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Review

Review of Non-Thermal Plasma Technology for Hydrogenation of Vegetable Oils and Biodiesel

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Abstract. The hydrogenation of lipid derivative compounds has received much attention as it is one of the key chemical reactions of industrial processes to improve the physical and chemical properties of those compounds such as thermal resistance, cold flow properties, oxidative stability, etc. The principle of hydrogenation of vegetable oil for margarine production relies on the addition of hydrogen to the carbon double bond positions of fatty acid molecules to become a single bond, increasing the saturated fatty acids until the texture becomes semi-solid. The partial addition of hydrogen to biodiesel improves its oxidation resistance. At present, industrial-scale using catalytic hydrogenation of lipid derivative compounds operates under high temperature and high-pressure environments, leading to a high *trans*-fat content in the products and requiring catalyst separation from the product. Non-thermal plasma (NTP) technology as a green process can be deployed to substitute conventional hydrogenation, on a laboratory scale for the time being, because no catalyst is required and the process can occur at near ambient temperature and low or atmospheric pressure. Moreover, *trans*-fat formation is several times lower than that of catalytic hydrogenation. The present review article provides more insight into the various types of NTP technology for lipid derivative compounds hydrogenation, including discussions on different experimental setup configurations, parameters affecting plasma hydrogenation, properties of synthesized products, as well as the advantages and drawbacks of environmentally-friendly plasma hydrogenation compared to conventional catalytic hydrogenation.

Keywords: Non-thermal plasma, hydrogenation, lipid derivative compound, vegetable oil, biodiesel.

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1. Introduction

Hydrogenation, an important chemical reaction for the industry, was discovered by a French chemist who introduced a nickel as a catalyst to facilitate the addition of hydrogen to organic compounds in the gas phase [1]. Generally, it is the chemical reaction between a reactant (unsaturated substrate) and molecular hydrogen, and is commonly used in combination with a catalyst at a wide range of temperatures and pressures depending on the type of catalyst and the substrate used. Hydrogenation has become an important chemical reaction for organic compounds, especially fats and oils, with carboxylic acids as a functional group because the reaction can change the chemical and physical properties of these organic precursors like oxidative and thermal stability, melting characteristics, miscibility, and viscosity, converting them into value-added products [2]. These products can be used in a variety of applications such as in hardening of vegetable oils for making margarine and shortenings, helping reduce production costs for manufacturers and helping extend the shelf life of the product, as well as reducing rancidity. In the case of hydrogenation of biodiesel, it reduces susceptibility to oxidation which improves oxidation stability and cetane number and thereby slightly degrades biodiesel quality in terms of cold flow properties.

Hydrogenation typically constitutes the addition of hydrogen atoms to unsaturated carbon bonds of oils and derivatives, for example, poly- or mono-unsaturated methyl esters (biodiesel), turning them into monounsaturated or saturated counterparts with the use of catalysts. Conventionally, the addition of hydrogen to vegetable oils or fatty acids compounds such as biodiesel requires a catalyst and elevated temperature (100 – 200^{o}C) and pressure (0.2 – 0.5 MPa) [3, 4]. Most of the catalysts used on an industrial scale are heterogeneous ones such as noble metals and metals on a support material, employing hydrogen gas as a source of hydrogen atoms. Homogeneous catalysts are also used but to a lesser extent. The advantages of using heterogeneous catalysts are reusability, ease of operation, high productivity, and high selectivity. Although the catalysts can be reused, some drawbacks are huge resources required in the preparation process, long and several preparation steps [5], and efficiency reduction with an increasing number of reuse cycles. In the catalyst preparation process, a large amount of waste is generated, resulting in costs for proper disposal. In addition, the use of a catalyst with high-temperature operations in the partial hydrogenation process often produces *trans* isomers. In the food industry for margarine production, *trans* isomers are generated through the process. The consumption of *trans* fatty acid (TFA) results in an increase in bad cholesterol levels in the body and contributes to cardiovascular disease and obesity, all of which are dangerous for consumers. Not only does TFA promote higher levels of bad lipoproteins, but it is also associated with the development of Alzheimer's disease, macular degeneration, gallstone disease, and inflammation which is a risk factor for many chronic non-communicable diseases (NCDs). Even the World Health Organization (WHO) and the U.S. Food and Drug Administration (FDA) have banned the consumption of TFA and forced food manufacturers to stop using ingredients containing TFA in their products. In Thailand, the announcement of the Ministry of Public Health on July 13th, 2018, stated that partially hydrogenated oil and food products containing TFAs from partially hydrogenated oil are prohibited from manufacturing, importing, and distribution [6]. The *trans* isomers, when formed by partial hydrogenation in biodiesel fuels, impair certain cold flow properties because of their high crystallization point. Therefore, by using technologies that do not require a catalyst, the catalyst preparation process, waste, and disposal costs would be eliminated. An alternative hydrogenation technology without the use of a catalyst is plasma technology, which is one of the green technologies that can be substituted for catalytic hydrogenation because the active species formed in the plasma region can function as a catalyst.

In recent years there has been a wide variety of plasma applications in materials science, chemical processing, food processing, medical treatment and disinfection [7]. Plasma technology can allow thermodynamically-unfavorable chemical processes to occur in an ambient environment, e.g., atmospheric pressure and room/near room temperature [8]. Most of the plasma utilized is cold plasma or non-thermal plasma (NTP), which is a novel technology that offers an appealing alternative for the effective hydrogenation of vegetable oils and derivatives to improve their characteristics and gain value added. NTP is a non-equilibrium plasma, a regime of plasma when the electron temperature is much higher than the temperatures of ion and neutral species ($T_e \gg T_i \approx T_n$, where e, i, and n represent electron, ion, and neutral species, respectively), thus, not being in equilibrium with one another [8, 9]. NTP operates at low temperatures and under atmospheric pressure with often high reaction rates. The energetic electrons created in NTP have sufficient energy to excite working gas molecules by excitation, dissociation, and ionization, producing various plasma species (e.g., excited atoms and molecules, ions, neutral molecules, as well as radicals) that can effectively catalyze and initiate chemical reactions [10]. Another advantage of the plasma technology is the compactness, portability, easy installation, and flexibility of the system allowing for increasing study of the utilization of plasma in many applications. Furthermore, plasma hydrogenation of vegetable oils can be performed at or near room temperature, thus reducing the likelihood of TFA formation [11]. However, the main challenges of hydrogenation via cold plasma techniques are the low reaction selectivity and the strategies to increase their energy efficiency and cost-effectiveness to compete with conventional catalyzed hydrogenation.

This review paper is focused on the literature survey on the hydrogenation of vegetable oils and biodiesel via the NTP technology, aiming to gather the knowledge, limitations, and opportunities for hydrogenation using the NTP technology based on several techniques. Specifically, this paper reviews progresses in (a) hydrogenation using different types of NTP, (b) studied parameters affecting the hydrogenation process, (c) probable mechanisms of hydrogenation via hydrogen plasma, (d) product properties resulting from plasma hydrogenation, and (e) advantages and drawbacks of using NTP for hydrogenation. To provide a complete picture, conventional hydrogenation research using catalysts is also briefly discussed in terms of catalyst types, reactor types, etc.

2. Catalytic Hydrogenation

2.1. Catalysts for Hydrogenation

Catalysts employed in hydrogenation to make the oil more saturated in the case of margarine and shortening manufacturing, as well as to improve certain properties of biodiesel, play a vital role in accelerating the reaction rate [3]. Under high temperatures and high pressure, the hydrogen gas molecules first adsorb on the catalyst surface, dissociate into hydrogen atoms, and then react with the reactants. Poly- and mono-unsaturated fatty acids are gradually hydrogenated through carbon double bonds (C=C) or carbonyl bonds (C=O) until they become either monounsaturated fatty acids or saturated ones [3]. In addition, the use of catalysts can regulate the reaction rate and be able to control the selectivity of the reaction toward the desirable product.

