, direct or indirect upgrading of triglycerides and fatty acids could be performed to produce diesel-like hydrocarbons (also known as “renewable diesel”). For a detailed discussion on terminology and historical perspectives of biodiesel and renewable diesel, see the review by Knothe (2010). In the context of this review, biodiesel upgrading refers to the conversion of vegetable oils, animal fats, bio-based triglycerides, fatty acids, and FAEEs into hydrocarbons by thermochemical and catalytic processes.

3.1. Upgrading routes

The main possible routes for obtaining fuels and chemicals from triglycerides, as representative molecules for bio-based oils and fats, are illustrated in Figure 2. It is imperative to understand that the deoxygenation pathways depicted in this scheme do not reveal any mechanistic information. Several studies have been performed to gain some insights into the mechanism of deoxygenation under different atmospheres. Detailed discussions about mechanisms of deoxygenation are presented in recent reviews by Gosselink et al. (2013) and Rogers and Zheng (2016).

Biodiesel consumption results in lower carbon monoxide, particulate matter, and unburned hydrocarbon emissions; however, it typically leads to higher NO_x emissions, as compared with petroleum diesel (Al-Dawody and Bhatti, 2013). However, the amount of oxygen in biodiesel or its parent oil is significantly higher than its nitrogen content and much higher than oxygen content in petroleum diesel. On the other hand, any effort to remove oxygen will result in parallel removal of nitrogen (and/or sulfur) (Bezergianni et al., 2010a). Hence, effective catalytic deoxygenation of bio-based oils will practically ensure obtaining a NO_x-free diesel. For this reason, (hydro)denitrogenation is not discussed in this review and interested readers are referred to the reviews elsewhere (Hoekman and Robbins, 2012; Yang et al., 2016).

Cracking is unattractive due to high yields of light hydrocarbons (C₁-C₄) and short-chain alkanes (C₅-C₁₅) with lower energy densities (Dupain et al., 2007; Sotelo-Boyas et al., 2010; Vinh et al., 2011). Commercial silica-alumina, zeolites, and fluid catalytic cracking catalysts are typically used for this type of reactions (Katicaneni et al., 1995; Dupain et al., 2007; Vinh et al., 2011). In contrast, deoxygenation appears promising since it produces diesel-like hydrocarbons with low oxygen content as compared with cracking and esterification processes. The fuel properties of renewable diesel (e.g., cetane number) obtained by catalytic deoxygenation of natural oils could even exceed its fossil-based counterpart (Snåre et al., 2009; Kiatkittipong et al., 2013; Phimsen et al., 2016). Furthermore, designing new catalytic systems and optimizing reaction conditions could maximize the yield of unsaturated hydrocarbons and alcohols, which can open new paths for production of higher value chemicals (Hollak et al., 2013). Note that the production of biodiesel followed by deoxygenation is possible but industrially irrelevant due to extra processing steps, which significantly increases capital and operating costs.

As concisely shown in Figure 2, two key processes for deoxygenating bio-based oils have been investigated thus far. One is deoxygenation in an inert atmosphere such as nitrogen, helium, or argon. Monometallic catalysts supported on Al₂O₃, SiO₂, and carbon (especially carbon-supported noble metals) are the catalysts of choice for selective deoxygenation under inert atmospheres (Snåre et al., 2006; Snåre et al., 2008; Morgan et al., 2012). Nevertheless, several issues including limited deoxygenation, rapid deactivation of catalyst due to coking, and most notably high selectivity toward unwanted reactions like cracking and aromatization have hampered the advancement of this method toward larger scales (Snåre et al., 2008; Lestari et al., 2009a). As an alternative, deoxygenation in the presence of hydrogen has been proposed. The idea originally came from hydrotreating petroleum-based fuels to remove unwanted heteroatoms such as sulfur and nitrogen to improve the quality of the products and address some environmental concerns (Furimsky, 1983). Unlike the previously mentioned method, in this process deoxygenation could occur through both hydrodeoxygenation (HDO) and decarboxylation/decarbonylation (DCO) pathways. In addition, undesired reactions such as cracking, aromatization, cyclization, oligomerization, and coking are significantly hindered in the presence of H₂ (Madsen et al., 2011). In principle, HDO pathway yields a

product with one carbon atom more than that of DCO. This is advantageous from both environmental and energy efficiency viewpoints since less CO and CO₂ are released in the product gas stream and more carbon ends up in the product liquid stream. Although it initially seems that more hydrogen is consumed in the HDO pathway as opposed to DCO, the successive methanation of CO and CO₂ would increase the overall hydrogen consumption (Srifa et al., 2015). Saturation of double bonds also generally occurs during HDO processes.

reactions such as oligomerization, cracking, and coking promoted in the absence of H₂ due to inherent hydrogen deficiency of bio-based oils. Thus, co-feeding hydrogen as a reactant seems necessary to sustainably obtain a high-quality product without the frequent need for catalyst regeneration cycles. Nevertheless, the high hydrogen pressures that are sometimes required for effective deoxygenation may be a limiting factor for commercial HDO processes.

