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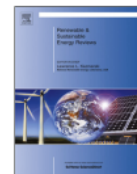
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Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism



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ABSTRACT

Deoxygenation process of fatty acid as a renewable resource to produce diesel-like hydrocarbons is one of the alternatives to address drastic shortage of crude oil-based fuels in the near future. Catalytic deoxygenation process of fatty acid is getting attention from both academia and industry. Researchers have tried different techniques in the fatty acid deoxygenation to enhance the production of diesel-like hydrocarbons. This review paper elucidates the influence of tmain operating conditions towards achieving optimum yield and selectivity 40 desired products. The reaction pathways, the reaction kinetics as w 15 as recent progress in deoxygenation of fatty acid for production of diesel-like hydrocarbons are also reviewed.

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1. Introduction

Growth in road transportation sector is currently steering the demand for fuel oils. It has been predicted that the world demand for diesel fuel will grow faster than any other refined oil products toward 2035, as illustrated in Fig. 1 [1]. Diesel fuel demand is

predicted to grow from 26 million barrels per day in 2012 to around 36 million barrels per day by 2035. Meanwhile, the demand for gasoline will moderately increase from about 23 million barrels per day in 2012 to 27 million barrels per day by 2035. In the same period, slight increases in demand will occur for ethane/LPG, naphtha, bitumen, lubricants waxes still gas, coke, direct use of crude oil, etc. On the other hand, demand for residual fuel will globally decrease in the coming years [1].

Due to consumption of diesel fuel derived from diminishing conventional crude oil that will continue in the next decades,

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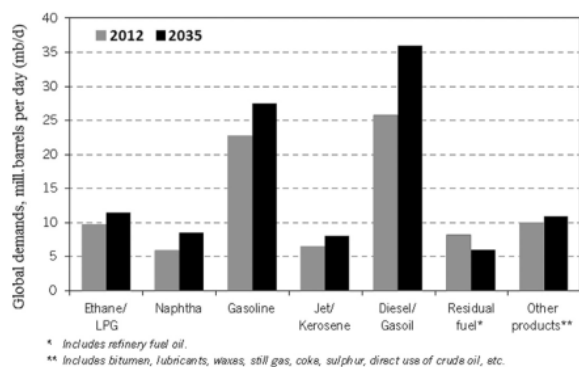


Fig. 1. Global demands for diesel fuel in 2012 and forecast in 2035 compared to other refined oil products [1].

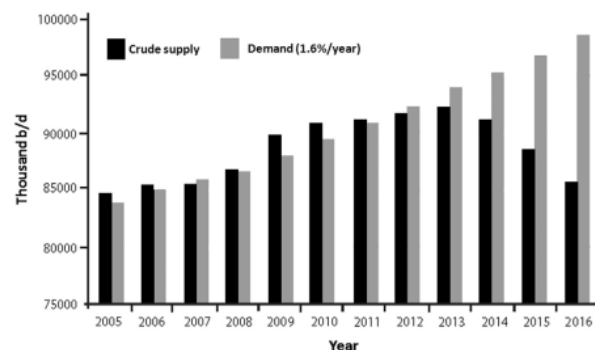


Fig. 2. Global crude oil supply and projected demand [2].

exhaustion of fossil fuels is predicted. Comparison between the most probable crude oil supply and the most likely demand requirements has been reported by the International Energy Agency (IEA) [2], as can be seen in Fig. 2. Conventional crude oil supply exceeded the demand from 2009 to 2011. However, in 2012 and 2013, the demand consistently exceeded supply. Then, from 2014 onwards, the conventional crude oil supply will be shortfall. Meanwhile, the demand will constantly increase due to rapid growth in human population.

Therefore, extensive studies on biofuels productions from various renewable feed stocks and related technologies have been carried out for many years [3–8]. Among others, fatty acids are renewable resources that can be produced in mass scale and used as feedstock for deoxygenation reactions to synthesize diesel-like hydrocarbons [9–14]. Diesel-like hydrocarbons contain *n*-alkanes and alkenes that are hydrocarbons similar to those found in diesel fuel obtained by refining crude oil in petroleum refineries [15]. Thus, this option provides interesting alternative to support future energy demand.

Fatty acids are found in plant oils/fats and animal oils/fats [16–21]. Besides of fatty acids, plant oils/fats and animal oils/fats contain triglycerides with the main constituent. Fatty acids are formed during enzymatic hydrolysis of triglyceride especially when the oils are kept in humid atmosphere [22–27]. Fatty acid can also be formed during purification of vegetable oils and fats [28–30]. It can be produced at a sufficiently high rate in many countries. For example, in the United States, tall oil fatty acid can be obtained by vacuum distillation of crude tall oil which is side stream from pulp and paper industry [31]. Tall oil fatty acid mainly consists of palmitic acid, oleic acid and linoleic acid. The total production of tall oil in the United States was 845,000 t in 2004 [32]. Meanwhile, Malaysia and Indonesia, as the world's top-two

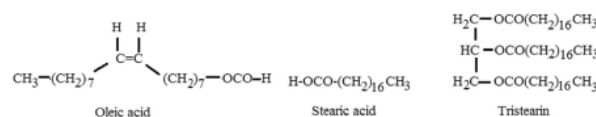


Fig. 3. Molecular structures of stearic acid, oleic acid and tristearin.

largest crude palm oil (CPO) producers, produce palm fatty acid distillate (PFAD) which is the by-product of physical refining process of CPO [33]. Malaysian refineries produced PFAD with the total amount of 750,000 t in 2008 [34]. PFAD contains more than 90% palmitic acid and is comparatively far cheaper than CPO. It is generally sold as a source of industrial fatty acids for non-food applications such as laundry soap industries [35–38]. It can also be used to produce renewable energy sources through suitable thermochemical means.

Fatty acids are carboxylic acids with long aliphatic chains, which are either saturated or unsaturated [39]. Saturated fatty acids are fatty acid that have no carbon-carbon double bond such as palmitic acid, stearic acid and lauric acid. Unsaturated fatty acids are fatty acids with one or more carbon-carbon double bonds for example: oleic acid, myristoleic acid and linoleic acid. Meanwhile, triglycerides are esters derived from glycerol and three fatty acids. They are named according to the fatty acid components, for example, tristearin contains three molecules of stearic acid. Other examples of triglyceride are trilaurin, tripalmitin and triolein. Molecular structures of stearic acid, oleic acid and tristearin can be seen in Fig. 3.

There are several alternative techniques recently developed to produce diesel like-hydrocarbon using fatty acid such as catalytic cracking, hydrotreating and catalytic deoxygenation. Catalytic cracking technology is used to break down high-molecular-mass into fragments of lower molecular mass [40–45]. Hydrotreating process involves the removal of oxygen through the introduction of hydrogen into the fatty acid or triglyceride molecules either using metal catalyst or oxide catalysts to produce *n*-alkanes [46–50]. Meanwhile, deoxygenation involves removal of the carboxyl group in the fatty acid as carbon and/or carbon monoxide using a supported metal catalyst, thereby producing alkane and alkene as diesel-like hydrocarbons [51]. Very encouraging results have been reported recently [46–48].