Partial hydrogenation of vegetable oils and biodiesel has been well-investigated with the use of several kinds of catalysts, both homogeneous and heterogeneous. Precious metals including Pt (Platinum), Pd (Palladium), or Rh (Ruthenium) are applicable [12, 13]. Metallic Ni on silica, alumina, or zirconia support is most acceptable from an economical and industrial point of view [12]. Homogeneous catalysts for fatty acid hydrogenation are less popular than heterogeneous ones due to the problems of catalyst separation from the product and the ability of regeneration [14]. However, some advantages of this type of catalyst are higher activity and less selectivity to the *trans* isomer. Ru compound ($RuCl_2(CO)_2(PPh_3)_2$), a promising catalyst, was used in the hydrogenation of canola oil by processing at high gas pressure (750 psi) and low temperature (110 ^oC) producing the *trans*-isomer of about 10.4% with a 61.5% decrease in iodine value (IV) [15]. A series of Ru catalysts had also been investigated for hydrogenation of fatty acid methyl esters (FAMEs) and the results revealed that it was a practical, scalable, and high-yield process [16]. Currently, rhodium trichloride ($RhCl_3$) as an effective homogeneous catalyst also breaks the limitations for catalyst separation, since this catalyst is highly soluble in polar solvents such as polyethylene glycol (PEG), while reactants and products are well soluble in nonpolar solvents such as toluene. Therefore, after the reaction, the separation of the two phases is simple and the catalyst can also be recycled [17]. Furthermore, aqueous sodium carbonate (Na_2CO_3) and sodium dichloropalladate (Na_2PdCl_2) were reported to increase the selectivity up to 93% for sunflower oil hydrogenation [3]. Consequently, the choice of employing homogeneous catalysts is still helpful in terms of reducing *trans* isomerization with high selectivity for *cis* isomerization [15, 18].

Heterogeneous catalysts, as opposed to homogeneous counterparts, exhibit a different physical state with reactants and products and are most frequently applied in a solid form. The obvious advantage of this type of catalyst is the convenient separation from the product. The Ni (nickel) catalyst, normally used on an industrial scale, on a high surface area support, in particular Raney-Ni, seems to be the most promising agent among the metals because it is cheap, abundant, exhibits high activity and selectivity on linoleic acid and linolenic acid [14]. In the food industry, Ni on titanium dioxide (Ni/TiO_2) was effective for the hydrogenation of soybean oil with a TFA level of 10.5% and a final iodine value (IV) of 70 [19]. Likewise, Li et al. [20] utilized the nickel–boron catalyst for hydrogenating soybean oil achieving a lower TFA formation of 8% and an IV of 77, but with a higher tendency toward the formation of stearic acid than the commercial nickel catalyst. Partial hydrogenation of polyunsaturated biodiesel using Ni-based catalysts has also been found to significantly enhance fuel quality. Nonetheless, Thunyaratchatanon et al. [21] showed that the Ni/SiO_2 catalyst exhibited relatively low efficiency in the partial hydrogenation of soybean biodiesel as the oxidation stability was improved by only 1 h and as the cloud point increased to 9^{o}C. 28 and 0.96 wt.% of *cis*- and *trans*- methyl oleate (C18:1) were obtained after 4 h of reaction time. Jatropha oil biodiesel, containing high amounts of free fatty acids (FFAs), was hydrogenated using Raney-Ni under the microwave heating approach. The conversion of C18:2 to C18:1 was more pronounced than that of C18:1 to C18:0 and the oxidation stability increased from 6 h to over 45 h [22]. Many studies of partially hydrogenated biodiesel revealed that the biodiesel based on high C18:3 or C18:2 contents might be readily converted to C18:1 which has a positive effect on the resistance to oxidation while still exhibiting a good cloud point. The oxidative stabilities of these hydrogenated FAMEs (H-FAME) were improved 2-30 times compared to the untreated FAMEs [23-25]. Hydrogenation of palm oil-based biodiesel was also studied using Ni/SiO_2. The results revealed that if the value of oxidation stability was too high, the fuel could be stored for a long period but had poor cold flow characteristics [26]. This is because palm biodiesel has a very high C18:1 fraction of almost 50%, which already exhibits excellent oxidation stability. The addition of hydrogen atoms to the unsaturated molecules enhances the C18:0 ratio considerably, resulting in very high oxidation stability. As C18:0 has a high cloud point, too much of it deteriorates the cold flow properties. To generate a good fuel, however, they need to be a good compromise between these two characteristics. However, the Ni catalyst has a short life span due to the loss of its activity caused by various types of substances poisoning in oil, including a trace amount of gaseous sulfur compounds and carbon monoxide as an impurity in commercial hydrogen gas, and phospholipids and sodium soaps presenting in a tiny amount in all refined oil [27, 28]. All of these have a deleterious impact on Ni catalysts with almost 15% being deactivated during the first hour of the hydrogenation process [28].

Besides Ni, Cu-based catalysts are among the most attractive catalysts used in partial hydrogenation. Soybean oil hydrogenated through the Cu/SiO_2 catalyst prepared by the chemisorption-hydrolysis method to improve its properties was studied by Trasarti et al. [29]. The results indicated that C18:1 increased from 24.9 to 52.2 wt.% while C18:3 was almost completely eliminated. The C18:2 concentration decreased from 52.7 to 31.3 wt.% and the unwanted *trans*-isomer was 13.8 wt.%. The saturated stearic acid content was constant during the reaction. Ravasio and the group [30] used Cu with different supports, Cu/SiO_2, Cu/Al_2O_3, and Cu/TiO_2, as catalysts for rapeseed oil methyl esters hydrogenation. The Cu/SiO_2 agent resulted in high C18:1 content of 88 wt.% with the *trans*- content of approximately 20 wt.% while the percentage of C18:0 remained unchanged [30]. Zaccheria et al. [31] reported an altered vegetable fatty acid methyl esters composition after hydrogenation with a Cu/SiO_2 catalyst, where the trends of these composition changes were in the same direction as the previous investigation. The selectivity of the ratio of diene to monoene was outstanding. The beneficial aspects of Cu-based catalysts compared to Ni ones are the higher selectivity of the hydrogenation of C18:3 to C18:1 which increases oxidation resistance, and the non-interference with the C18:0 content as too much of it would worsen the cold flow properties [29, 30].

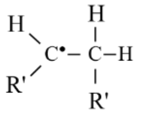
The utilization of noble metals, e.g., Rh, Pd, and Pt as catalysts for hydrogenation, especially in natural oils, has been widely suggested. The report showed that the ranking order of noble metal activity on the addition of hydrogen to natural oils was as follows: Pd > Rh > Pt > Ir > Ru, and *cis-trans* isomerization in the order of Pd > Rh > Ru > Ir > Pt [14, 32]. All of these noble metals exhibit higher activity than Ni. The different activities of these metals may be due to the physical characteristics such as the specific surface area of the catalyst or the concentration-dependent ability of hydrogen to reach the active sites on the catalyst [32]. Numwong et al. [33] reported that Pt and Ni catalyzed the hydrogenation of the *trans*-monoene and it became saturated immediately. Therefore, Pt and Ni catalysts exhibited lower selectivity for *trans*-isomers. McArdle et al. [34] developed a Pt supported on mesoporous SiO_2 for sunflower oil hydrogenation with strong catalytic activity and small TFA content, and it was found that the more Pt loading, the higher the catalytic activity. Later, it was observed that adding Ni to Pt/SiO_2 to form a bimetallic system would improve *cis*–isomer selectivity [35]. Furthermore, some reports found that Pt catalysts with various support materials provided different TFA levels. $Pt/BaSO_4$ was successful in both lowering TFA and increasing saturated fatty acid (SFA) [36].

2.2. Parameters Affecting Hydrogenation

The type of vegetable oil feedstock is one of the key parameters affecting hydrogenation as it determines the physical and chemical properties of the resulting product such as oxidative stability, cold flow properties, acidity, and viscosity. Vegetable oils contain 90-98% triglycerides and a small fraction of mono- and diglyceride [37, 38]. Different kinds of vegetable oils exhibit varying fatty acid compositions. The choice of feedstocks is dependent on geographical and climatic conditions, together with the availability at the requested time. Thus, feedstocks can be supplied differently in different regions and at different times. In tropical countries, palm oil and Jatropha oil are commonly used as feedstock in biodiesel production because of large-scale planting and government support. Sunflower oil and rapeseed oil are more commonly used in Europe while soybean oil predominates in the U.S. [39].