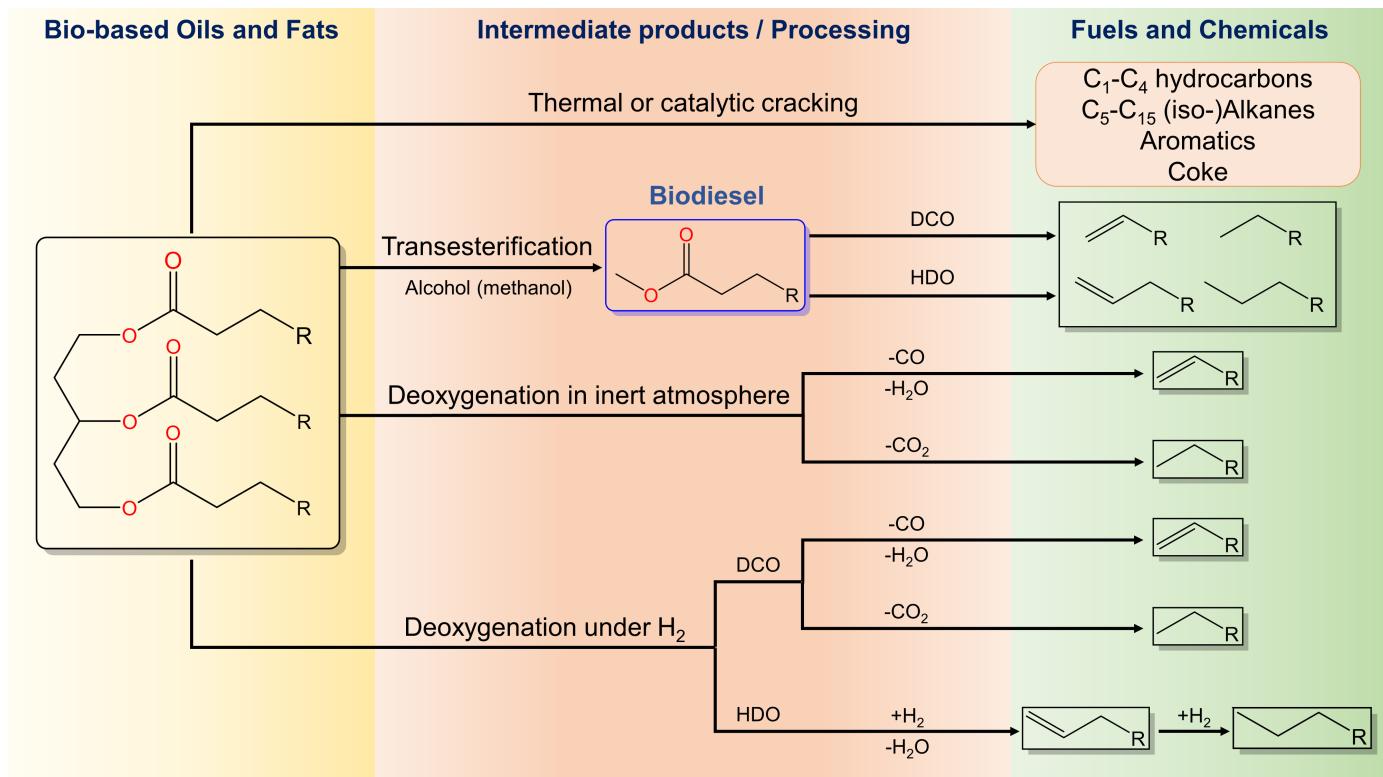


Fig. 2. Possible reaction pathways for obtaining fuels and chemicals from triglycerides as representative molecules for bio-oils.

It should be noted that the hydrocarbon chain in the structure of triglycerides and/or fatty acids (i.e., -R) could be long or short, as well as saturated or unsaturated depending on the source of the triglyceride. For instance, crude palm kernel oil comprises mainly of saturated fatty acids such as lauric acid (C₁₂, 54.5%), myristic acid (C₁₄, 12.1%), and palmitic acid (C₁₆, 7.7%) (Ng et al., 2003). Rapeseed oil, on the other hand, contains primarily unsaturated C₁₈ fatty acids: 63.7% oleic acid, 15.4% linoleic acid, and 14.3% linolenic acid, with one, two, and three double bonds, respectively (Sotelo-Boyas et al., 2010). Deoxygenation under H₂ usually saturates this chain if unsaturated originally (Han et al., 2011a; Coumans and Hensen, 2017), whereas after deoxygenation under inert gases, the double bonds could remain intact (Snåre et al., 2008).

The extent of DCO and HDO routes under H₂ depends on feedstock composition, reaction conditions, and the choice of catalyst (Kiatkittipong et al., 2013). The results of selected investigations for deoxygenating vegetable oils and their surrogate compounds are summarized in Tables 1-3. It is evident from these results that conventional hydrotreating catalysts have a higher selectivity for HDO than DCO reactions (Table 1). Supported noble metal catalysts, on the contrary, prefer DCO over HDO in the presence of hydrogen. Comparing deoxygenation processes in the absence and presence of hydrogen indicates the superiority of the latter. Even in the case of Pd/C catalysts (initially believed to work identical under Ar/He and H₂ environments), hydrogen has been proven beneficial (Immer et al., 2010; Rozmyslowicz et al., 2012). For instance, higher catalyst stability and quicker kinetics were reported for stearic acid deoxygenation under 10% H₂ compared with He atmosphere using a 5% Pd/C catalyst (Immer et al., 2010). This is because undesired side

3.2. Upgrading catalysts

Catalysts investigated to date for biodiesel upgrading can be categorized in three main groups. The first group comprises of hydrotreating catalysts including Ni- and Co-promoted Mo or W sulfides conventionally supported on silica and/or alumina materials. The second category includes supported metals with a focus on carbon-supported noble metals such as Pd and Pt. Lastly, transition metal carbides, nitrides, and phosphides have been recently reported to be active for HDO reactions and selective toward long-chain paraffins or olefins. Taking into account the considerable effect of support material in improving reactivity, selectivity, and stability of catalysts, it is imperative to acknowledge the role of different supports beside the active phase of upgrading catalysts.

3.2.1. Conventional hydrotreating catalysts

Transition metal sulfide-based catalysts were originally developed in refineries to remove heteroatoms (i.e., sulfur, nitrogen, oxygen, and metals) from distillate fuels by hydrotreating at elevated temperatures and pressures (Parkash, 2003). The presence of these heteroatoms could worsen fuel properties, corrode engines and storage units, deactivate catalysts in downstream units, and raise environmental concerns due to the emission of SO_x and NO_x (Parkash, 2003; Srivastava and Hancsok, 2014). Biodiesel suffers from some other problems such as low energy density and chemical stability and poor cold flow properties due to the presence of heteroatoms,

Table 1.

Summary of some literature findings on catalytic deoxygenation using conventional hydrotreating catalysts.

Entry	Feed	Catalyst	T (°C)	P _{H₂} (bar)	Contact time/Space velocity	Reactor	Yield of major products*	Side products**	Reference
1	Rapeseed oil	NiMoS/γ-Al ₂ O ₃	350	80	3 h	batch	75% (C ₁₃ -C ₂₂)	iso.-DCO ₂	Sotelo-Boyas et al. (2010)
2	Rapeseed oil	NiS/Al ₂ O ₃	280	35	0.25 h ⁻¹	fixed-bed	56% (C ₁₇ :0)	FA (40%)	
3	"	MoS/Al ₂ O ₃	"	"	"	"	72% (C ₁₈ :0)	DCO ₂ -alc.	Kubička and Kaluža (2010)
4	"	NiMoS/Al ₂ O ₃	"	"	"	"	70% (C ₁₈ :0) 24% (C ₁₇ :0)	-	
5	Rapeseed oil [a]	CoMoS/MCM-41	320	35	1 h ⁻¹	fixed-bed	53% (HCs)	DCO-DCO ₂ FA-FE	Kubička et al. (2010)
6	"	CoMoS/MCM-41	"	70	"	"	93% (HCs)	DCO-DCO ₂	
7	Palm fatty acid distillate	NiMoS/γ-Al ₂ O ₃	375	40	1 h	batch	75% (diesel) ^[b]	DCO-DCO ₂	
8	Degummed crude palm oil	NiMoS/γ-Al ₂ O ₃				batch	70% (diesel) ^[b]	DCO-DCO ₂	Kiatkittipong et al. (2013)
9	Palm kernel oil	NiMoS/γ-Al ₂ O ₃	330	50	1 h ⁻¹	trickle-bed	53% (C ₁₀ -C ₁₂)	DCO-DCO ₂ met.	Itthibenchapong et al., (2017)
10	Palm oil [c]	NiMoS/γ-Al ₂ O ₃	300	50	0.25 h ⁻¹	fixed-bed	54.7% (C ₁₈ :0) 34.3% (C ₁₆ :0)	DCO-DCO ₂	
11	"	NiMoS/γ-Al ₂ O ₃	300	50	1 h ⁻¹	"	47.4% (C ₁₈ :0) 30.7% (C ₁₆ :0)	DCO-DCO ₂	Srifa et al. (2014)
12	"	NiMoS/γ-Al ₂ O ₃	300	15	1 h ⁻¹	"	43.9% (C ₁₈ :0) 29.3% (C ₁₆ :0)	DCO-DCO ₂	
13	"	NiMoS/γ-Al ₂ O ₃	420	50	1 h ⁻¹	"	22.3% (C ₁₆ :0) 12.7% (C ₁₈ :0)	DCO-DCO ₂ cra.	
14	Spent coffee oil [d]	NiMoS/γ-Al ₂ O ₃	400	40	2 h	batch	34% (C ₁₂ -C ₁₈) 20% (C ₅ -C ₁₁)	DCO-DCO ₂	Phimsen et al. (2016)
15	Canola oil	NiMoS	375	90	8 h	batch	90% (diesel) ^[e]	cra.-dim.	
16	"	CoMoS	"	"	"	"	78% (diesel) ^[e]	DCO-cra. dim.-olf.	Zhang et al. (2014)
17	Jatropha oil [f]	NiMoS/SiO ₂ -Al ₂ O ₃	350	40	7.6 h ⁻¹	fixed-bed	75% (C ₁₁ -C ₂₀) 8% (C ₅ -C ₁₀)	DCO-DCO ₂ iso.-cra.	Liu et al. (2011)
18	Sunflower oil [g]	NiMoS/Al ₂ O ₃ /F	350	40	1 h ⁻¹	semi-batch	75% (C ₁₁ -C ₂₁)	iso. (35%)-cra.	Kovács et al. (2011)
19	Waste cooking oil [h]	Commercial NiMoS	330	83	1 h ⁻¹	fixed-bed	90% (diesel) ^[a]	DCO-DCO ₂	Bezergianni et al. (2010a)
20	Waste cooking oil [h]	Commercial NiMoS	330	83	1 h ⁻¹	fixed-bed	91% (C ₁₅ -C ₁₈)	DCO-DCO ₂ iso. (6%)	
21	"	Commercial NiMoS	398	"	"	"	61% (C ₁₅ -C ₁₈)	iso.(36%) cra.(21%) dim.(14%)	Bezergianni et al. (2010b)
22	C ₁₈ fatty acids	NiWS/SiO ₂ -Al ₂ O ₃	300	50	not specified	fixed-bed	33% (C ₁₈ :0) 14% (C ₁₇ :0)	DCO-DCO ₂ cra.	Yang et al. (2013b)
23	Methyl oleate	NiMoS/γ-Al ₂ O ₃	260	60	6.5 h ⁻¹	fixed-bed	34% (C ₁₈ :0) 9% (C ₁₇ :0)	DCO-DCO ₂	Coumans and Hensen (2017)
24	Methyl palmitate	NiMoS/γ-Al ₂ O ₃	260	15	2 h	batch	35% (C ₁₅ :0) 8% (C ₁₆ :0)	dim.	Han et al. (2012)
25	Caprylic acid	NiMoO/γ-Al ₂ O ₃	360	17	6 h ⁻¹	fixed-bed	12.5% (C ₈ :0) 5.6% (C ₈ :1)	iso.	Boda et al. (2010)
26	Palmitic acid	MoO ₃ /CNT	220	40	6 h	batch	92% (C ₁₆ :0)	DCO-DCO ₂	Ding et al. (2015)
27	Methyl laurate [f]	NiMoO/SAPO-11	325	30	5 h ⁻¹	fixed-bed	87% (C ₁₂ :0) 11% (C ₁₁ :0)	iso. (5%)	Chen et al. (2015)