During the past few year, researchers reported mechanism and kinetic model of fatty acid deoxygenation over supported metal catalyst to produce diesel-like hydrocarbons. It also reported that operating parameters were important to optimize selectivity/yield of diesel like-hydrocarbon in the deoxygenation process. The operating parameters include supported metal catalyst type, feed type, temperature, reaction atmosphere, feed rate (residence time), catalyst amount and the presence of solvent. This review summarizes reaction pathways and kinetic models of deoxygenation fatty acid. Subsequently, the roles of the operating conditions that are employed for optimum yield and selectivity of diesel-like hydrocarbon are highlighted. This paper also highlights recent progress in deoxygenation of fatty acid to produce diesel-like hydrocarbons. In addition, highlights on future directions for this option are also provided.

2. Reaction pathways and kinetic models of deoxygenation of fatty acid to produce diesel-like hydrocarbons

Lestari et al. [51] proposed general saturated fatty acid deoxygenation reaction steps under inert atmosphere over supported metal catalyst that involve several reaction pathways, as can be seen in Fig. 4. Under inert atmosphere, the presence of hydrogen during the process is achieved via dehydrogenation of unsaturated

compound [52]. The reaction pathways consist of liquid and gas phase reactions. Liquid phase reactions of the fatty acid deoxygenation process involve direct decarboxylation and decarbonylation reactions that occur simultaneously, as illustrated in reactions 1 and 2 in Fig. 4. Direct decarboxylation removes carboxyl group in the fatty acid to produce *n*-alkane by releasing carbon dioxide molecule. Meanwhile, direct decarbonylation removes carboxyl groups by releasing carbon monoxide and water molecules to produce alkenes. Furthermore, deoxygenation of saturated fatty acid in the presence of hydrogen involves indirect decarboxylation and direct hydrogenation to produce *n*-alkanes, as illustrated in reactions 3 and 4. Furthermore, CO₂, CO, hydrogen and water produced from the liquid phase decarboxylation/ decarbonylation will undergo gas phase reactions. The gas phase reactions include methanation of CO₂ and CO as shown in reactions 5 and 6, respectively. Besides, water-gas-shift reaction also occurs during the deoxygenation process, as shown in reaction 7.

Reaction pathway of deoxygenation of a specific saturated fatty acid has been proposed by Snare et al. [53] who used stearic acid

as reactant. Fig. 5 shows the reaction pathway of stearic acid deoxygenation over various supported metal catalysts under inert atmosphere at 300 °C. First, main reactions of decarboxylation and decarbonylation of stearic acid simultaneously occur to produce *n*-hexadecane (C₁₇H₃₆) and 1-hexadecene (C₁₇H₃₄), respectively, as can be seen in reactions 1 and 2. Then, some of the *n*-hexadecane and 1-hexadecene are isomerized and/or hydrogenated/dehydrogenated, as can be seen in reactions 5–9, to generate minor amounts of C₁₇ cyclic and aromatic molecules as well as hydrogen source. Subsequently, some of stearic acid is hydrogenated using the hydrogen source to produce minor amount of another alkane (C₁₈H₃₈), as in reactions 3. Some of 1-hexadecene will undergo hydrogenation/dehydrogenation to produce *n*-hexadecane, as in reaction 3. Cracking reaction of stearic acid (reaction 10) may also occur leading to the production of lower fatty acids (C₁₀–C₁₇ acid) and shorter hydrocarbons (C₁₃–C₁₆). Besides, conversion of stearic acid to symmetrical ketone and dehydrogenation of stearic acid and unsaturated hydrocarbons can occur to the formation of heavier products, as shown in reaction 11, 12, and 13 in Fig. 5. Thus, fatty acid provides alternatives to produce various hydrocarbons as fuels in the future should some technical hurdles in the processes involved can be properly managed.

For unsaturated fatty acid deoxygenation under inert atmosphere, its reaction pathway has also been proposed by Snare et al. [54]. The unsaturated fatty acid type that they used was oleic acid. Fig. 6 shows the reaction pathway of oleic acid deoxygenation. This can be explained as follows: positional and geometrical isomerizations of oleic acid initially occur to generate elaidic and vaccenic acid. Then, oleic acid and its isomer are dehydrogenated to form polyunsaturated and aromatic by-products as well as source of hydrogen. Subsequently, the double bond (the remaining oleic acid and its isomer) are hydrogenated to generate stearic acid by using the source of hydrogen. Further deoxygenation reaction results in heptadecane hydrocarbon fuel as the main product and minor amounts of unsaturated positional isomers (1-, 3-, and 8-heptadecene) as well as C₁₇ aromatics. Thus, more unsaturated hydrocarbons can be produced when unsaturated fatty acid is used as feedstock.

Furthermore, Kitiyanan et al. [55] reported that kinetic model for oleic acid deoxygenation under inert atmosphere can be

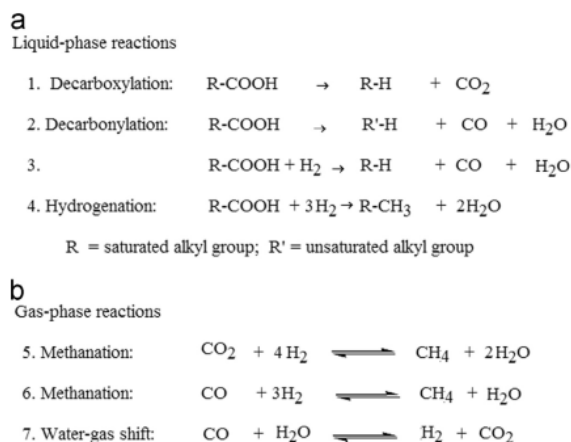


Fig. 4. General saturated fatty acid deoxygenation reaction steps under inert atmosphere over supported metal catalyst adapted from [51].

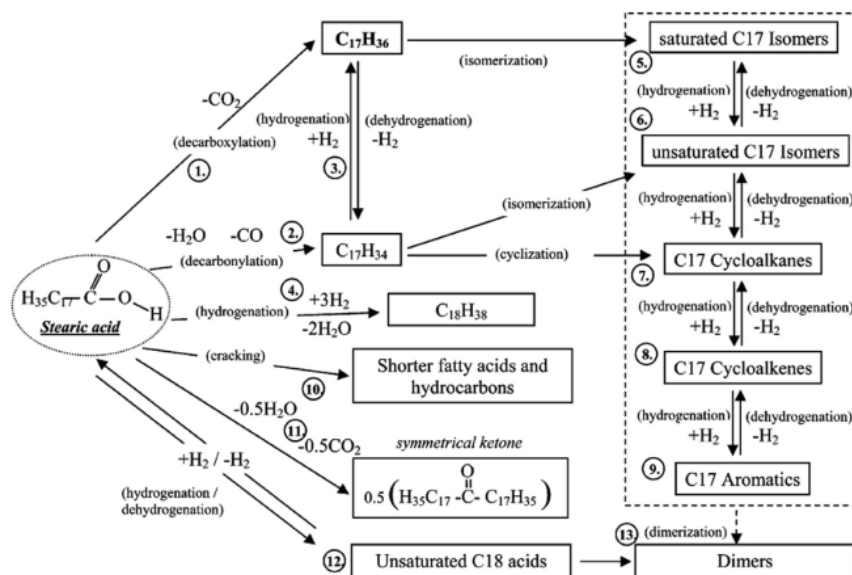


Fig. 5. Reaction pathway of stearic acid deoxygenation over supported metal catalysts under inert atmosphere [53].