Palm oil contains nearly 45% saturated fatty acids, so when used in biodiesel production, the resulting product exhibits high oxidative stability (OS) but poor cold flow properties. Soybean, sunflower, and rapeseed oils, on the other hand, possess low OS but good cold flow properties due to high unsaturated contents. In particular, the high polyunsaturated linoleic acid content causes a negative impact on the OS [3, 40]. Therefore, hydrogenation is preferred for oils with high unsaturated fatty acid contents to improve their undesirable properties.

Conventional hydrogenation relies on hydrogen gas as a hydrogen source. Hydrogen gas is initially fed into the reactor. It then dissolves into the oil and diffuses to the surface of the catalyst. The dissolution rate of hydrogen is related to the difference between the solubility of hydrogen at a given temperature and pressure and its concentration [41]. Hydrogenation is the addition of hydrogen atoms to the fatty acid chains in which the addition rate depends on the concentration of adsorbed hydrogen atoms. As the adsorbed atomic hydrogen concentration is proportional to the catalyst concentration, the rate of hydrogenation could be enhanced by adding more catalysts [41]. Increased hydrogen pressure and reaction temperature can boost the activity of the catalyst, resulting in a rapid hydrogenation rate [42]. In terms of *trans* configuration reduction, increasing hydrogen pressure enriches hydrogen saturation at the catalyst surface and subdues isomerization. Beers et al. [43] explained this phenomenon that when a hydrogen atom is added to a C=C bond, the half-hydrogenated intermediate,



, is created, and it could bond an available hydrogen atom adsorbed on the catalyst surface in the near area to react with another hydrogen atom at the carbon atom ($C^{\bullet}-C$) to form saturation. This likelihood occurs before the molecule revolves around a single carbon bond that was previously a carbon−carbon double bond. Hence, fewer *trans* isomers could be generated under high-pressure circumstances. It was observed that at a hydrogenation pressure of 0.2 MPa using a Ni catalyst with soybean oil, the *trans*-isomer was produced at roughly 35–40% with a saturated stearic level of approximately 15%. When increasing the hydrogen pressure to 2.5 MPa, 28% of TFA content was noticed, but simultaneously greater saturated content was also formed, leading to solid fats. However, to achieve the stereoisomeric *trans* content of less than 10%, a hydrogen pressure of more than 10 MPa would be required and the existing equipment could not withstand such pressure. Therefore, the use of very high hydrogen pressure may not be practical for the industry [43].

As above mentioned, the hydrogenation activity increases as a function of reaction temperature. When the temperature rises, the viscosity of the oil falls, promoting the mass transfer of a gas-liquid-solid system and intraparticle transfers. Furthermore, increasing the temperature improves the chance of atoms/molecules overcoming the activation energy barrier and frequency of the chemical reactions involved. [42]. The majority of catalytic processes, including hydrogenation, are accelerated by raising the reaction temperature. The high reaction temperature promotes the polyunsaturated fatty acids conversion, resulting in a significant quantity of saturated ones and both *cis*- and *trans*-monoenic (C18:1) [44]. Because higher temperature expedites the reaction rate and the hydrogen concentration on the catalyst surface decreases as the temperature rises, selectivity of the *trans* isomer increases with increasing reaction temperature. Toshtay and Auezov [45] reported a 16.2% increase in TFA (C18:1) content as the temperature rose from 90°C to 150°C for hydrogenated rapeseed oil with the Pd catalyst. The alteration of polyunsaturated compositions including *trans* isomerization with temperature was also observed in the partial hydrogenation of biodiesel. Higher reaction temperatures promote the conversion of polyunsaturated FAMEs. At 80°C and 120°C, polyunsaturated ones were converted by 53% and 73%, respectively. The increase in temperature also caused an increase in the saturated molecules with the transformation of *cis* C18:1 into *trans* C18:1 molecules at 120°C of almost 10% [46].

The efficiency of agitation can influence *trans* isomer formation. Increasing the agitation speed enhances the likelihood that hydrogen is transported from the oil to the catalyst surface to suppress *trans* molecules formation and encourage the formation of saturated ones. When mixing is inefficient, hydrogen transfer through the oil to the catalyst surface may be sluggish. This condition could result in less hydrogen on the catalyst surface and more *trans* isomer production than expected [47]. Musavi et al. [48] examined the hydrogenation of soybean oil with different stirring rates and discovered that the higher the stirring speed, the significantly lower *trans* content was obtained. By raising the stirring rate from 500 to 1,000 rpm, the maximum *trans* level was reduced from 43.69 to 30.60%. Industrial hydrogenation plants face limitations on the mass transfer of hydrogen due to lower mixing efficiency. Increasing the agitator speed or using a recirculation reactor are all positive ways to increase the process efficiency.

2.3. Reactor Configuration

2.3.1. Batch reactors

Batch reactors are commonly used in industrial plants owing to their simplicity and adaptability to a variety of chemical reactions and raw materials. They are also called slurry reactors when powdery solid catalyst is suspended in liquid feedstock as a slurry phase. Two types of these reactors are used industrially, including agitated tanks and loop tanks. The agitated tank, a so-called ‘dead-end’ reactor, is widely employed in hydrogenated oil applications. The hydrogen gas as bubble form is fed into the agitated vessel at the bottom center corresponding to the impeller position which is a high-shear zone [49], and the bubbles spread throughout the existing hot oil and catalyst. The vicinity of the impeller tips distributes the highest turbulence resulting in the best product yield [50]. Another type of reactor is known as a loop reactor. The reaction mixture is circulated in an external loop and pumped through a nozzle. There exists a high shear region at the nozzle, causing the mixture to flow at a high velocity and creating a more intense mixture of hydrogen and reactants than in a dead-end reactor. Only after reaching a specific temperature will the reaction begin to move at a significant rate. Therefore, the reactor must be provided with an appropriate heat exchanger to maintain the desired reaction temperature. However, a cooling system also needs to be equipped due to an exothermic reaction of hydrogenation [43].

The dead-end vessel is preferred due to less energy use, high adaptability in raw material handling, and less capital and operating cost. Nevertheless, heterogeneous batch reactors have problems with the limited rate of hydrogen gas diffusion into the catalyst because of the low solubility of hydrogen in organic matter, high mass transfer resistance in the gas-liquid phase, and the reactant adsorption on the active site. Thus, this reactor has been advocated for the investigation of the supercritical-fluid technique to overcome the transport problem of hydrogen gas in liquid oil and to improve the reaction rate. The supercritical fluid state is excellent due to its unique characteristics. It employs a one-phase system in which gas behaves like a liquid and easily diffuses into the surface of a solid. Herein, this method can reduce mass transfer resistance and enhance the transfer rate [51, 52].

2.3.2. Fixed-bed reactors

In a fixed-bed reactor, the solid catalyst is packed along a vertical vessel with the feedstock oil, and hydrogen gas flowing through. The reactant mixture is converted into a product when passing through the catalyst packed bed. The flow directions of liquid and gas reactants can be divided into co-current or counter-current flows. The co-current can be further divided into upflow or downflow. When choosing a reactant flow pattern, it is important to consider the operating conditions, feedstock type, reaction temperature, flow rate of the reactants, and so on to minimize the mass transfer resistance. However, co-current flow reactors are more frequently used in the industry as they can operate at higher flow rates while counter-current ones encounter a restriction with fluid flooding in the reactor [53]. A suitable reactor should be determined by the velocity of the gas or liquid, level of conversion, and the type of reaction system [54]. Moreover, a good liquid distribution must be maintained and hot spots in the reactor should be avoided. This reactor is operated as a continuous process that runs until the properties of a product are below standard as the catalyst is deactivated and must be replaced. However, the operating parameters such as temperature, pressure, and gas and liquid flow rates can be adjusted to achieve the desired product.

2.3.3. Membrane reactors

One of the methods of improving the diffusion of hydrogen gas onto the catalyst surface is the use of a membrane reactor. Novel membrane reactors have the advantage of compact size and low operating energy, thus providing higher energy efficiency values than conventional reactors. The principle of the membrane reactor is that one side of the membrane is deposited with the catalyst allowing the oil phase to pass through the catalyst side and diffuse into the catalyst layer. On the opposite side of the membrane, hydrogen gas molecules directly flow to react with the catalyst. This concept can reduce the diffusion distance and diffusion resistance of H_2 [55]. In a study by Veldsink [55], a 3-phase catalytic membrane reactor was used with Pd as an active catalyst to hydrogenate sunflower seed oil. The results revealed that the formation of C18:0 was caused by the direct conversion of C18:2. Furthermore, strong selectivity resulted in a high *trans* degree. The finding also reported that the catalytic membrane demonstrated significant catalyst deactivation; however, the catalyst activity could be recovered slightly [55]. Ilinitch et al. [56] stated that Pd with a polymeric membrane could decrease *trans* isomers selectivity more than a conventional slurry reaction using Pd/C as the catalyst. The improved selectivity is related to the higher mass transport in the membrane pores. For the industrial application of a membrane reactor, it is important to develop a membrane suitable for the diffusion of the reactants with good catalyst deposition, durability, and viable renewability.