*: Yields are approximate numbers and at different conversions; (C_xy) x = number of carbons, y = number of unsaturated (double) bonds.**: iso.=isomerization; DCO=decarbonylation; DCO₂=decarboxylation; FA=fatty acid; FE=fatty ester; met.=methanation; cra.=cracking/hydrocracking; dim.=dimerization; olf.=olefin; alc.=alcohol.[a] H₂/feed molar ratio=50; [b] hydrocarbon yield in the 180-360 °C boiling range; [c] H₂/feed volume ratio=1000; [d] H₂/feed molar ratio=2; [e] hydrocarbon yield in the 200-350 °C boiling range; [f] H₂/feed volume ratio=800; [g] H₂/feed volume ratio=500; [h] H₂/feed volume ratio=4071.

most noticeably oxygen. Therefore, the same principles could also apply to remove oxygen from bio-oils and bio-fats using conventional hydrotreating catalysts, although the amount of oxygen in bio-oils (28-40 wt%) is considerably higher than the amount of oxygen (<1 wt%) and sulfur (<4 wt%) in petroleum-based fuels (Mortensen et al., 2011). The oxygen atoms present in the feed are able to oxidize transition metal sulfides to their less reactive oxide phase, especially in the absence of a sulfur source. Hence, a constant flow of H₂S or some other sulfur-containing compound may be required (Furimsky, 2000).

Transition metal sulfides have proven effective catalysts for HDO, but essentially inept in the absence of H₂ and H₂S as expected by their deoxygenation pathway, i.e., a reverse Mars-Van Krevelen mechanism (Zhao et al., 2013). In this mechanism, H₂ interacts with sulfur atoms on the MoS₂ surface and forms H₂S and a coordinatively unsaturated site. This vacant site can chemisorb oxygenates, the oxygen atom of which oxidizes the catalyst while hydrocarbon products are formed with or without further hydrogenation (Romero et al., 2010). Thus, it is clear that the presence of H₂ is necessary for the catalyst to proceed with deoxygenation. That is also why these catalysts are exclusively active for HDO rather than DCO pathway. Moreover, in the absence of H₂S or another sulfur source, oxygen could replace sulfur atoms, forming less active molybdenum oxide species on the surface. The results of some experiments using hydrotreating catalysts are compiled in Table 1.

The main advantages of conventional hydrotreating catalysts are as follows. Firstly, they are very active for deoxygenation and selective to HDO, which assures high hydrocarbon yields. Secondly, this class of catalysts is produced in large scales and studied comprehensively and extremely well due to their industrial presence for decades. Thus, minimal training and intellectual efforts are needed for synthesizing, characterization, and eventually commercialization (Ruddy et al., 2014). Additionally, they are robust, meaning that they are not very sensitive to other heteroatoms that may exist in biomass feedstocks.

There are several drawbacks for these catalysts, on the other hand. One of the main drawbacks is the need for continuous co-feeding of a sulfur source such as H₂S to maintain catalytic activity, which deprives the resulting biofuel from its sulfur-free nature (Badawi et al., 2011). This is particularly important as strict regulations for sulfur levels in diesel fuel are mandated by governments (Stanislaus et al., 2010). Additionally, hydrotreating is typically done at high pressures of hydrogen, requiring expensive equipment including heavy-duty compressors and special reactors, increasing both capital and operating costs. Another disadvantage is the sensitivity of these catalysts to the presence of water, a ubiquitous substance in bio-based feedstocks (Senol et al., 2005a). Last but not least, this class of catalysts is prone to coking, especially with feedstocks that have unsaturated C=C bonds, known to be coke precursors (Furimsky and Massoth, 1999). These shortcomings in the performance of transition metal sulfide catalysts call for research on new non-sulfide materials for catalyzing deoxygenation reactions.

The same mechanistic principles can be applied to transition metal oxides. However, the oxide form of these catalysts is less reactive than the sulfide form for deoxygenation reactions (Senol et al., 2005b). Although supported molybdenum oxides have been recently found to be active for HDO of some model compounds (Boda et al., 2010; Chen et al., 2015; Ding et al., 2015), their activity seems to be inferior to the sulfide form at elevated pressures used in hydrotreating processes (Senol et al., 2005b).

3.2.2. Supported metallic catalysts

To address some issues of conventional hydrotreating catalysts for bio-oil deoxygenation, supported mono- and bi-metallic catalysts gained substantial research attention (Table 2). This category of catalysts is comprised mainly of supported noble metals and base metals. These catalysts do not require co-feeding of a sulfur source, are not very sensitive to water, and are able to activate H₂ at low/moderate temperatures. Therefore, they are promising candidates for converting bio-oils into liquid fuels.