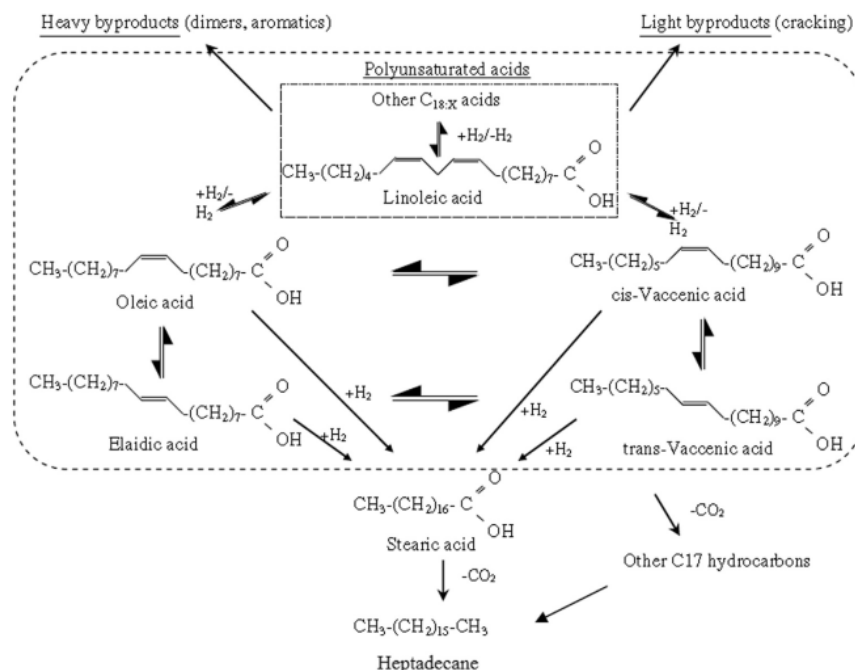


Fig. 6. Reaction pathway of oleic acid deoxygenation over supported metal catalysts under inert atmosphere [54].

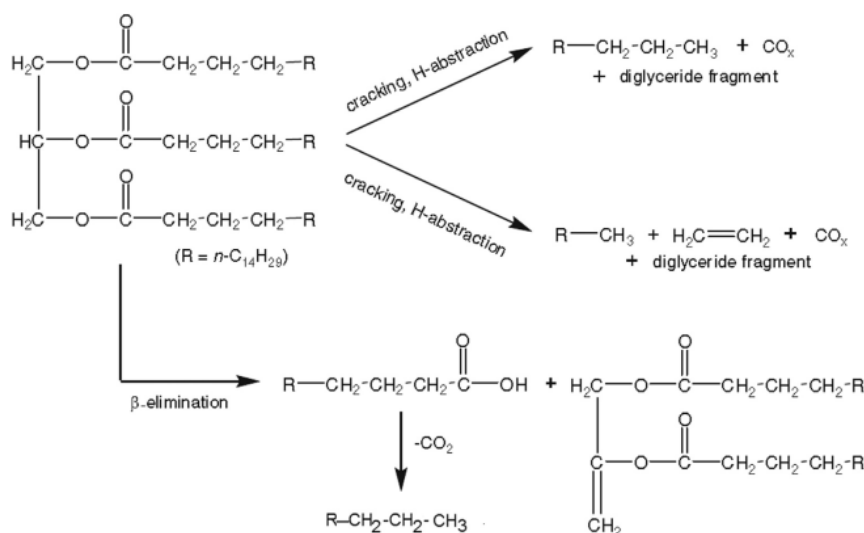


Fig. 7. Reaction pathway for tristearin deoxygenation over supported metal catalyst under inert atmosphere [56].

suggested to follow the first order with respect to oleic acid, as in Eq. (1):

$$\text{Rate} = \frac{-d[\text{C}_{\text{OA}}]}{dt} = k[\text{C}_{\text{OA}}] \quad \text{or} \quad \text{Rate} = \frac{-d[\text{C}_{\text{OA}}]}{[\text{C}_{\text{OA}}]} = kdt \quad (1)$$

where, k is rate constant, t is reaction time and $[\text{C}_{\text{OA}}]$ is concentration of oleic acid.

Reaction pathway of tristearin deoxygenation over various supported metals (Ni, Pt, and Pd) under inert atmosphere at 300 °C has been proposed by Morgan et al. [56] as in Fig. 7. First, some tristearins liberated stearic acid via a β -elimination process. This also generates unsaturated glycol difatty ester as a co-product. Subsequently, the stearic acid is decarboxylated to give n -heptadecane.

Meanwhile, the other tristearins can undergo cracking reactions that involve either scission of the C–C bond between the ester carbonyl carbon and a carbon of the hydrocarbon chain, or scission between the β and γ carbon atoms to produce C17 and C15 hydrocarbons, respectively as well as diglyceride fragment and CO_x gas.

The C17 and C15 hydrocarbons correspond to n -heptadecane and n -pentadecane, respectively, as the main products. Besides, the C17 and C15 might correspond to heptadecene and pentadecene that lead to the hydrogen generation during bond scission. It has been reported that hydrogen is consistently detected in the gaseous products. Scission between the β and γ carbon atoms forms ethene as a co-product. It is assumed that the unsaturated glycerol units (diglyceride fragments) produced from reactions 1,

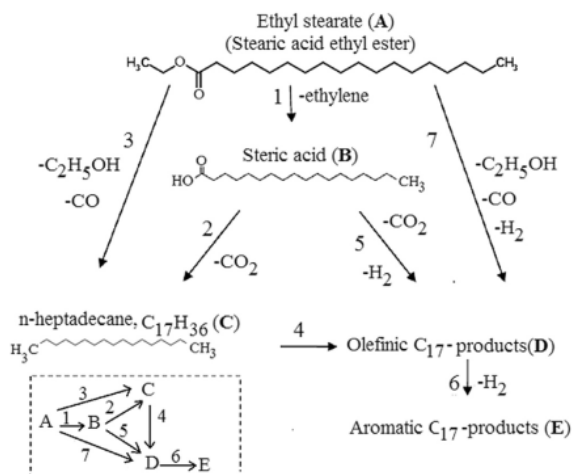


Fig. 8. Reaction pathway for deoxygenation of stearic acid ethyl ester over a commercial Pd/C catalyst [58].