A comparison of the advantages and disadvantages of each reactor type is shown in Table 1.

Table 1. Advantages and disadvantages of each reactor type.

Reactor type	Pros	Cons
Batch	• Simplicity and flexible operation • Widely used in industry • Can be used for wide variety of chemical reactions	• High mass transfer resistance • Long transport distance between H_2 and oil • Low energy efficiency
Fixed-bed	• No catalyst separation step • Suitable for large scale • Low operating cost • Can control product quality • Can be used with automation	• Less feasible for working on small scale • Unsuitable for high-fluctuation production as reactor may not work at full efficiency • Large thermal gradient may occur • The existing pressure drop between beds • Ineffective temperature control
Membrane	• Compact construction • Flexible operation • High energy efficiency	• Difficulty of catalyst regeneration • High catalyst deactivation

3. Discharge Plasma Hydrogenation

3.1. Why Plasma is Used for Hydrogenation?

Plasma, the fourth state of matter, consists of free electrons, positive and negative ions, excited species, and neutral species of atoms/molecules [8]. Plasma can be divided into naturally occurring plasma and man-made plasma. Most man-made plasma is created electrically at low or atmospheric pressure by supplying sufficient energy to gas or gas mixture, e.g., air, argon, and helium, which can be characterized by its temperature: thermal plasma and non-thermal plasma, and by electric fields [57]. The thermal (high temperature) plasma is almost fully ionized and is typically obtained by arcing a large amount of current in the air at atmospheric pressure [58]. A well-known example is plasma cutting which can reach a temperature of more than 10,000 K for metal cutting . The non-thermal plasma (NTP) or cold plasma employs a sufficiently high electric field to produce a partially ionized gas at low temperatures [59]. The greatest temperature in NTP is the electron temperature (~ 10^5 K), while heavy particles, ions, and excited species keep relatively low temperatures (~ 300 K) [59]. High-energy electrons create active species and radicals that behave as catalysts, rapidly reacting in substances and promoting reaction pathways. Thus, no physical catalysts would be required. Cold plasma can be operated at low or atmospheric pressure [8]. The low-pressure NTP such as radio-frequency (RF) plasma (commonly used frequency is 13.56 MHz) and microwave discharges (typically used frequency is 2.45 GHz) are employed for surface treatments, decontamination of food and thin film coating, etc [60, 61]. Atmospheric-pressure NTP, for instance, corona discharge has been investigated for electrocharging face masks and fabrics, especially in N95 mask to achieve high filtration efficiency, whereas, dielectric barrier discharge (DBD), and plasma jet have been studied in a wider range of applications such as disinfection [62], ozone generation for water treatment [63], and elimination of volatile organic compounds [64].

As mentioned above, highly active species generated from the plasma discharge can function as catalysts. Therefore, the use of cold plasma in chemical processes instead of a chemical catalyst, or incorporating together with a catalyst, has been extensively investigated such as the hydrogenation pathway in vegetable oils or biodiesel [10, 65-67]. An effective application of plasma to a chemical process relies on a suitable reactor design with effective plasma-reactant physical contact and satisfactory operating parameters.

The following are advantageous green aspects of plasma applications to chemical reactions.

- Absence of catalyst preparation process.
- No catalysts are disposed of or recycled after process termination, so no waste is generated.
- Operation at room temperature or slightly higher (approximately 30 – 90°C), so no heating system is required.
- Reduce the residence period of reagents to achieve a steady state.

A comparison between plasma hydrogenation and catalytic hydrogenation in terms of studied parameters and their effects is shown in Fig. 1. However, plasma exhibits certain drawbacks such as the difficulty to control the reaction mechanism because it depends on the reactive species present in the plasma state, low selectivity to the given products, difficult to scale up and make it a continuous process as well as low energy efficiency [7, 68].

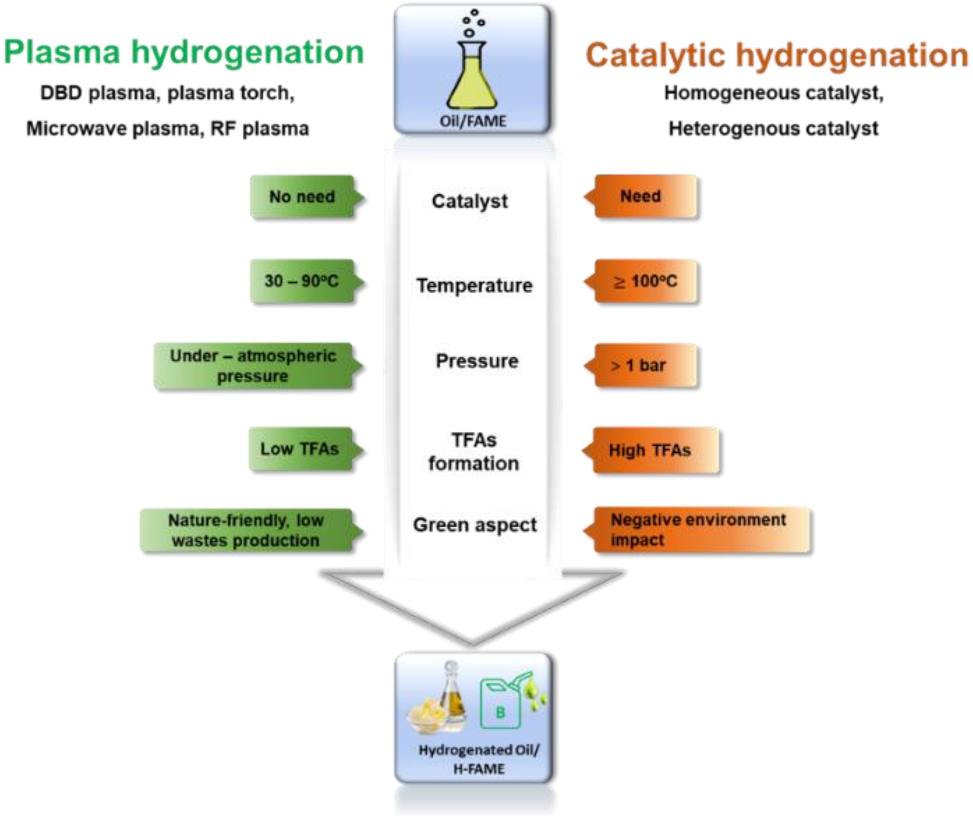


Fig. 1. Comparison between plasma hydrogenation and catalytic hydrogenation.