Murzin's group pioneered the deoxygenation of vegetable oils and many model compounds using a variety of supported metallic catalysts (Kubickova et al., 2005; Snåre et al., 2006; Mäki-Arvela et al., 2007; Snåre et al., 2007; Lestari et al., 2008; Mäki-Arvela et al., 2008; Snåre et al., 2008; Simakova et al., 2009; Lestari et al., 2009b and c; Bernas et al., 2010; Lestari et al., 2010; Simakova et al., 2011). Their studies show that supported noble metals are

generally selective to DCO and thus produce C_{n-1} products. They suggest that HDO may proceed on bifunctional catalysts in the presence of hydrogen, where metal sites are active for hydrogenation/hydrogenolysis and the support's acidic sites are responsible for deoxygenation (*via* dehydration). Among monometallic catalysts, noble metals, especially Pd, have shown excellent performance for deoxygenation of various model compounds and bio-oils. Despite their effectiveness, the high price and scarcity of noble metals are important prohibitive factors for cost-effective production of bio-based fuels.

The strong affinity of these catalysts for hydrogen promotes the hydrogenation of coke precursors adsorbed on the surface and ensures a longer lifetime for the catalyst (Zhu et al., 2011). These catalysts also have a high resistance under hydrothermal conditions, which makes them excellent candidates for deoxygenation of bio-based feedstocks (Ruddy et al., 2014). However, studies suggest that leaching and sintering of the active phase might be major problems for utilization of these catalysts over extended periods (Han et al., 2011b). In addition, some works indicate their sensitivity to sulfur, nitrogen, and trace inorganic contaminants (e.g., iron) that might be present in biomass and bio-oil (Nagy et al., 2009; Ardianti et al., 2011; Choudhary and Phillips, 2011), although the utilization of bimetallic alloys have increased their tolerance to sulfur and nitrogen (Nagy et al., 2009). This category of catalysts is not a good choice for producing alkenes/alkynes since they saturate the double/triple bonds of triglycerides, FFAs, and FFAEs prior to breaking their structures or oxygen removal (Madsen et al., 2011).

A comparison between Pd/C and NiMoS/ γ -Al₂O₃ indicates that the former is superior, in terms of activity and selectivity to diesel-range hydrocarbons, for pure fatty acid feedstocks, but inferior in the case of bio-oils (Kiatkittipong et al., 2013). Despite similar observations in other studies (Boda et al., 2010; Madsen et al., 2011; Phimsen et al., 2016), there is no systematic study undertaken to address this phenomenon. Based on turnover frequencies calculated for deoxygenating oleic acid over four alumina supported monometallic catalysts, catalytic activities were found to be in the order: Co > Pd > Pt > Ni. It was also emphasized that DCO was more dominant in the case of Pd, Pt, and Ni catalysts, whereas the Co/Al₂O₃ catalyst deoxygenates palm oil through both DCO and HDO pathways (Srifa et al., 2015). Similar results were obtained for deoxygenation of spent coffee oil using Pd/C and NiMoS/ γ -Al₂O₃ (Phimsen et al., 2016).

At this point, supported noble metals do not seem to be an industrially relevant option mainly because of their high prices, sensitivity to contaminants, as well as leaching and sintering problems. Other monometallic catalysts such as Co and Ni have shown promise as alternatives for noble metals, but important issues such as sensitivity to trace contaminants, deactivation, and stability still remain unresolved. These issues should be addressed before any attempts can be made on industrialization of these catalysts for producing renewable diesel fuels.

3.2.3. Transition metal carbides, nitrides, and phosphides

Transition metals in different forms have recently emerged as effective deoxygenation catalysts (Table 3). Among them, molybdenum and tungsten have gained much attention due to their unique HDO abilities. Mo₂C and W₂C have shown promising results in deoxygenation of various vegetable oils and model compounds (Han et al., 2011a and b; Han et al., 2012; Sousa et al., 2012; Hollak et al., 2013; Gosselink et al., 2013; Qin et al., 2013; Wang et al., 2013; Stellwagen and Bitter, 2015). Compared with Pd and Pt catalysts, transition metal carbides exhibited higher catalytic activity, better selectivity toward HDO rather than DCO, and much higher resistance to leaching and deactivation (Han et al., 2011b). Mo₂C/CNF was found to be an excellent catalyst for arriving at paraffinic hydrocarbons due to its high hydrogenation ability, while W₂C/CNF was shown to be appropriate for producing olefins (Hollak et al., 2013). Mo₂C was more stable presumably because of lower concentration of coke precursors, i.e., olefins, in the product stream. Additionally, Mo₂C was less sensitive to oxidation compared with W₂C. The oxide phase was found to be responsible for dehydration reactions and thus producing unsaturated hydrocarbons (Stellwagen and Bitter, 2015). Hence, it seems that a tradeoff exists between catalytic activity and selectivity toward olefins.

Transition metal nitrides are studied even more extensively than carbides for hydrodesulfurization and hydrodenitrogenation (Furimsky, 2003).

Table 2.

Summary of some literature findings on catalytic deoxygenation using supported metallic catalysts.