2 and 3 in Fig. 5 will undergo cracking reactions to the formation of volatile products, e.g., C1–C3 hydrocarbons and hydrogen abstraction [40].

In addition, it has been reported by Chiappero et al. [57] that a kinetic model for triglyceride deoxygenation under inert atmosphere in a semi-batch mode is suggested to follow the first order with respect to triglyceride as in Eq. (2).

$$\text{Rate} = -dC_{TG}/dt = k dC_{TG} \quad (2)$$

where k is the rate constant and C_{TG} is the concentration of triglyceride. The kinetic behavior has been reported to be successfully identified for several types of triglyceride such as trilaurin and trimyristin. By using Eq. (1), trilaurin and trimyristin had reaction rates of $1.2 \times 10^{-2}/\text{min}$ and $1.16 \times 10^{-2}/\text{min}$, respectively.

Meanwhile, reaction pathway of deoxygenation of fatty acid ester in a semi-batch reactor over a commercial Pd/C catalyst at 300 °C has been verified using stearic acid ethyl ester as reactant [58]. The reaction pathway is shown in Fig. 8 and can be explained as follows: stearic acid ethyl ester initially liberates stearic acid (reaction 1). Subsequently, stearic acid is decarboxylated to form *n*-heptadecane (reaction 2). However, dehydrogenation of the produced *n*-heptadecane concurrently occurs to form heptadecene (reaction 4) and aromatic compound (reaction 6). Besides, stearic acid can be directly converted into heptadecene (reaction 5) via dehydrogenation of the stearic acid to generate unsaturated fatty acid intermediate followed by a fast decarboxylation reaction [54]. Stearic acid ethyl ester is also be directly converted into *n*-heptadecane via reaction 3 and into heptadecene via reaction 7.

Additionally, kinetic model for stearic acid ethyl ester deoxygenation under inert atmosphere has been suggested to follow the first order with respect to stearic acid ethyl ester as in Eq. (3):

$$\text{Rate} = -dC_{SAEE}/dt = k dC_{SAEE} \quad (3)$$

where, k is rate constant and C_{SAEE} is the concentration of stearic acid ethyl ester. The rate constant, k is related to an Arrhenius equation, which gives the relationship between pre-exponential factor (A) and activation energy (E) in Eq. (4). The activation energy (E) based on Eqs. (3) and (4) has been reported to be 573 kJ/mol [58].

$$k = A \exp [-E/(RT)] \quad (4)$$

Furthermore, a kinetic model has been developed for deoxygenation of stearic acid ethyl ester with intermediate products on

the basis of the reaction pathway in Fig. 6 using Langmuir–Hinshelwood mechanism. Langmuir–Hinshelwood mechanism assumes that the reactant must first adsorb on the catalyst surface. Subsequently, the reaction takes place at the active site, and the product then desorbs from the catalyst [59]. A reasonable simplification is made by disregarding adsorption constants for gaseous products (i.e., CO₂, ethylene, etc.) in the denominator. It was also assumed that surface reactions are rate limiting and adsorption reactions are more rapid than the surface reactions. The rates of reaction steps, r_i ($i=1, 2, 3, 4, 5, 6, 7$), based on Fig. 6 are proposed as follow:

$$r_1 = \frac{k'_1 C_A}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (5)$$

$$r_2 = \frac{k'_2 C_B}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (6)$$

$$r_3 = \frac{k'_3 C_A}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (7)$$

$$r_4 = \frac{k'_4 C_C}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (8)$$

$$r_5 = \frac{k'_5 C_B}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (9)$$

$$r_6 = \frac{k'_6 C_D}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (10)$$

$$r_7 = \frac{k'_7 C_A}{1 + K_A C_A + K_B C_B + K_A C_C + K_D C_D + K_E C_E} \quad (11)$$

where A=stearic acid ethyl ester, B=stearic acid, C=*n*-heptadecane, D=olefinic C₁₇ products, E=aromatic C₁₇ products, K_i =equilibrium reaction constant, k'_i =apparent reaction constant, C_i =concentration lance.

A system of ordinary differential equations (ODE) that is obtained by using the kinetic rate expressions into the mass balances of components on the basis of reactions in Fig. 6 can be seen in the following expressions:

$$\frac{1}{\rho_B} \frac{dC_A}{dt} = -r_1 - r_3 - r_7 \quad (12)$$

$$\frac{1}{\rho_B} \frac{dC_B}{dt} = r_1 - r_2 - r_5 \quad (13)$$

$$\frac{1}{\rho_B} \frac{dC_C}{dt} = r_2 + r_3 - r_4 \quad (14)$$

$$\frac{1}{\rho_B} \frac{dC_D}{dt} = r_4 + r_5 - r_6 + r_7 \quad (15)$$

$$\frac{1}{\rho_B} \frac{dC_E}{dt} = r_6 \quad (16)$$

where ρ_B =catalyst amount used in the reaction.

3. Factors influencing the deoxygenation process

Achieving high content of diesel-like hydrocarbons in liquid products is important in deoxygenation of fatty acid and triglyceride in order to avoid further separation step such as distillation to meet a quality standard as a fuel [10]. Process conditions significantly influence yield and selectivity of diesel-like hydrocarbon as well as product composition. The process conditions reported in the literature include the use of supported metal catalyst type, feed type, temperature, reaction atmosphere, residence time,

catalyst loading and type of feed. Mature understandings on the influences of specific process conditions are yet to be established in view of the complex reactions involved. However, some recent works reported managed to shed some light on this area [48,50,60].

3.1. Supported metal catalyst type

Various supported metal catalysts i.e. Pd, Pt and Ni on γ - Al_2O_3 have been investigated for deoxygenation of waste fat containing a mixture of oleic acid and tripalmitin in the presence of solvent under hydrogen atmosphere. It has been observed that Pd/ γ - Al_2O_3 catalyst is more active than the Pt/ γ - Al_2O_3 catalyst and also more selective for production of the C17 and C15 diesel-like hydrocarbons [60]. The higher activity was due to the higher content of active metal (Pd) in the Pd/ γ - Al_2O_3 catalyst than the active metal (Pt) in the Pt/ γ - Al_2O_3 catalyst. However, although Ni/ γ - Al_2O_3 catalyst contained the highest active metal (Ni) among the three catalysts, it showed the poorest activity for production of C17 and C15 diesel-like hydrocarbons. This result was attributed to the largest particle size of active metal (Ni) in Ni/ γ - Al_2O_3 catalyst. The average particle size of Ni in Ni/ γ - Al_2O_3 catalyst was 8.2 nm. Meanwhile, Pd and Pt had the average particle sizes of 4.6 nm and 5.4 nm, respectively. The result was in agreement with reports [52–53] that Ni/ γ - Al_2O_3 was less active catalyst than Pd/ γ - Al_2O_3 and Pt/ γ - Al_2O_3 .