3.2. Types of NTP and Configuration for Hydrogenation

3.2.1. Dielectric barrier discharge plasma

The dielectric barrier discharge plasma or DBD plasma typically operates at about atmospheric pressure (usually 10^4 – 10^5 Pa). It is one of the most common plasmas used in chemical processes such as the production of ozone, production of organic compounds via polymerization or even removal of organic pollutants [69], and improvement of heavy oils structure. The configuration principle is very simple: an AC power supply with an amplitude of 1 – 100 kV and frequency between a few kHz and MHz delivers the power to two electrodes (one is the earth electrode), and a dielectric material (glass, quartz, ceramic, Teflon, etc.) is sandwiched between the electrodes [70]. The distance between the two electrodes, the discharge gap, is approximately 0.1 mm to several mm depending on the installation of each research. The plasma region where the microfilaments form a thin layer is between these electrode plates. The dielectric layer helps control the electrical discharge, reduces electric arc formation, and prevents electrode deposition [71]. The most typical shape of electrodes in DBD plasma are plate type and coaxial cylinder type. A high-voltage, high-frequency device like a neon sign transformer has been widely employed as a plasma generator for the DBD system in the oil hydrogenation experiment because it is practical, inexpensive, and easy to operate. In 2016, Yepez and Keener [72] carried out the production of partially hydrogenated soybean oil using High-Voltage Atmospheric Cold Plasma (HVACP) system as shown in Figure 2(a). The system was a parallel-plate DBD plasma utilizing the transformer to amplify the AC voltage from 120 V to 130 kV. A plastic container was used as a reaction chamber where two acrylic sheets as a dielectric layer were placed at the top and bottom. Two circular aluminum electrodes were installed above and below each respective acrylic sheet. The experiments were performed at 90 kV and the results showed that the HVACP system with N_2/H_2 gas could lower the IV of soybean oil from 133 to 92 within 12 h of operation time without the TFA formation. The DBD plasma was also utilized to produce margarine from refined palm olein by the group of Puprasit et al. [73]. The system configuration as depicted in Fig. 2(b) comprised an 800 mL rectangular borosilicate glass reaction chamber that was placed on the lower electrode with the upper electrode and dielectric glass sheet positioned inside the reaction chamber above the surface of the feedstock. An adjustable neon sign transformer with a maximum output of 10 kV and 30 mA at 25 kHz was used as a high-voltage, high-frequency power source. Likewise, Kongprawes et al. [65] used the same configuration setup and equipment as [73] to hydrogenate soybean biodiesel to improve its properties such as OS and cold flow characteristics. Hydrogen atoms were added to the double carbon bonds of the feedstock which were converted into single carbon bonds. In a further investigation by Kongprawes et al. [10], H-FAME derived from palm oil was synthesized using a similar system but with modifications to treat larger FAME volume and improve mass transfer by the installation of a reactant circulation loop. This DBD plasma generating system is illustrated in Fig. 2(c). The coaxial DBD reactor for heavy oil processing in a liquid-phase as presented in Fig. 2(d) was carried out by Liu and the group [74]. A microsecond-pulse power source with voltage of 15 kV, pulse repetition frequency of 1 kHz was connected to electrode to generate plasma. The heavy oil was bubbled to better contact with the plasma resulting the improvement of chemical reaction rate [74].

Although the DBD system offers a simple operation and straightforward configuration, the resulting reactive species density is low. A novel geometry of needle-in-tube DBD plasma or plasma torch is designed to address this low-density problem. A hollow dielectric tube into which a needle electrode is inserted can limit and force the produced free radicals to travel through the reactant layer before leaving the reaction chamber to maximize physical contact with the reactant. Three sets, each consisting of a stainless-steel needle inside a hollow quartz tube, were developed for the partial hydrogenation of palm FAME. A neon transformer with 15 kV and 40 mA maximum output was employed as a plasma generator. The quartz tubes were immersed in the FAME layer and an aluminum electrode plate was placed underneath the Pyrex glass chamber [75]. Hydrogen gas was supplied into the inlet port of each quartz tube. The resulting plasma was a large filament similar to arc formation causing the temperature of the liquid during the experiment to be about 30°C higher than that of the parallel-plate DBD system under the same power consumption. This geometry demonstrated in Fig. 3(a) revealed that several tiny bubbles were created at the reactant layer, generating a stirring motion on their own and enhancing the liquid-plasma phase reaction. Besides using the neon sign transformer to produce plasma, a tesla coil transformer was also employed in the production of margarine from palm oil. The high-voltage output from the coil was connected to a stainless steel needle electrode to generate plasma. A ground electrode plate was placed beneath a glass reaction chamber that also functioned as a dielectric material. The Ø1 mm needle electrode was centrally mounted inside a quartz tube with the end opening submerging into palm oil to confine free radicals and to allow the to encounter the oil as much as possible to increase the reaction efficiency before they recombined and left the chamber [76]. The needle-in-tube system energized by the tesla coil is displayed in Fig. 3(b).

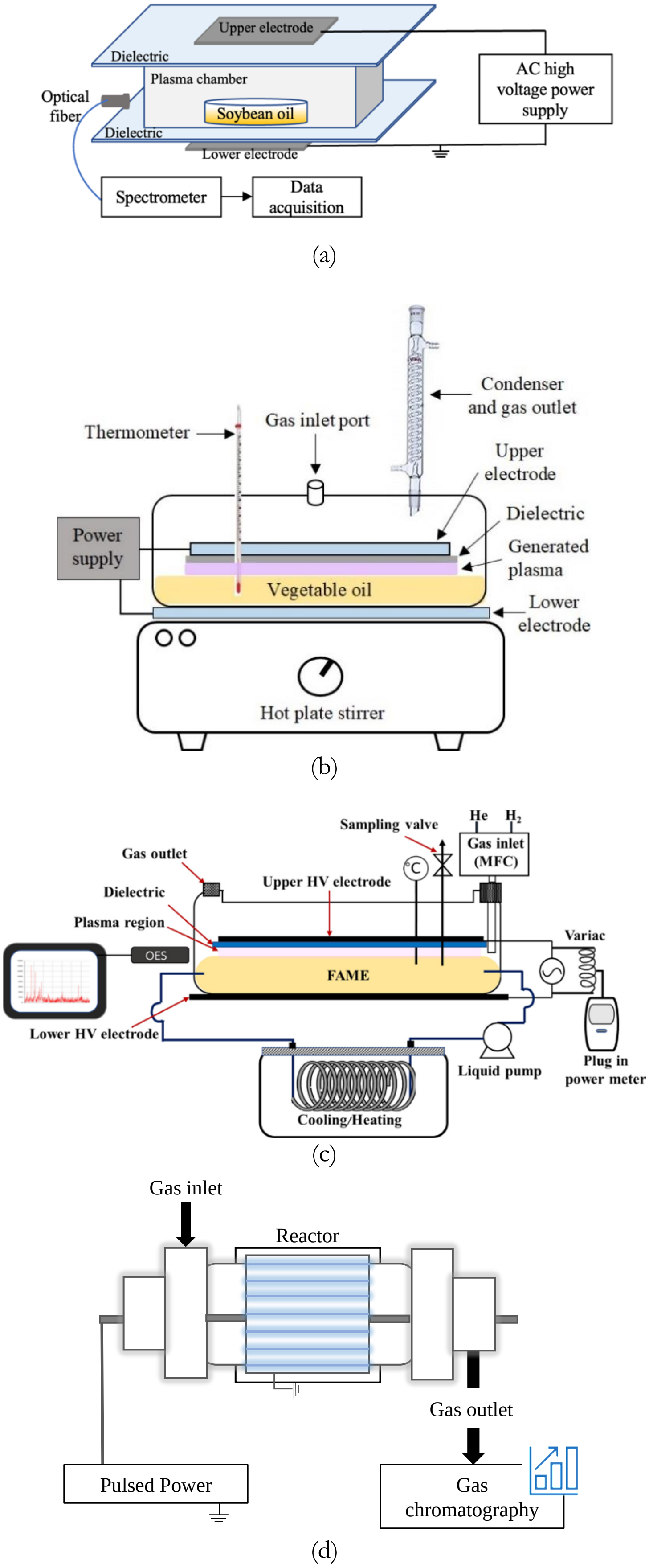
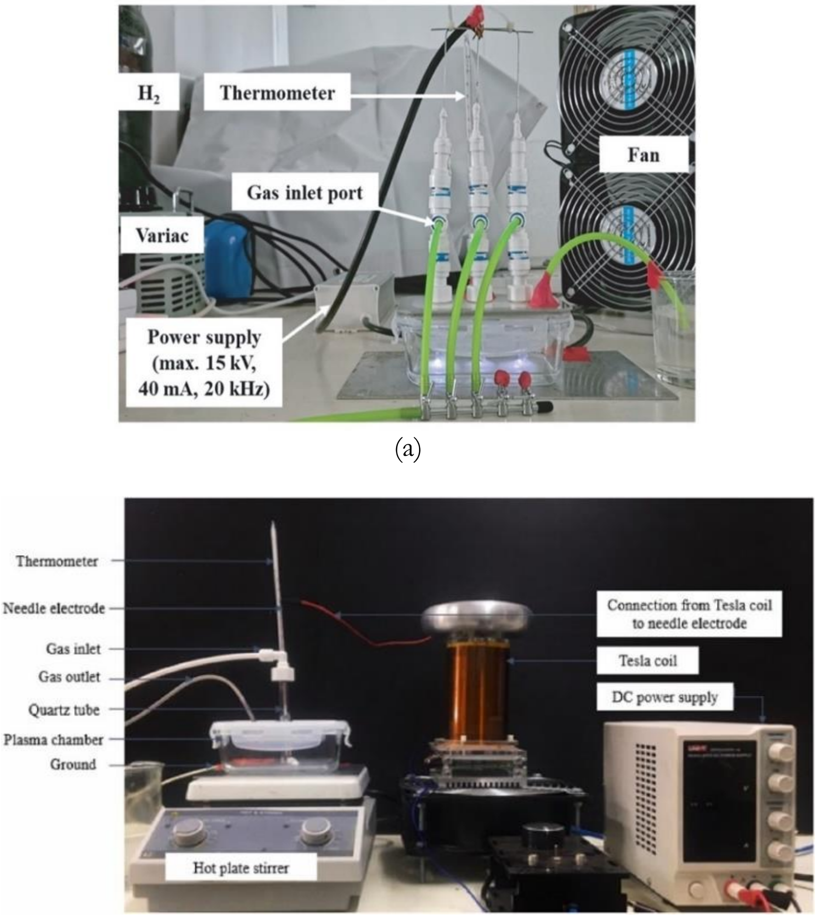