Entry	Feed	Catalyst	T (°C)	P (bar)	Contact time/ Space velocity	Reactor	Yield of major products*	Side products**	Reference
1	Rapeseed oil	Pt/H-ZSM-5	380	110 (H ₂)	3 h	batch	41% (C ₅ -C ₁₂) 21% (C ₁₃ -C ₂₂)	iso.-cra.	Sotelo-Boyas et al. (2010)
2	"	Pt/H-Y	"	"	"	"	36% (C ₁₃ -C ₂₂) 28% (C ₅ -C ₁₂)	iso.	
3	Jatropha oil ^[a]	PtPd/Al ₂ O ₃	350	30 (H ₂)	h ⁻¹	fixed-bed	81.4% (C ₁₇ :0) 13.9% (C ₁₅ :0)	-	Gong et al. (2012)
4	Spent coffee oil ^[b]	Pd/C	400	40 (H ₂)	2 h	batch	31% (C ₁₂ -C ₁₈) 17% (C ₅ -C ₁₁)	met.	Phimsen et al. (2016)
5	Palm fatty acid distillate	Pd/C	375	40 (H ₂)	0.5 h	batch	80% (diesel) ^[c]	-	Kiatkittipong et al. (2013)
6	Degummed crude palm oil	Pd/C	400	"	1 h	batch	70% (diesel) ^[c]	-	
7	Microalgae oil	Fe-MSN	290	30 (H ₂)	6 h	batch	51% (C ₁₃ -C ₂₀)	not discussed	Kandel et al. (2014)
8	Oleic acid	Fe-MSN	"	"	"	"	82% (C ₁₈ :0) 12% (C ₁₇ :0)	not discussed	
9	Triplamitin	Pt/γ-Al ₂ O ₃	325	20 (H ₂)	5 h	batch	43% (C ₁₅ :0)	-	Madsen et al. (2011)
10	Oleic acid	Pt/γ-Al ₂ O ₃	-	20 (H ₂)	5 h	-	95% (C ₁₇ :0)	-	
11	Oleic acid	Pt/γ-Al ₂ O ₃	-	9 (H ₂)	1 h	-	71% (C ₁₇ :0)	-	
12	Oleic acid	Co/γ-Al ₂ O ₃	330	50 (H ₂)	2 h ⁻¹	trickle-bed	50% (C ₁₈ :0) 44% (C ₁₇ :0)	met.	
13	"	Pd/γ-Al ₂ O ₃	"	"	"	"	72% (C ₁₇ :0)	est.	
14	"	Pt/γ-Al ₂ O ₃	"	"	"	"	51.1% (C ₁₇ :0)	SA-est.	Srifa et al. (2015)
15	"	Ni/γ-Al ₂ O ₃	"	"	"	"	25.5% (C ₁₇ :0)	SA-est.	
16	Stearic acid	Pd/C	300	6 (He)	6 h	semi-batch	95% (C ₁₇ :0)	-	Snåre et al. (2006)
17	"	Pt/C	"	"	"	"	75% (C ₁₇ :0)	cra.	
18	"	PdPt/C	"	"	"	"	59.1% (ΣC ₁₇)	-	
19	"	Rh/C	"	"	"	"	15.2% (ΣC ₁₇)	dim.-cra.-ket.	
20	"	Ru/C	"	"	"	"	8.6% (ΣC ₁₇)	dim.-cra.-ket.	
21	"	Ni/SiO ₂	"	"	"	"	10.5% (ΣC ₁₇)	cra.	
22	"	Pd/Al ₂ O ₃	"	"	"	"	10% (ΣC ₁₇)	ket.-dim.	
23	"	Pt/Al ₂ O ₃	"	"	"	"	9.2% (ΣC ₁₇)	ket.-dim.	
24	Stearic acid	Pd/C	300	15 (He)	0 h	semi-batch	24.7% (C ₁₇ :0), 8.3% (C ₁₇ :1)	-	Immer et al. (2010)
25	"	Pd/C	"	15 (He)	5 h	"	98% (C ₁₇ :0)	-	
26	"	Pd/C	"	15 (10%H ₂ -He)	1 h	"	98% (C ₁₇ :0)	-	Boda et al. (2010)
27	Caprylic acid	Pd/C	360	17 (H ₂)	6 h ⁻¹	fixed-bed	20.3% (C ₇ :0)	-	
28	palmitic acid	Pd/CNT	280	40 (H ₂)	6 h	batch	78.3% (C ₁₅ :0) 12.1% (C ₁₆ :0)	cra.	
29	methyl palmitate	Pd/CNT	240	15 (H ₂)	2 h	batch	34.5% (C ₁₅ :0)	not discussed	Ding et al. (2015)
30	"	Pt/CNT	"	"	"	"	22.4% (C ₁₅ :0) 3.5% (C ₁₆ :0)	not discussed	
31	Methyl oleate ^[d]	Ni/SBA-15	340	30 (H ₂)	20 h ⁻¹	fixed-bed	46% (C ₁₇ :0) 12% (C ₁₅ :0)	DCO-DCO ₂ cra.	Yang et al. (2012)

* Yields are approximate numbers and at different conversions; (Cx:y) x = number of carbons, y = number of unsaturated (double) bonds.

**: iso.=isomerization; cra.=cracking/hydrocracking; met.=methanation; est.=esterification; SA=stearic acid; dim.=dimerization; ket.=ketonization; DCO=decarbonylation; DCO₂=decarboxylation.[a] H₂/feed volume ratio=600; [b] H₂/feed molar ratio=2; [c] hydrocarbon yield in the 180-360 °C boiling range; [d] H₂/feed volume ratio=300 at 6 h on stream.

These materials are known to adsorb and activate hydrogen and can act as bifunctional catalysts with both metallic and acidic sites, which is beneficial for HDO of bio-oils (Miga et al., 1999). Nevertheless, very few studies have tested these catalysts for converting vegetable oils and model compounds into diesel-like hydrocarbons. Wang et al. (2012) examined the ability of NiMo nitride and carbide supported on ZSM-5 for hydrocracking of soybean oil. Complete conversions and high yields of hydrocarbon fuels (~50%) were

obtained for both catalysts. The nitride catalyst showed a higher selectivity toward DCO and methanation, which is undesired for producing fuels. However, this might not remain true if the support material was of a less acidic nature. In another study, γ-Al₂O₃-supported transition metal nitrides were investigated for HDO of oleic acid and canola oil (Monnier et al., 2010). Mo₂N/Al₂O₃ exhibited higher activity, oxygen removal, and alkane selectivity than vanadium and tungsten nitrides. Molybdenum nitride was

very selective toward HDO, producing almost exclusively *n*-octadecane from oleic acid. A high oxygen removal of ~90% and diesel fuel yield of 38-48% were obtained by hydrotreating canola oil over Mo₂N/Al₂O₃ for 450 h time-on-stream, indicating the high stability of the catalyst.

Transition metal phosphides (Ni and Mo phosphides) have also shown promising results for deoxygenation of bio-based feedstocks (Gong et al., 2012; Yang et al., 2012; Yang et al., 2013a; Chen et al., 2014; Zarchin et al., 2015; Yang et al., 2015; Peroni et al., 2016). Alumina-supported sulfided-NiMoP and PtPd catalysts demonstrated similar extents of deoxygenation for non-edible jatropha oil, but through different pathways (Gong et al., 2012). Sulfided-NiMoP maintained activity for 120 h time-on-stream, after which the activity reduced significantly, presumably due to the oxidation of the sulfide phase. Most recently, Peroni et al. (2016) examined the deoxygenation of palmitic acid by bulk and Al₂O₃-supported Ni₂P and MoP catalysts in a trickle fixed-bed reactor at 40 bar H₂ and 453-573 K. The results revealed that Ni₂P catalysts were intrinsically more active than MoP catalysts, although bulk MoP demonstrated the highest specific activity, meaning that its surface was more exposed to the reactants. DCO was generally more pronounced than HDO since the yields of pentadecane were higher than hexadecane. Besides these two products, hexadecanol, hexadecanoil, and palmityl palmitate (esterification product) were also observed in considerable amounts. Deactivation mechanisms were not discussed in this chapter.

Considering the literature findings stated above, transition metal carbides, nitrides, and phosphides seem promising candidates for substituting transition metal sulfides for deoxygenation purposes. Nevertheless, direct comparison of these catalysts with each other and with other types of catalysts is required to understand the deficiencies and strengths of each category. Moreover, deactivation mechanisms, catalytic stability, life cycle assessment, and the economics are only some of the issues that should be addressed for designing effective commercial-scale catalytic systems.

3.2.4. Role of support

Support materials can play a substantial role in catalyzing biodiesel upgrading. Several support materials have been investigated for deoxygenation of bio-oils and their model compounds. Alumina and zeolite supports were conventionally used for hydrotreating petroleum fuels. Lewis acid sites on Al₂O₃ can activate oxygenated species and facilitate deoxygenation through DCO pathway (Rogers and Zheng, 2016). Nevertheless, the presence of water in bio-based feedstocks can reduce the specific surface area of γ -Al₂O₃ by crystallization to Boehmite (Laurent and Delmon, 1994). Brønsted acid sites on zeolites promote HDO through hydrogenation-dehydrogenation reactions, but are also responsible for cracking, isomerization, and rapid deactivation via coking (Liu et al., 2011). Silica supports are known to be inert toward deoxygenation reactions and thus are interesting materials specifically for studying the role of active sites without any interferences from the support (Liu et al., 2011). Reducible metal oxides such as ZrO₂, CeO₂, TiO₂, and Cr₂O₃ in their reduced forms can chemisorb oxygenates through oxygen vacancies and facilitate deoxygenation.