Meanwhile, Ni supported on mesoporous carbon (Ni/C) has been reported to be more active and selective catalyst for diesel-like hydrocarbons compared to Pd or Pt supported on mesoporous carbon in deoxygenation of triglycerides (tristearin, triolein and soybean oil) under inert atmosphere (N_2) [56]. The higher activity of the nickel supported on mesoporous carbon was due to its higher content of Ni as active metal (20 wt%) with small particle size (4 nm) in the Ni/C catalyst. Pd/C had active metal content of 5 wt% with particle size of 6 nm while Pt/C had metal content of 1 wt% with particle size of 3.7 nm. Furthermore, various Ni functionalized mesostructured cellular foam silica (NiMCF) with different characteristics have been investigated as catalysts for solventless deoxygenation of palmitic acid under inert atmosphere [61]. It was found that NiMCF catalyst that had the highest nickel content (17.57 wt%) with the smallest particle sizes (1 to 3 nm) was the highest active and selective catalyst for solventless palmitic acid deoxygenation to produce diesel-like hydrocarbons. Metal particles were active sites to produce *n*-alkane and alkene in fatty acid deoxygenation through decarboxylation and decarbonylation reaction, respectively [62]. In general, it can be concluded that metal incorporated mesoporous materials having high metal content with small particle sizes are suitable catalysts for fatty acid deoxygenation to produce diesel-like hydrocarbons.

3.2. Feed types

Various feeds, i.e. saturated fatty acid (behenic acid, $\text{C}_{21}\text{H}_{43}\text{COOH}$ and stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$) and fatty acid ester (stearic acid ethyl ester, $\text{C}_{17}\text{H}_{35}\text{COOC}_2\text{H}_5$) have been deoxygenated over commercial Pd/C catalyst in the presence of dodecane as solvent at 300 °C under 5% H_2 in argon for 360 min [52]. It was found that initial reaction rate for stearic acid (0.63 mmol/min- g_{cat}) was higher than that for behenic acid (0.36 mmol/min- g_{cat}), while initial reaction rate for stearic acid ethyl ester (0.70 mmol/min- g_{cat}) was slight higher compared to stearic acid. However, deactivation of Pd/C catalyst was more severe for deoxygenation of stearic acid ethyl ester than for that of stearic acid. It was observed that after a prolonged reaction time of 360 min, the conversion of stearic acid ethyl ester was only 38%, while the conversion of stearic acid was 60%. The more severe deactivation of the Pd/C

catalyst was mainly ascribed to higher amounts of unsaturated products that were produced through stearic acid ethyl ester deoxygenation.

The large quantities of unsaturated compounds decreased the selectivity to *n*-alkane. At a conversion of 30%, deoxygenation of stearic acid ethyl ester gave *n*-alkane selectivity of 40% which was much lower than that of stearic acid (86%). Meanwhile, deoxygenation of behenic acid achieved *n*-alkane selectivity of 78% at the conversion of 30%. This indicated that decarboxylation reaction was more dominant in fatty acid deoxygenation than in fatty acid ester deoxygenation. This was due to the easier breaking the COO–H bond in fatty acid compared to the COO–R bond in fatty acid ester, because the alkyl group in ester is a nucleophilic group as reported in the literature [63]. It was also reported that deoxygenation of stearic acid ethyl ester produced CO as the predominant gaseous compound because of the stability of the ethoxy group in ester. It can be concluded from the results that deoxygenation of fatty acid (such as behenic acid and stearic acid) was more selective to produce *n*-alkane as diesel-like hydrocarbons through decarboxylation when compared to deoxygenation of fatty acid ester (stearic acid ethyl ester). Deoxygenation of saturated fatty acid with a shorter chain achieves a bit higher *n*-alkane selectivity.

Furthermore, deoxygenations of palmitic acid has been compared with deoxygenation of stearic acid using Pd supported on mesoporous carbon catalyst in the presence of dodecane as solvent in a semi batch reactor at 300 °C under 5% H_2 in argon [64]. Reaction rate of palmitic acid deoxygenation was found to be the same as reaction rate of stearic acid deoxygenation. Deoxygenation of palmitic. This result was in agreement with those reported for deoxygenations of heptadecanoic acid, stearic acid, nonadecanoic acid, arachidic acid and behenic acid [65]. The catalytic deoxygenations of palmitic acid and stearic acid resulted in formation of *n*-pentadecane and *n*-heptadecane, respectively, as the main liquid products.

3.3. Reaction atmosphere

Effect of reaction atmosphere on conversion and yield/selectivity of desired products (*n*-undecane ($\text{C}_{11}\text{H}_{24}$) and undecene ($\text{C}_{11}\text{H}_{22}$) in deoxygenation of lauric acid ($\text{C}_{12}\text{H}_{24}\text{O}_2$) has been studied using two different reaction atmospheres, i.e. pure Ar (Inert) and pure H_2 [66]. The reactions were carried out in a semi-batch reactor under the presence of hexadecane as a solvent using Pd supported on mesoporous carbon as catalyst. It was found that in the first 100 min of reaction, yields of the desired products using the experiment in inert atmosphere were higher than those obtained in the experiment carried out in hydrogen rich atmosphere. On the other hand, from 100 min until 300 min of reaction, the yields obtained in the experiment under inert atmosphere were lower than those under hydrogen rich atmosphere.

The lower yields in the reactions under the rich hydrogen in the first 100 min of reaction were due to initial high formation of intermediates which were gradually converted into the desired products. Meanwhile, in the reaction under inert atmosphere, the desired products were formed via decarboxylation and decarbonylation. Fatty acid deoxygenation pathways under the rich hydrogen atmosphere, as can be seen in Fig. 9. These can be explained as follows: with high saturation of the palladium surface with hydrogen, hydrogenation of carboxylic group in fatty acid primarily occurs forming an aldehyde ($\text{R}-\text{CHO}$) as an intermediate (reaction 1). The aldehyde highly decomposes through decarbonylation reaction producing hydrocarbon and CO (reaction 2, and 3). Some of the aldehydes can be further hydrogenated to lauryl alcohol, $\text{R}-\text{CH}_2-\text{OH}$, (reaction 4). Subsequently, decomposition of lauryl alcohol forming mainly undecane is a more favorable step

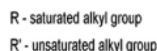


Fig. 9. Fatty acid deoxygenation pathways under rich hydrogen atmosphere in a batch reactor using Pd/C catalyst in the presence of solvent [66].



Fig. 10. Lauril alcohol decomposition mechanism over Pd catalyst [66].

than further hydrodeoxygenation of alcohol to dodecane ($R-CH_3$). Lauryl alcohol decomposes through dehydrogenation to the aldehyde intermediate (reaction 5) and thereafter decarbonylate to hydrocarbon over Pd surface (reaction 6). Decomposition of lauryl alcohol is illustrated in Fig. 10.