Fig. 2. Experimental setup of DBD plasma generating systems: (a) DBD for hydrogenation of soybean oil, edited from [72], (b) DBD for margarine production, reproduced from [73] with permission from Elsevier, (c) DBD for H-FAME production, reproduced from [10] with permission from Springer Nature, and (d) Coaxial DBD for heavy oil processing, edited from [74].



(a)

(b)

Fig. 3. Experimental setup of different needle-plate DBD reactors: (a) DBD for H-FAME production, reproduced from [75] with permission from Wiley and (b) DBD for margarine production, reproduced from [76] with permission from Elsevier.

The applications of DBD plasma for hydrogenation of oil or FAME without a co-catalyst had satisfactory results. The synthesized products met the requirements; for instance, hydrogenated FAME (H-FAME) exhibited an increase in the OS while the cold flow properties were within the standards of both ASTM D 6751 and EN 14214. For hydrogenation of vegetable oils using DBD plasma, the final products were satisfactory in several physicochemical properties. They exhibited an IV in a range of 23-30, an acid value of less than 0.37 mg KOH/g, saturated fatty acid content of 57-68%, and a slip melting point of 21-36°C [73, 76]. On the other hand, the commercial ones showed an IV in the range of 17-46 [77-79], an acid value of less than 4 mg KOH/g [79], saturated fatty acid content of 48-50% [78], and a slip melting point of 35.5-37.8 °C [77, 78, 80]. It should be noted that, the properties of margarine produced in each country are depending on the raw material types and objectives for using margarine.

DBD plasma is highly useful not only in hydrogenation applications but also in many other fields. It is easy to use, requires inexpensive equipment, and plasma generation can naturally generate UV radiation. However, there are some disadvantages of DBD plasma, namely the relatively low plasma density compared to other plasmas such as microwave plasma, arc plasma, etc., which results in a longer reaction time to achieve the desired degree of hydrogenation.

3.2.2. Microwave plasma discharge

Microwave energy, an electromagnetic wave, generated from a magnetron can be used to generate microwave plasma discharges with a typical frequency of 2.45 GHz (exceeding 300 MHz is suitable) at low or atmospheric pressure with any gas. Microwave wavelengths span between 3 mm and 30 cm and different microwave frequencies are used for industrial, medical, and scientific purposes [61, 81]. Microwave plasma may be produced based on the pulsed or continuous wave with incident microwave energy ranging from watts to kilowatts. The absorbed energy can be quite large, reaching up to 90% of the incident value. Microwave-powered plasma is a non-electrode discharge that offers several advantages, e.g., higher electron density, high efficiency in creating reactive species, operating in a broad range of pressures (10^{-3} Pa – atmospheric pressure), ease of control of microwave-to-plasma conversion by using an external applicator, and reduced chance of gas or plasma phase contamination from electrode corrosion [82].

The fundamental components of a microwave plasma system comprise a microwave power generator (often a magnetron), circulator (a device to protect the magnetron from reflected power), microwave power detectors (incident power and reflected power), matching circuit (manual or automatic stub tuners), microwave-to-plasma applicator, and discharge chamber. The microwave-to-plasma applicator is the most important part of the system since it allows microwave radiation to transfer into the plasma [83]. It can determine the efficiency of the plasma generator, the levels of minimal and maximal plasma powers, the structure of the electromagnetic field in the plasma, the electron density, as well as the homogeneity and size of the plasma. The existing technology of microwave-to-plasma applicators is such as cavity microwave plasma generators, waveguide microwave plasma generators, surface wave plasma generators, and initiated microwave discharges [81].

Microwave plasma generation is based on the principle that the microwave electric field produced by a magnetron travels along a waveguide and then transmits energy to the existing free electrons to oscillate. These energized electrons, moving at high velocity, engage in collision phenomena. They can dissipate their energy by colliding with working gas molecules, and neutral and ionic species in a large number of elastic and inelastic collisions, resulting in excitation and ionization processes [84]. These ions and exited species as chemically active species can be used in the chemical and physical processes of materials. Mostly, microwave plasma has been used in the chemical vapor deposition (CVD) process for the growth of diamond films which is a highly successful method with a higher plasma density than any other plasma-based technology [85]. Microwave plasmas are also utilized as an emission and ionization source in chemical spectrometry equipment such as optical emission spectrometers (OES) and mass spectrometers (MS) [84]. However, to the best of our knowledge, there has been only one study on the use of microwave hydrogen plasma in oil processing, especially to enhance the oil properties. Wongjaikham et al. [66] experimented with microwave plasma hydrogenation to enhance the OS value of FAMEs. The microwave plasma generating system comprised a magnetron and power supply circuit disassembled from a 1,000 W household microwave oven connected to an isolator, a waveguide, and a downstream plasma source, respectively. A variac was used to modulate the power output from the magnetron. The downstream plasma source was connected to a 2-L borosilicate glass reaction chamber, and beneath the chamber was installed a stainless steel plate connected to a negative high-voltage power supply to draw the positive hydrogen ions to react with the reactant to increase the reaction rate. Figure 4 shows this experimental setup. The results indicated that the microwave plasma system can efficiently bond atomic hydrogen to the carbon double bonds in FAME. Moreover, the interaction of the microwave plasma in combination with the negative high voltage bias caused a greater reduction in C18:3, C18:2, and C18:1 and a greater increase in C18:0 than in the absence of the high voltage. This negative high voltage generated an intense electric field to attract positive hydrogen ions to react with the FAME layer. OS was reported to increase from 12.5 to 21.6 h [66]. Therefore, the microwave plasma system can be applied in the process of FAME properties improvement or other applications by replacing the reactant and working gas.