Since its emergence, carbon in various forms has revolutionized catalysis research by its unique properties, viz., high surface area, ability to highly disperse the catalytic active phase, and inertness or functionality (Rodríguez-Reinoso, 1998). Carbon is able to accommodate various functional groups depending on the source as well as chemical and thermal treatment techniques used to prepare it (Lam and Luong, 2014). In addition, it can be produced by simple techniques from inexpensive sources such as carbohydrates or aromatic compounds (Lam and Luong, 2014). Carbon materials have been used extensively as supports for biodiesel upgrading studies and are expected to play a crucial role in industrialization of these catalysts in the future. In a study by Snare et al. (2006), high initial rates for deoxygenation of stearic acid by carbon-supported metallic catalysts compared with alumina and silica-supported catalysts were attributed to the effect of carbon in preventing sintering and/or coking due to its structural properties. Activated carbon was responsible for a noticeable increase in the activity and selectivity of Mo₂C for deoxygenating methyl stearate and methyl palmitate to *n*-octadecane and *n*-hexadecane, respectively (Table 3 entries 19-23) (Han et al., 2011a).

Mesoporous silicates (e.g., MCM-41, SBA-15, and SBA-16) have also been studied as supports for biodiesel upgrading catalysts (Wang et al., 2013). These materials are interesting because of their ability to disperse the active phase and their suitable structure for the diffusion of large molecules, such as those

present in vegetable oils (Stöcker, 2008). For instance, mesoporous silica nanoparticles have been proven as effective catalyst supports for upgrading microalgae oil using iron nanoparticles (Kandel et al., 2014). Furthermore, stearic acid deoxygenation on Pd/SBA-15 and Pd/C catalysts showed a higher turnover frequency in the case of Pd/SBA-15, indicating the effectiveness of the mesoporous support (Lestari et al., 2010). These materials can also accept new active sites via ion-exchange, adsorption, or grafting techniques (Nava et al., 2009). Most importantly, the amount and strength of acid sites can be tuned by changing the structure of silica-alumina as well as the amount of aluminum (Al) incorporated into the silica framework (Si/Al ratio) (Nava et al., 2009). Mesoporous aluminum silicates could, therefore, be an excellent choice for the support of HDO catalysts as they can provide a tunable amount of weak/moderate acid sites while improving the dispersion of the active phase and facilitating the diffusion of feedstock molecules.

3.3. Effect of operating parameters

Studying the effect of operating parameters on conversion and yield of desired products is very important as such information is necessary for scaling up the upgrading process and evaluating the economics. The key parameters for all types of catalysts include pressure, temperature, and contact time. In addition, the influence of sulfidation on conventional hydrotreating catalysts cannot be ignored. Although the choice of reactor is of great importance, it is extremely difficult (if not impossible) to make comparisons between systems with different reactor types. This is mainly because of different geometries and sizes, as well as different operating parameters used in various studies. Hence, more data with similar operating conditions is required to enable the evaluation of the effect of reactor configuration. The chain length and degree of saturation of feedstocks are also known to affect the upgrading product yields and the extent of side reactions. However, the modifications applied due to using different feedstocks would be considered fine-tuning and would not fit into the scope of this text. Other parameters such as the choice of solvent in batch studies could also play some role in the outcome of the deoxygenation reactions for biodiesel upgrading. However, the effect of these parameters is less significant than those considered in the following sections.

3.3.1. Sulfidation

Conventional hydrotreating catalysts, comprising mainly of transition metal sulfides, have been the predominant choice for deoxygenation of vegetable oils. The extent of sulfidation in transition metal sulfides has been demonstrated to significantly influence the activity, selectivity, and stability of the catalyst (Kubička and Horáček, 2011; Coumans and Hensen, 2017). Thus, the amount of H₂S or other sulfiding agents co-fed into the system could be of great importance for an efficacious upgrade. The sulfiding agent is responsible for keeping the catalyst in its highly active sulfide form, otherwise changed to the less active oxide form through oxygen atoms of the bio-oil feed (Furimsky and Massoth, 1999; Kubička and Horáček, 2011). It can also compensate for the activity loss due to the inhibiting effect of water on catalysts (Şenol et al., 2007).

3.3.2. Pressure (H₂ pressure)

In general, pressure plays a significant role in the thermodynamics of reactions. In the context of biodiesel upgrading, higher hydrogen pressures heavily favor HDO over DCO by facilitating hydrogenolysis and hydrogenation reactions (Madsen et al., 2011; Zhao et al., 2013). Even in the case of Pd/C catalysts that remove oxygen exclusively through DCO under either inert or hydrogen atmospheres (Snare et al., 2007; Lestari et al., 2009b), hydrogen has been shown to influence the kinetics of deoxygenation and improve the activity and stability of the catalyst (Immer et al., 2010; Rozmysłowicz et al., 2012). Elevated hydrogen pressures ensure higher carbon yields in the diesel range by suppressing side reactions such as cracking and decarboxylation (Kandel et al., 2014). In addition, hydrogen has been found to benefit catalyst stability by preventing coke-forming oligomerization reactions through hydrogenation of coke precursors, i.e., unsaturated hydrocarbons (Do et al., 2009). The importance of hydrogen in deoxygenation of vegetable oils and model compounds has

Table 3.

Summary of some literature findings on catalytic deoxygenation using transition metal carbide, nitride, and phosphides.