Furthermore, Kubickova et al. [67], Lestari et al. [64] and Madsen et al. [60] reported that fatty acid deoxygenation in the presence of Pd/C catalyst using reaction atmosphere with small quantity of H₂ in inert gas (5% H₂ in argon or 5% H₂ in helium) gave higher catalytic activities compared to those using inert or rich hydrogen atmospheres. This was because the presence of a small quantity of H₂ in inert gas in the reactions generated lower amounts of unsaturated hydrocarbons and aromatic hydrocarbons leading to coke formation and also generated a smaller molecular weight compounds in the product mixture. The coke formation and accumulation of different compounds on the catalyst surface can contribute to catalyst deactivation. As such, the presence of a small quantity of H₂ in inert gas is expected to preserve the catalytic activity for a longer time.

3.4. Reaction temperature

Bernas et al. [68] reported that reaction temperature significantly affected conversion and yield/selectivity of diesel-like hydrocarbon in deoxygenation of diluted dodecanoic acid over 1% Pd/C catalyst in a continuous reactor under inert atmosphere. The increase in temperature from 300 to 360 °C resulted in the increase in conversion from 10% to 60% with 17-ecane and undecene as the main products. 17-ecane, while, for deoxygenation of diluted stearic acid over 4% Pd/C in a semi-batch reactor under inert atmosphere, the increase in temperature from 270 to 330 °C made time needed for 100% conversion shorter i.e. from 270 min to 20 min and *n*-heptadecane selectivities generated were nearly the same i.e. around 50% [69]. Furthermore, the increase in temperature from 300 to 360 °C for deoxygenation of diluted ethyl stearate resulted in an increase in conversion (from 40 to 100%). On the other hand, *n*-heptadecane selectivity decreased from 70 to 40%. The deoxygenation was carried out in a semi-batch reactor under the flow of 5% H₂ in argon for 360 min [67].

Effect of temperature in deoxygenation of tall oil fatty acid (TOFA) over Pd/C catalyst has been studied at various temperatures from 300 °C to 350 °C in the presence of dodecane as a solvent under the flow of 1% H₂ in argon for 360 min [31]. It was found that total conversion of the fatty acid increased with an increase in reaction temperature and only minor sintering of Pd/C (Sibunit) occurred at a reaction temperature of 350 °C. The main products in the liquid phase at temperature reaction of 300 °C were desired products (*n*-heptadecane and *n*-heptadecene) with a higher amount of *n*-heptadecane compared to *n*-heptadecene.

At higher reaction temperatures, 325 °C and 350 °C, the ratio between *n*-heptadecane and *n*-heptadecene was lower. This indicated that dehydrogenation occurred to a larger extent [40]. Selectivity to the desired products decreased with the increase in temperature due to the more extensive catalyst deactivation at higher temperatures because of enhanced formation of an aromatic C17 compound. The aromatic compound was typically undecylbenzene type. Aromatic compound is formed after the deoxygenation via dehydrogenation of *n*-C17-heptadecane leading to cyclization. Besides that, conversion of linoleic acid in TOFA into its C18 fatty acid isomers was enhanced at higher temperatures.

3.5. Catalyst amount

Catalyst amount used for stearic acid deoxygenation significantly can influence reaction rates and selectivity of the desired products (*n*-heptadecane and heptadecene) [52]. The effect of catalyst amount in stearic acid deoxygenation has been studied at 300 °C under 6 bar of helium in dodecane by using Pd/C catalyst at different amounts (0.2, 0.5, and 1 g). It was reported that the reaction rates and conversion increased linearly with the amount of the catalyst in the range. Besides that, the increase in catalyst amount resulted in a slower catalyst deactivation and a higher selectivity to *n*-heptadecane. Thus, this parameter is critical in optimizing the yield of the desired products.

Furthermore, Kwon et al. [70] studied the effect of catalyst amount in deoxygenation of methyl laurate at 350 °C in a batch reactor in the presence of H₂ using various amounts of NiMo/Al₂O₃ catalyst (0–0.126 g). They found that the conversion and selectivity of linear hydrocarbons (undecane and dodecane) increased with the catalyst amount. Meanwhile, lauric acid as an intermediate product and undesired products decreased when the catalyst amounts was increased. This result indicated that the use of smaller amounts of catalyst in the presence of H₂ led to higher polymerization of methyl laurate toward the formation of undesired products.

3.6. Feed rate (residence time)

Maki-Arvela et al. [71] studied the effect of feed rate on the activities in lauric acid deoxygenation using four different volumetric feed flow rates, i.e. 0.1 ml/min, 0.25 ml/min, 1 ml/min and 1.5 ml/min. The reaction was carried out using Pd/C catalyst under the presence of dodecane as solvent in a continuous reactor. It was found that when the feed rate was decreased from 1 ml/min to 0.25 ml/min, the conversion level increased from 4% to 45% because of the increase in the residence time of feed in the reactor. Feed rate is inversely proportional to residence time. The increase in feed rate resulted in the decrease in the conversion level due to a shorter residence time that resulted in extensive catalyst deactivation. It can be concluded that, catalyst deactivation during lauric acid deoxygenation was significant when contacting the catalyst with a large quantity of lauric acid.

3.7. Use of solvent

Effect of solvent on catalytic activity has been studied for deoxygenation of methyl stearate over catalyst of 5% Pd/BaSO₄ under hydrogen atmosphere in a batch reactor at 270 °C for 6 h [72]. It was reported that deoxygenation reaction carried out without using a solvent produced no alkanes, although the methyl stearate conversion was nearly 100%. This could be due to formation of macromolecules via coupling reactions among intermediates on the catalyst surface. This result agreed with that of solventless deoxygenation of sunflower oil as reported in the literature [73].

Meanwhile, when organic solvents such as hexane was used for the methyl stearate deoxygenation, high stearic acid conversion (99.5%) with high yield of *n*-alkane (95.7%) were achieved. Furthermore, using hexane as solvent in deoxygenation of sunflower oil over catalyst of 5% Pd/BaSO₄ under hydrogen atmosphere also successfully gave high yield of desired products of around 79.2% [72]. This result was because the high diffusivity of supercritical hexane that could reduce mass-transfer resistance of reactants in the reactions, which facilitated the contact of hydrogen and the reactants with the catalyst. Besides that, the solvent has high solubility with alkanes. The high solubility enhances desorption of alkanes generated on the catalyst surfaces. As such, the coupling reactions among alkyl intermediates adsorbed on the active sites of the catalysts to form unidentified macromolecules were effectively inhibited. However, the presence of an excess of solvent made the deoxygenation slow due to a volume expansion reaction.