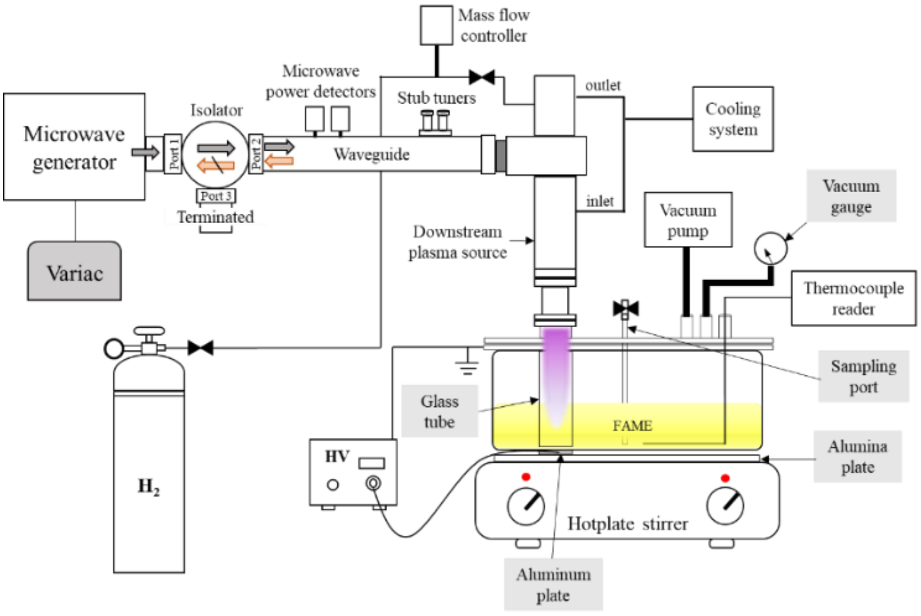
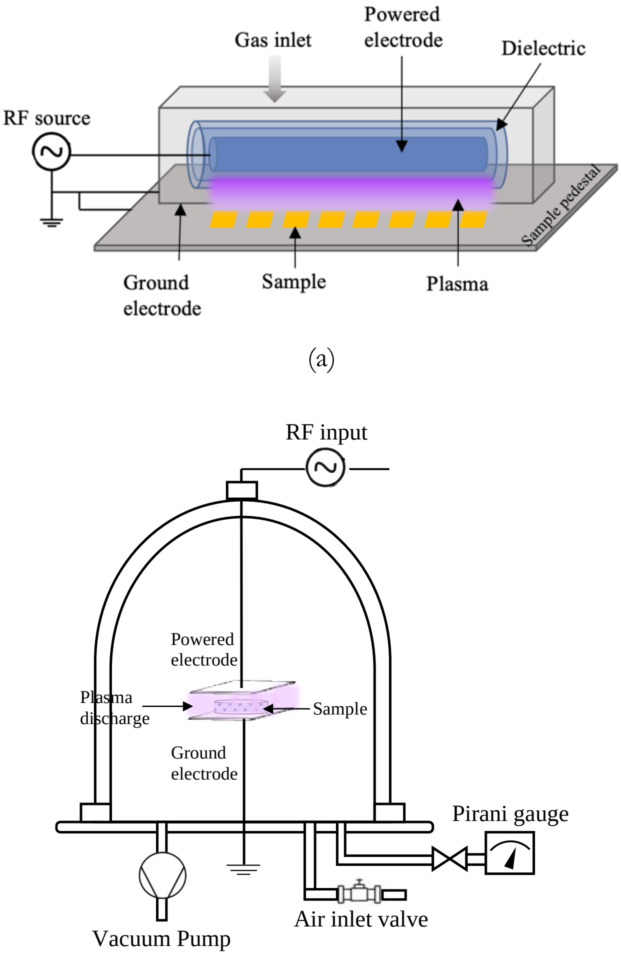


Fig. 4. Experimental setup of microwave plasma generating system for H-FAME production, reproduced from [66] with permission from Elsevier.

3.2.3. Radio frequency (RF) plasma

The generation of RF plasma uses radiofrequency electromagnetic fields as an energy source. The standard industrial frequency for RF plasma is 13.56 MHz. Several approaches can be applied to create an RF field, for instance, the application of RF voltage to parallel-plate electrodes, the use of circulating RF current in the coils or antennas through submersion in the plasma, or separation by a dielectric window. There are three major types of RF plasma: capacitively coupled plasmas (CCPs), inductively coupled plasmas (ICPs), and helicon wave sources (HWSs) [61]. The utilization of RF plasma includes culinary processes such as decontamination, chemical processes such as treatment of fabrics and polymers, semiconductor processing and metal cutting, etc. In the chemical processes based on RF plasma treatment of a lipid-containing product, Kim et al. [86] investigated the application of atmospheric pressure RF plasma to inactivate microorganisms and studied the fatty acid profile of beef jerky. The RF plasma treatment system as shown in Fig. 5(a) comprised the in-line plasma treatment system of 160 mm in length. The hollow cylindrical quartz tube as a dielectric layer was inserted with electrodes throughout its length. The sample pedestals were positioned in this RF system in such a way that they could be exposed to the plasma. The plasma discharge took place between the dielectric barrier and the ground electrode using argon as the working gas. To avoid overheating the discharge unit, a cooling system was employed. The results reported that there was no detection of significant changes in the beef jerky's fatty acid profile after RF plasma treatment of 200 W for 5 min. Upadhyay and the group [87] investigated RF plasma treatment of lipid-containing chia flour. The experiment illustrated in Fig. 5(b) employed a bell-shaped plasma reactor built from a glass tube. Two parallel stainless steel electrode discs 3 cm apart for sample plasma treatment were capacitively connected to the 13.56 MHz RF power generator. To create plasma, air (24°C) was employed to operate at a pressure of 15 Pa. The finding observed a 9% decrease in the polyunsaturated fatty acid composition of chia seed powder at 60 W for 15 min. However, undesirable TFA of 0.24% was also detected after the experiment.



(a)

(b)

Fig. 5. Drawing of various geometric configurations: (a) atmospheric pressure RF plasma, edited from [86] and (b) low-pressure RF plasma, edited from [87].

3.3. Parameters Affecting Plasma Hydrogenation

3.3.1. Effect of working gas concentration and flow rate

The gas used for the hydrogenation reaction of vegetable oils and derivatives is hydrogen. The plasma density and stability are related to the optimal carrier gas flow rate entering the system, affecting the reaction rate and the desired product. In addition to using solely pure H_2 gas, mixing H_2 with other gases is another option for the hydrogenation method. H_2 (5%) blended with N_2 (95%) for partially hydrogenated soybean oil production was carried out by Yepez and Keener [72]. 30 L of the mixed gas was added to the chamber only once for 3 min and then sealed and reacted, respectively. The results showed that the hydrogenation was very efficient, for C18:3 and C18:2 were significantly reduced to C18:1 and C18:0 within 12 h. In other investigations, variable quantities of H_2 mixed with He were studied in partial hydrogenation based on the DBD plasma regime. The higher the H_2/He ratio, the greater the atomic hydrogen formation resulting in a faster hydrogenation rate [10, 65, 76]. The varying flow rate of H_2/He mixture gas (20 - 100 mL/min) was also investigated for hydrogenation of bio-oil. The 60 mL/min gas flow rate gave the highest deoxidation rate and high heating value of refined bio-oil [88]. The use of 100% H_2 fraction without other carrier gases has also been carried out to hydrogenate fatty acid compounds. When the flow rate of H_2 into the system was different, the resulting plasma density and reaction rate were affected. The higher H_2 flow rate generated more active hydrogen radicals, providing higher plasma density and homogeneity of plasma distribution, and speeding up the chemical reactions. However, an appropriate flow rate that is not too low and not too high would provide the best effect on the reaction. Some researchers have suggested that too low a flow rate had fewer free radicals, and the resulting plasma was unstable [75]. Excessive flow rates also led to rapid species recombination, as well as species rapidly leaving the system through the outlet port, resulting in fewer hydrogen free radicals reacting with unsaturated C=C bonds [71, 76]. In addition, the use of high gas flow rates increases the production cost unreasonably. The optimal volume of the reactor (L)/H_2 flow rate (L-min^{-1}) for hydrogenating biodiesel in the studied DBD parallel system was 4 L/L-min^{-1} [63] while that for the DBD torch system was 0.35 L/L-min^{-1} [64]. For certain techniques such as microwave plasma which can generate higher density plasma than DBD plasma, the gas flow rate can be increased up to 8.5 L/min with the excess hydrogen recycled [66], and the volume of the reactor/H_2 flow rate was 0.24 L/L-min^{-1}.

3.3.2. Effect of applied input power

The applied input power presents one of the most significant variables for plasma generation affecting the hydrogenation rate. For DBD plasma, the plasma discharge power is directly proportional to the input power. Higher input power also results in higher discharge voltage, generating higher energy electrons in larger quantities, resulting in greater collision frequency with hydrogen gas molecules enhancing the effectiveness of hydrogenation. The optimal conversion of polyunsaturated fatty acid compounds into saturated ones in the DBD reactors driven by a neon transformer was reported at an applied input power of 100 W [10, 75]. According to the reports, the more input power supplied to the systems, the higher the discharge voltage resulting in larger and brighter plasmas. However, the input power of more than 100 W produced less plasma and the plasma eventually disappeared with a further increase in the input power. In addition, the increase in input power could raise the reaction temperature; e.g., a difference in input power of 50 W increased the system temperature up to 38^{o}C [75]. It was obvious that more input power supplied into the system generated more energetic species, such as electrons and quasi-stable particles, to interact with the reactant through energy transfer affecting the reaction temperature.