Entry	Feed	Catalyst	T (°C)	P _{H₂} (bar)	Contact time/Space velocity	Reactor	Yield of major products*	Side products**	Reference
1	Maize oil	Mo ₂ C/CNT	260	25	3 h	batch	44% (C _{18:0}) 13% (C _{16:0})	-	
2	Maize oil	Mo ₂ C/AC	"	"	"	"	40% (C _{18:0}) 10% (C _{16:0})	iso.	Qin et al. (2013)
3	Maize oil	Mo ₂ C/CNF	"	"	"	"	36% (C _{18:0}) 11% (C _{16:0})	-	
4	Methyl palmitate	Mo ₂ C/CNF	"	"	"	"	92% (C _{16:0})	-	
5	Sunflower oil	β-Mo ₂ C/γ-Al ₂ O ₃	360	50	5 h ⁻¹	trickle-bed	67% (C _{12-C₁₈})	dim.	Sousa et al. (2012)
6	Soybean oil	NiMoC/Al-SBA-15	400	45	1 h ⁻¹	fixed-bed	93% (C _{12-C₂₂})	-	
7	"	NiMoC/γ-Al ₂ O ₃	"	"	"	"	73% (C _{12-C₂₂})	cra.	Wang et al. (2013)
8	"	NiMoC/USY	"	"	"	"	48% (C _{12-C₂₂}) 13% (C _{5-C₁₂})	cra.	
9	Soybean oil	NiMoC/ZSM-5	450	45	not specified	fixed-bed	13% (C _{12-C₂₂}) 16% (C _{5-C₁₂})	DCO-DCO ₂ cra.-met.	Wang et al. (2012)
10	"	NiMoN/ZSM-5	"	"	"	"	12% (C _{12-C₂₂}) 11% (C _{5-C₁₂})	DCO-DCO ₂ cra.-met.	
11	Soybean oil	Ni ₂ P/SiO ₂	370	30	1 h ⁻¹	trickle-bed	80% (C _{15-C₁₈})	DCO-dim.	Zarchin et al. (2015)
12	"	Ni ₂ P/HY (20h used)	"	"	"	"	79% (C _{15-C₁₈})	DCO-cra.-iso.	
13	Jatropha oil [a]	NiMoP/Al ₂ O ₃	350	30	2 h ⁻¹	fixed-bed	37% (C _{18:0}) 37% (C _{17:0})	DCO-DCO ₂ iso.	Gong et al. (2012)
14	Rapeseed oil	Mo ₂ C/CNT	260	20	3 h	batch	86% (paraffin)	iso. (46%)	
15	Methyl palmitate	Mo ₂ C/CNT	240	15	2 h	"	51% (C _{16:0}) 29% (C _{16:1})	-	Han et al. (2011b)
16	Methyl palmitate	Mo ₂ C/CNT	240	25	2 h	"	96% (C _{16:0})	-	
17	Methyl palmitate	Mo ₂ C/OMC	260	15	5 h	batch	79% (C _{16:0}) 11% (C _{16:1})	-	Han et al. (2012)
18	"	Mo ₂ C/AC	-	-	2 h	"	81% (C _{16:0})	dim.	
19	Methyl stearate	Mo ₂ C	280	10	5 h	batch	28% (C _{18:0}) 4% (C _{17:0})	iso.-olf.	
20	Methyl stearate	Mo ₂ C/AC	"	"	4 h	"	89% (C _{18:0})	DCO-iso. olf.	
21	Methyl palmitate	Mo ₂ C/AC	"	"	4 h	"	91% (C _{18:0})	DCO-iso. olf.	Han et al. (2011a)
22	Ethyl stearate	Mo ₂ C/AC	"	"	4 h	"	90% (C _{18:0})	DCO-iso. olf.	
23	Stearic acid	Mo ₂ C/AC	"	"	4 h	"	75% (C _{18:0}) 13% (C _{17:0})	iso.-olf.	
24	Stearic acid	Mo ₂ C/CNF (<3 nm)	350	30	5 h	batch	85% (C _{18:0})	DCO-DCO ₂	
25	"	Mo ₂ C/CNF (10 nm)	"	"	3 h	"	51% (C _{18:0}) 44% (C _{17:0})	-	Stellwagen and Bitter (2015)
26	"	W ₂ C/CNF (<3 nm)	"	"	5 h	"	82% (C _{18:0})	DCO-DCO ₂	
27	"	W ₂ C/CNF (12 nm)	"	"	3 h	"	60% (C _{18:0}) 30% (C _{17:0})	est.	
28	Oleic acid	Mo ₂ C/CNF	350	50	3 h	batch	84% (C _{18:0})	alc.-ald.	Hollak et al. (2013)
29	-	W ₂ C/CNF	"	"	"	"	43% (C _{18:1}) 25% (C _{18:0})	alc.-ald.	
30	Oleic acid	Mo ₂ N/γ-Al ₂ O ₃	380	71.5	0.45 h ⁻¹	fixed-bed	9% (C _{18:0}) 4% (C _{10:0})	DCO-DCO ₂ cra.	Monnier et al. (2010)
31	Methyl oleate [b]	Ni ₂ P/SBA-15	340	30	20 h ⁻¹	fixed-bed	68% (C _{17:0}) 14% (C _{18:0})	-	Yang et al. (2015)
32	"	Ni ₂ P/SBA-15	250	"	"	"	5% (C _{18:0}) 3% (C _{17:0})	-	
33	Methyl laurate [c]	Ni ₂ P/SiO ₂	340	30	14 h ⁻¹	fixed-bed	85% (C _{11:0}) 12% (C _{12:0})	-	
34	"	NiMoP/SiO ₂	"	"	"	"	66% (C _{11:0}) 32% (C _{12:0})	-	Chen et al. (2014)
35	"	MoP/SiO ₂	"	"	"	"	75% (C _{12:0}) 7% (C _{11:0})	-	

Table 3.
(continued).

Entry	Feed	Catalyst	T (°C)	P _{H₂} (bar)	Contact time/ Space velocity	Reactor	Yield of major products*	Side products**	Reference
36	Methyl laurate [c]	Ni ₂ P/SiO ₂	340	20	10 h ⁻¹	fixed-bed	82% (C ₁₁ :0) 15% (C ₁₂ :0)	-	
37	"	Ni ₂ P/MCM-41	"	"	"	"	86% (C ₁₁ :0) 12% (C ₁₂ :0)	-	Yang et al. (2013a)
38	"	Ni ₂ P/SBA-15	"	"	"	"	87% (C ₁₁ :0) 13% (C ₁₂ :0)	-	
39	Methyl oleate [b]	Ni ₂ P/SBA-15	340	30	20 h ⁻¹	fixed-bed	71% (C ₁₇ :0) 11% (C ₁₈ :0)	-	Yang et al. (2012)
40	Palmitic acid	MoP	300	40	1 h ⁻¹	trickle-bed	47% (C ₁₅ :0) 22% (C ₁₆ :0)	alc.	Peroni et al. (2016)
41	"	Ni ₂ P/γ-Al ₂ O ₃	"	"	"	"	76% (C ₁₅ :0) 22% (C ₁₆ :0)	-	

* Yields are approximate numbers and at different conversions; (Cx:y) x = number of carbons, y = number of unsaturated (double) bonds.

** iso.=isomerization; dim.=dimerization; cra.=cracking/hydrocracking; DCO=decarbonylation; DCO₂=decarboxylation; met.=methanation; olf.=olefins; est.=esterification; alc.=alcohols; ald.=aldehydes.

[a] H₂/feed volume ratio=600; [b] H₂/feed volume ratio=300 at 6 h on stream; [c] H₂/feed molar ratio=50.

been confirmed by exploring the effect of hydrogen pressure (Donnis et al., 2009; Kubička et al., 2009; Kandel et al., 2014), H₂ partial pressure in mixtures with He (Do et al., 2009; Immer et al., 2010), and hydrogen donor solvents (Mäki-Arvela et al., 2007). High pressures of hydrogen are required not only to obtain higher extent of deoxygenation, but also to prolong catalyst activity. However, the expensive compressors and leak-proof reactors that are required for increasing the pressure and maintaining it at those levels make it economically unfeasible. Therefore, new reactor configurations and catalytic systems would have to be designed and employed to lower the operating pressures while effectively deoxygenating bio-oils.

3.3.3. Temperature

The effect of temperature on kinetics and thermodynamics of reactions is unquestionable. Higher temperature almost always translates into faster kinetics and thus, the production of final products at a higher rate. However, this is not necessarily equivalent to better economics since increasing the temperature requires extra energy. More importantly, faster kinetics do not always correspond to better results as temperature also influences the selectivity of the products. In another word, one can obtain the products at a higher rate by raising the temperature, but the products obtained might not be the ones desired. This is in fact the case for deoxygenation processes. As the temperature rises, the reaction proceeds faster and the degree of deoxygenation increases significantly, both of which are favorable (Şenol et al., 2005a; Bezergianni et al., 2010a). Nevertheless, high temperatures (typically >400 °C) give rise to undesired cracking (C₄-C₁₄) and heavy (C₁₉-C₃₀) products and reduce the yields of diesel fuel in the product stream (Bezergianni et al., 2010b; Kiatkittipong et al., 2013; Phimsen et al., 2016). They also increase the isomerization products that can improve the cold flow properties of diesel fuel at the expense of cetane number (Bezergianni et al., 2010b). It has been found in some works that higher temperatures also increase the DCO to HDO ratio, resulting in lower carbon yields (Kubička and Kaluža, 2010; Yang et al., 2013b; Ithibenchapong et al., 2017). Therefore, temperature should be controlled carefully to obtain high yields of products at a high rate without compromising carbon efficiency and fuel properties. The effect of operating temperature on catalyst coking and stability has yet to be examined.