4. Recent progress in deoxygenation of fatty acid

Initially, Snare et al. [53] studied stearic acid deoxygenation in the presence of dodecane as solvent in a semi-batch reactor using noble metals (Pd, Pt, Ru, Ir, Os and Rh) as well as non-noble metal (Ni) as active components. The catalyst supports explored were Al₂O₃, SiO₂ and activated carbon. It was found that Pd supported on mesoporous carbon (5 wt% Pd/C) was the most efficient catalyst for stearic acid deoxygenation in especially through decarboxylation to produce *n*-heptadecane. The 5 wt% Pd/C catalyst successfully converted stearic acid completely with >98% selectivity toward deoxygenated C₁₇ products. It was also reported that activities of metals incorporated on the same support for the deoxygenation increased in the order of Os < Ru < Ir < Rh < Ni < Pt < Pd. A continuous process of methyl stearate deoxygenation was also successfully carried out using the 5 wt% Pd/C catalyst at 360 °C that gave 100% of conversion with 95% of *n*-heptadecane selectivity [58]. Since then, a number of works in the literatures

reported deoxygenation of various fatty acids to produce diesel like hydrocarbons over supported metal catalysts under various operating conditions and various reactor types. These works are summarized in Table 1.

As can be seen from Table 1, Maki-Arvela et al. [52] observed deoxygenation of various fatty acids and their derivative using 5 wt% Pd/C catalyst in a semi-batch reactor for 5 h under various operating conditions i.e. temperatures (300 to 320 °C), gas atmosphere (argon, nitrogen and hydrogen), solvents (dodecane, mesitylene) and initial feed concentrations (0.2–1.0 g). It was reported that high yields of the desired product, *n*-heptadecane were achieved in stearic acid deoxygenation at 300 °C under helium. Moreover, deoxygenations of a saturated fatty acid i.e. lauric acid over 1 wt% Pd/C catalyst were carried out in continuous process using various solvents (dodecane, mesitylene and decane) at lower temperatures (255–300 °C) to study the stability and deactivation of the catalyst [71]. Catalyst deactivation was identified to be the most prominent when using solvents such as mesitylene and dodecane. The deactivation of catalyst resulted from poisoning by gas products of CO and CO₂ and coking.

Subsequently, 5 wt% Pd/C were examined in deoxygenations of unsaturated fatty acids (oleic acid, linoleic acid) and unsaturated fatty acid ester (methyl oleate) either in a semi-batch or in a continuous reactor under various operating conditions i.e. atmospheres (argon, hydrogen and synthetic air), temperatures (300–360 °C) and pressures (15–27 bar) [54]. It was found that the unsaturated fatty acids and unsaturated fatty acid ester were successfully deoxygenated to produce diesel-like hydrocarbons via initial hydrogenation of double bonds and subsequent deoxygenation of corresponding saturated feeds. Then, the application of continuous process for the reaction confirmed stability of the catalyst. Arend et al. [74] studied solventless deoxygenation of oleic acid over 2 wt% Pd/C in a continuous reactor under hydrogen atmosphere at various conditions. Deoxygenations of dodecanoic acid over 1 wt% Pd/C were also carried out in a continuous reactor [68]. Furthermore, tall oil fatty acid and lauric acid deoxygenations over Pd/C catalysts were successfully demonstrated in a semi-batch reactor with encouraging results [31,66,75].

Pd supported on SBA-15 mesoporous silica was also studied for deoxygenation of stearic acid using dodecane as solvent in a semi-batch reactor at 300 °C under a flow of 5% H₂ in Ar [76]. The catalyst achieved stearic acid conversion of 94% with *n*-heptadecane selectivity of 94% for a reaction time of 5 h. Meanwhile, when 4 wt% Pd/C catalyst was used, deoxygenation of a mixture of stearic acid and palmitic acid using the same conditions achieved a total conversion of about 97% with *n*-heptadecane and *n*-pentadecane selectivity of 99% for a reaction time of 2 h [64]. Furthermore, Pd incorporated on different supports (i.e. Pd/C, Pd/SiO₂, and Pd/Al₂O₃) was demonstrated to be promising catalyst for stearic acid deoxygenation in a semi-batch reactor at 300 °C using dodecane as solvent under flow of 10% hydrogen in helium [77].

Immer et al. [78] observed stearic acid deoxygenation using Pd/C catalyst in the presence of dodecane or heptadecane using a semi-batch reactor. Complete stearic acid conversion with 98% selectivity to *n*-heptadecane was achieved after 5 h. Besides, the use of Pd/C catalyst for deoxygenation of C₁₈ free fatty acid in heptadecane has also been studied using fed-batch reactor [79]. Continuous processes of solventless deoxygenations of stearic acid over Pd/C catalyst were successfully carried out either under inert atmosphere or under the flow of H₂ in Ar [60,80]. Stearic acid conversions of around 12–15% with *n*-heptadecane (C₁₇H₃₆) as the main liquid product were achieved using these processes.

Besides using catalysts derived from Pd which is high price-rare metal, some researchers also investigated fatty acid deoxygenation using low cost catalysts such as Ni/MgO–Al₂O₃, Ni/Al₂O₃ and MgO/Al₂O₃ in a batch reactor under solvent free and inert

Table 1
Fatty acid deoxygenation over various supported metal catalysts to produce diesel-like hydrocarbons.

Catalyst	Feed	Solvent	Reactor type	Conditions	Reference
22 5 wt% Pd/C	Stearic acid Ethyl stearate Behenic acid Nonanoic acid Oleic acid	Dodecane Mesitylene	Semi-batch	T=300–320 °C Atmosphere=argon; nitrogen; hydrogen Initial feed concentration=0.1–1.6 mol/l Catalyst amount=0.2–1 g Reaction time=5 h	[52]
1 wt% Pd/C	Lauric acid	Dodecane Mesitylene Decane	Continuous	T=255–300 °C; feed rate=0.1–1.5 ml/min Atmosphere=argon; hydrogen; synthetic air Initial feed concentration=0.22; 0.35; 0.44 mol/l Catalyst amount=0.3–0.5 g	[71]
2 5 wt% Pd/C	Oleic acid Linoleic acid Methyl oleate	Solvent free Mesitylene	Semi-batch	T=300–360 °C; Catalyst amount=1 g Atmosphere=argon (25 ml/min) Initial feed concentration=0.83 mol/l and 100 wt% (solvent free) Reaction time=6 h	[54]
			Continuous	T=300 °C; Atmosphere=argon Catalyst amount=0.2 g Residence time=8 min Liquid flow rate=0.05 ml/min	
2 wt% Pd/C	Oleic acid	Solvent free	Continuous	T=380–450 °C; Catalyst amount=1–5 g Atmosphere=hydrogen (5–95 ml/min) Residence time=0.5–15 s WHSV=1.6 and 7.9 h ⁻¹	[74]
1 wt% Pd/C	Dodecanoic Acid	Solvent free, Dodecane	Continuous	T=300–360 °C; Atmosphere=argon Initial feed concentration=0.5–4.4 mol/l Catalyst amount=2–12 g Residence time=0.5–15 s WHSV=0.8–1.7 h ⁻¹	[68]
1 wt % Pd/C 4 wt% Pd/C	Tall oil fatty Acid	Dodecane	7 Semi-batch	T=300–350 °C Atmosphere=1% H ₂ in Ar; 100% H ₂ Reaction time=360 min Amount of catalyst=0.5 g Feed concentration=0.15–0.6 mol/L	[75]
5 wt% Pd/C	36 Lauric acid Lauric aldehyde Lauric alcohol	Hexadecane	Semi-batch	T=300 °C ; Atmosphere=100%Ar; 100 % H ₂ Reaction time=5 h Feed concentration=0.05 mol/L Amount of catalyst=0.1 g	[66]
1 wt% Pd/C	26 oil fatty Acid	Dodecane	Semi-batch	25 300–350 °C; Atmosphere= 100 % H ₂ Reaction time=330 min Feed concentration=0.15–0.6 mol/L Amount of catalyst=0.5 g	[31]
3 wt% Pd-SBA-15	Stearic acid	Dodecane	Semi-batch	T=300 °C ; Atmosphere=5 % H ₂ in argon Reaction time=5 h Feed concentration=0.05 mol/l Amount of catalyst=0.5 g	[76]
2 4 wt % Pd/C	A mixture of Palmitic acid 10 and Stearic acid (SA)	Dodecane	Semi-batch	T=300 °C ; Atmosphere=5 % H ₂ in argon Reaction time=180 min Feed concentration=0.05 mol/l Amount of catalyst=0.5 g	[64]
5 wt% Pd/C 5 wt % Pd/SiO ₂ 5 wt% Pd/Al ₂ O ₃	Stearic acid	Dodecane	Semi-batch	T=300 °C Atmosphere=5–10 % hydrogen in argon Solvent amount=22.5 g; feed amount=5.6 Mmol Catalyst amount=336 mg Reaction time=5 h	[77]
5 wt% Pd/C	Stearic acid Linoleic acid	Dodecane Heptadecane	Semi-batch	T=300 °C; reaction time=5 h Atmosphere=helium ; 10 % H ₂ in Ar. Feed concentration =1.6 g reactant in 23 g solvent Catalyst amount=350 mg	[78]
5 wt% Pd/C	C18 free fatty acid	Heptadecane	Fed-batch	T=300 °C; reaction time=24 h Atmosphere=5–10 % hydrogen in argon feed flow rate=6–30 µl/min Solvent amount=12.4 g; catalyst amount=336 mg	[79]
5 wt% Pd/C	Stearic acid	Solvent free	Continuous	T=360 °C ; Atmosphere=Ar; 5 % H ₂ in argon Feed rate=0.075 ml/min; Catalyst amount=10 g	[80]
2 wt% Pd/C	Stearic acid	Dodecane Solvent free	Continuous	T=300 °C; catalyst amount=10 g Atmosphere=argon; 5 % H ₂ in argon Initial feed concentration=10 wt%; pure stearic acid Feed rate=42 ml/min	[60]
MgO/Al ₂ O ₃	Oleic acid	Solvent free	Batch	T=300–400 °C; Reaction time=3 h Atmosphere=N ₂ ; feed amount=55 g Catalyst amount=2.75 g	[81]
Ni/MgO–Al ₂ O ₃	Oleic acid	Solvent free	Batch	T=300–400 °C; Reaction time=3 h Atmosphere=N ₂ ; feed amount=55 g Catalyst amount=1.375 g	[62]

atmosphere conditions [62,81]. Solventless deoxygenation of oleic acid through decarboxylation over hydrotalcite catalysts (MgO/Al₂O₃) with different MgO contents that has been carried out in an autoclave reactor at 300 °C for 3 h without the use of hydrogen [81]. However, the results confirmed that during the decarboxylation of oleic acid, saponification reaction of MgO was also involved. Saponification was dominant at 300 °C so that MgO disappeared after the decarboxylation process. Meanwhile, hydrotalcites that catalyzed oleic acid decarboxylation at higher temperatures (350 or 400 °C) exhibited very low selectivity of heptadecane since molecular cracking was dominant mechanism in the reaction during the decarboxylation process.

Roh et al. [62] investigated deoxygenation oleic acid through decarboxylation carried out in an autoclave reactor under solvent free condition without the use of H₂ flow. The catalysts were 20 wt % Ni supported on MgO–Al₂O₃ catalysts with different calcination temperatures (300, 400 and 500 °C). The catalysts achieved oleic acid conversions ranging from 26% to 31% with corresponding heptadecane selectivity ranging from 4.8% to 5.5% at 300 °C for 3 h. These results proved the plausibility of fatty acids as feedstock for production of hydrocarbons to be used as renewable energy sources in the future.

5. Conclusions

As an effort to address the drastic shortages of crude oil supplies in the near future, deoxygenation of fatty acid as a renewable resource using supported metal catalyst to produce diesel-like hydrocarbons is becoming more attractive. It is due to the feedstock availability in many countries and liquid products containing hydrocarbons similar to those found in diesel fuel obtained by refining crude oil in petroleum refineries. Reaction pathways and kinetic models of fatty acid deoxygenations over supported metal catalyst are critically reviewed. The key technology of fatty acid deoxygenation using supported metal catalyst to obtain a high yield or selectivity to the diesel-like hydrocarbons can be constructed by detailed understanding on roles of the operating conditions such as supported metal catalyst type, feed type, temperature, reaction atmosphere, catalyst loading, feed rate (residence time) and the use of solvent.

Metal incorporated mesoporous materials having high metal content with small particle are recommended catalysts for fatty acid deoxygenation to produce high yield or selectivity of diesel-like hydrocarbons. Furthermore, deoxygenation of fatty acid is more selective to produce diesel-like hydrocarbons compared to that of fatty acid ester. Deoxygenation of saturated fatty acid with a shorter chain achieved slightly higher selectivity to diesel-like hydrocarbons. Fatty acid deoxygenation under small quantity of H₂ in inert gas is recommended for higher yield of diesel-like hydrocarbons compared to that under inert or rich hydrogen atmospheres as this condition results in lower coke formation. The recommended temperature for the fatty acid deoxygenation is at around 300 °C for reactions in a batch or semi batch reactor. At higher reaction temperatures, it could lead to dehydrogenation reaction in a larger extent. Meanwhile, the higher amount of the catalyst gives positive effect to the reaction rates and selectivity to diesel-like hydrocarbons of *n*-alkane. Besides that, it resulted in a slower catalyst deactivation.

In general, most of the recently demonstrated catalysts for the deoxygenation process were noble metals (Pd, or Pt) supported on mesoporous carbon. However, catalysts based on noble metals are expensive and unattractive for commercial applications. For future research, more economical catalysts (e.g. Ni, Co, Cu-based catalysts) need to be fully developed to obtain mesoporous catalysts with high metal content with small particles. Besides that,

examination of performance of the catalysts on laboratory scale and on a pilot scale as well as optimized catalyst regeneration method are needed to put the catalytic fatty acid deoxygenation to practical use.

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