3.3.4. Contact time

Contact time is an important parameter in determining the kinetics of a reaction. The effect of time on conversion and yields could provide useful information for optimizing and scaling up a process. The effect of time, particularly in batch and semi-batch reactors, is typically evaluated to obtain useful information about deoxygenation pathways as well as product evolution (Foraita et al., 2017). Reaction pathways are interesting because they enable scientists to rationally design new catalytic systems, while product evolution

over time may indicate an opportunity to maximize the yield of some products (Stellwagen and Bitter, 2015). Although longer reaction times guarantee higher conversions and normally the production of saturated compounds under H₂ atmosphere (Immer et al., 2010; Foraita et al., 2017; Hollak et al., 2013), they could also result in lower overall diesel yields due to excessive cracking and DCO reactions (Kiatkittipong et al., 2013; Phimsen et al., 2016). In continuous systems, activity and selectivity over reaction time or time-on-stream is indicative of the catalyst's deactivation, stability, and surface/structure changes (Do et al., 2009; Lestari et al., 2009a; Kubička and Horáček, 2011; Kovács et al., 2011), whereas space velocity can regulate the contact time between feed and catalyst, determining the feed's conversion and product selectivity (Kubička et al., 2010; Kubička and Kaluža, 2010).

3.4. Challenges and opportunities

The primary challenge for producing renewable diesel is to secure the availability of feedstocks that do not compete with food production and make optimal use of land, water, and fertilizers (Escobar et al., 2009; Srinivasan, 2009). This is particularly imperative for developing countries and regions of the world that suffer from drought or harsh climates. Regarding biodiesel upgrading, the leading challenge is to design a catalyst with high resistance to water, coke, and minor minerals present in vegetable oils and animal fats, while being active for their conversion and selective toward HDO rather than DCO. This is a non-trivial challenge since numerous parameters play roles in the outcome. The trade-off between ignition properties (i.e., cetane number) and cold flow properties (cloud point and freezing point) of *n*-alkanes and *iso*-alkanes presents a major challenge for direct production of a petro-diesel substitute from bio-based feedstocks. In another word, the resulting product stream will not be able to replace petro-diesel if it only contains long-chain *n*-alkanes; rather, it acts as a cetane enhancer. Thus, isomerization ability of the upgrading catalyst should also be taken into consideration if feasible one-step production of renewable diesel is the ultimate goal. Another challenge is the use of more representative model compounds to obtain information about the performance of catalysts using real feedstocks as discussed in detail in a review by Gosselink et al. (2013).

Despite the above-mentioned challenges, the commercial production of renewable diesel fuels during recent years, with fuel properties exceeding petroleum diesel (Satyarthi et al., 2013; Phimsen et al., 2016), bodes well for a prosperous future in large-scale production of green diesel. NExBTL was introduced in 2005 as the first renewable diesel by the Finnish company, Neste Oil (Rantanen et al., 2005). Since then, several commercial plants have been built by Neste Oil, UOP/Eni, Petrobras/H-Bio, British Petroleum, Conoco Philips/Tyson, and Dynamic Fuels/Syntroleum/Tyson (Aslam et al., 2015). Currently, these commercial plants are mainly built

adjacent to the existing refineries to avoid high capital costs of constructing a completely new plant. However, improving the economics of biorefineries by integrating processes such as HDO and steam reforming, and even making use of light hydrocarbons and acid gases may increase the feasibility of stand-alone units. As far as fuel quality, an initial (hydro)-deoxygenation step followed by a (hydro)-isomerization process ensures a high cetane number, excellent cold flow properties, and environmental friendliness of the obtained renewable diesel compared with petroleum diesel and biodiesel (**Table 4**).

Table 4.

Summary of chemical characteristics of petroleum diesel, biodiesel, and Honeywell Green Diesel (UOP, 2017).

Parameter	Petroleum ultra-low sulfur diesel	Biodiesel (fatty acid methyl ester)	Renewable diesel
Oxygen (%)	0	11	0
Cetane number	40-55	50-65	75-90
Energy density (MJ/kg)	43	38	44
Sulfur (ppm)	< 10	< 2	< 2
Cold flow properties	Baseline	Poor	Excellent
Oxidative stability	Baseline	Poor	Excellent

Aside from renewable diesel production, another opportunity is to produce commodity chemicals by tuning the surface characteristics of catalysts and optimizing the reaction conditions maximizing the yield of mono- or poly-unsaturated hydrocarbons (linear alpha/internal olefins). The smaller olefins can be used as precursors for polymeric materials, while the bigger olefins can be utilized as building blocks of important lubricants, surfactants, and even eco-friendly drilling fluids (Gee et al., 1996; Vora et al., 2009). The challenge here is the tradeoff between the olefin concentration in the product stream and the deactivation rate of the catalysts due to coking as explained in *Section 3.2.3*. Therefore, designing new catalytic systems that are able to produce unsaturated hydrocarbons from bio-based feedstocks without rapid deactivation may be an interesting venue for future research. Practically speaking, the need for biofuels may not allow for utilization of vegetable oils for olefin production, yet there is a use for this research since olefins are produced as side products, especially from highly unsaturated feedstocks.

4. Conclusions

Biodiesel has been introduced as a clean, biodegradable, and biocompatible diesel substitute produced *via* transesterification of fresh vegetable oil, animal fats, waste cooking oil, and microalgae oil. In efforts to obtain an alternative method for purifying biodiesel, multiple methods have been studied in addition to the traditional water washing methods – washing with ionic liquids or supercritical carbon dioxide, adsorbents such as silica or biomass, ion exchange techniques and organic and inorganic membranes are covered in this work. These methods must successfully minimize the presence of total and free glycerol, water, and cations (either free or in soaps) within the crude biodiesel to produce a finished biodiesel product that meets ASTM and EN standards. In most cases, these methods are employed in conjunction with one another to produce a truly clean product; an equilibrium-based method will have different strengths in purification than an affinity-based or filtration-based method. Additionally, the effectiveness of these methods is dependent on the feedstock.

The stability and compatibility issues of biodiesel fuels have compelled scientists to search for effective upgrading processes. The deoxygenation of vegetable oils and animal fats to produce hydrocarbons in the range of diesel fuel has thus become an attractive alternative. Several catalytic systems have been tested for this task, but the future trend is expected to go toward non-sulfided catalysts ideally with high activity and stability in H₂-moderate environments, reduced sensitivity to water and trace contaminants, and selectivity to HDO. The presence of hydrogen could lead to the dominance of HDO over DCO, improving carbon efficiency. In addition, hydrogen appears to reduce the extent of undesired side reactions (i.e., cracking and coking).

The optimization of HDO processes poses a great challenge to the large-scale production of renewable diesel due to insufficient industrially relevant information in the field. Besides, the current commercial approach comprises of a two-step process (HDO followed by hydroisomerization) to produce high-quality diesel fuel. The integration of these two steps could be very appealing from economics perspective, although the price of catalysts also plays a key role in economic evaluations.

In sum, despite academic and industrial efforts and achievements, further development of deoxygenation technologies to feasibly produce biorenewable diesel fuels depends heavily on the price of fossil fuels as well as governmental mandates and regulations (i.e., incentives and tax reductions). Hence, a future deprived from fossil-based fuels and/or filled with environmental awareness in political administrations would guarantee major achievements in the production of renewable diesel fuels.

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