For the NTP technique, the input power of a particular microwave plasma system could be increased up to 500 W [66]. This is advantageous for creating a higher plasma density with more energetic electrons resulting in a higher concentration of atomic hydrogen, making it possible to treat a large amount of reactant, as well as being scalable.

3.3.3. Effect of electrode gap distance

The design of the distance between the electrodes in a DBD system is an important factor for plasma creation. Experiments with different purposes and configurations always have different optimal gap distances. For an initial plasma generation, it requires a certain distance to produce plasma, probably from 0.1 mm to the centimeter scale [89]. A smaller gap distance between electrodes produces a high-intensity electric field but with less plasma formation. However, an increase in electrode spacing also raises energy consumption. The optimal electrode spacings of parallel-plate and needle-plate geometries for hydrogenation of biodiesel were 35 and 10 mm, respectively [65, 75]. These electrode gaps resulted in the appropriate conversion of polyunsaturated FAMEs into monounsaturated and saturated ones with satisfying end product properties including the highest OS value. As reported that a too-small gap can create a spark or an arc, and a too large gap generated a lower intensity microfilament discharge to react with FAME resulting in less conversion rate. In addition, the larger the gap distance, the more energy was necessary to exceed the gas breakdown voltage to form plasma causing a lower density plasma [90]. For margarine production with DBD plasma system The length between the two electrodes was reported to be 17 mm [73]. Similar to the distance between the two electrodes, gas-filled gap is the distance between the upper electrode and the surface of the reactant. The effect of varying gas-filled gaps (1, 3, and 5 mm) on H-FAME production was examined. The research revealed that the greatest conversion rate was achieved with a 1 mm gap [10]. This study elucidated that a smaller gas-filled gap resulted in higher plasma intensity and a reduction in the distance traveled by hydrogen radicals to react with the reactant.

3.3.4. Effect of reaction temperature

For conventional catalytic hydrogenation experiments which are thermally activated reactions, the temperature is a key factor in directly increasing the catalyst activity because raising the temperature elevates the reaction speed leading to a faster reaction rate and higher conversion. This statement suggests that a similar observation applies to the electrochemical hydrogenation of soybean oil. The research has demonstrated that when the temperature is raised to 70°C , the iodine value of the oil diminishes by more than 22% [91]. On the contrary, increasing the temperature for the hydrogenation of fatty acid compounds with the plasma system may present a negative effect since it produces more *trans* isomers. In plasma systems, the key to the formation of plasma species such as dissociated and excited ones that act as catalysts is the energy transfer by electron impact [92], wherein is governed by the voltage and frequency supplied to the system. These have a greater effect on the hydrogenation rate with the plasma system than the temperature. The variation of the reaction temperature for the hydrogenation of oil and biodiesel was studied. In the parallel-plate DBD reactor revealing the results of FAME hydrogenation, the reaction temperature rose due to plasma heating, as well as the exothermic hydrogenation reaction, and remained constant at 38°C throughout the experiment, which was the optimal parameter to reduce the polyunsaturated FAMEs [10]. A similar finding was revealed in the research on the hydrogenation of vegetable oils, where the temperature increased to 50°C from DBD plasma application, which contributed to the fastest hydrogenation [73]. These results are in line with plasma hydrogenation taking place at sub-atmospheric conditions like microwave plasma. The microwave plasma increased the liquid reactant temperature until it stabilized at 30°C, which was less than that of the DBD plasma system [66]. It is not to be mistaken that microwave plasma was colder than DBD plasma. During plasma application, the temperature of the plasma applicator tube became very high and it required sufficient and continuous water circulation through the tube to effectively remove the excessive heat; otherwise, the tube could be damaged from overheating. With most of the excessive thermal energy removed via this forced convention mechanism, the resulting plasma temperature became low. On the contrary for the DBD plasma system, the reactant was the primary heat removal media.

In the same investigation on microwave plasma hydrogenation, increasing the reaction temperature to 60 – 100°C using a hotplate stirrer did not significantly increase the rate of hydrogenation. This conforms to the basic principle that exothermic hydrogenation should be performed at a lower temperature to propel the reaction forward. Also, running at too high temperatures allows for the formation of *trans* isomerization, which is undesirable for margarine production. The *trans* isomer formation as a function of temperatures during catalytic hydrogenation was investigated and the results revealed that the maximum *trans* content increased from 21.57 to 31.46% as the temperature increased from 150 to 180°C [48]. However, operating at a too low temperature, such as 20°C, not only did not enhance the reaction rate but also thickened the oil, worsening the physical contact between the plasma and the surface of the oil. A cooling system must be equipped for operating at low temperatures, which consumes energy.

3.3.5. Effect of reaction time

Determining the optimal hydrogenation reaction time should depend on the desired result or product properties. For example, H-FAME production requires consideration of the OS and cold flow properties values; the hydrogenation of vegetable oils was determined by IV and saturated/unsaturated fatty acids content; and the margarine production was determined by the texture, amount of saturated fatty acids, AV, IV, etc. For hydrogenation of soybean oil using DBD plasma based on the HVACP system (high voltage output of 90 kV), it took a maximum reaction duration of 12 h with an oil volume of 10 mL to achieve an IV of approximately 92 [72], which is suitable for pourable oil applications [4]. With this treatment time, the total saturated fatty acids level increased to 32.3% while polyunsaturated ones decreased to 41.5% with no TFA formation. For the latter study of the same HVACP system, 15 g of soybean oil was hydrogenated until some solid fractions appeared, which took 6 h of treatment time. The resulting solid fractions consisted of 22.5% saturated and 21.6% polyunsaturated fatty acids [93] with an IV of 84. The reason why the latter experiment required much less reaction time was probably because 100% hydrogen gas was used, while the previous experiment used a 5:95 mixture of hydrogen and nitrogen gas, consequently reducing the polyunsaturated fatty acids by an additional ~ 20% compared to the former research. However, the use of pure hydrogen resulted in a 2.8% increase in TFA from the conversion of the *cis* isomer since hydrogen plasma species are more reactive than nitrogen plasma [93].

Another DBD plasma system to hydrogenate palm oil for margarine production in a batch regime (25 mL) required 8 h to achieve a desired semi-solid texture comparable to commercial margarine. The final IV and TFA were reported as 36.8 and 1.44 – 5.24%, respectively [73]. Besides using the parallel-plate DBD reactors for margarine production, stainless steel needle-in-glass tube reactor similar to the plasma jet formation has also been investigated. Palm olein of 25 mL was used as a feedstock and the optimal hydrogenation time of 15 h was reported to obtain the spreadable product with an IV of 23.56 [76]. It is worth observing that this study required a much longer reaction time than the previous research [73] to obtain the appropriate texture of the product but the IV was lower. This may be due to the needle electrode being able to generate plasma only at the tip of the needle, as well as the experiment was set up with only one needle. Although the needle electrode provides a higher plasma density than the parallel-plate electrode, using a single needle requires more reaction time because the parallel-plate configuration can produce a full plate of plasma with a larger reaction surface area.

For the hydrogenation with biodiesel as a precursor resulting in H-FAME, the double carbon bonds of biodiesel are typically partially hydrogenated to improve certain properties such as OS. DBD reactors have also been used for the hydrogenation of biodiesel. Kongprawes and colleagues [10, 65] synthesized hydrogenated biodiesel and discovered that 5 and 5.5 h were the best plasma treatment durations with the maximum OS of 20 and 10 h for palm and soybean biodiesels, respectively. However, not only the composition of FAME was different for different feedstocks affecting the optimal processing time, but the varying amounts of feed biodiesel used in experiments also played a role. The hydrogenated soybean biodiesel research used 35 mL of reactant volume, while the palm biodiesel research used nearly 10 times more volume. Another geometric configuration of the DBD reactor used for the hydrogenation of biodiesel was the plasma torch, i.e., the electrode needle centered in a hollow glass tube. This configuration can deliver high-density plasma at the tip of the needle and if multiple needles are installed, the reaction rate can be increased. Kamjam et al. [75] used this design to execute the partial hydrogenation of 30 mL palm biodiesel and found that 1 h was the optimal time to enhance the OS by 10.7 h while the cloud point value (16°C) was within acceptable standards. Another study in the use of needle electrodes is the hydrogenation of bio-oil. It was found that 90 min reaction time gave the best deoxidation rate and high calorific value [94]. In addition to the widespread use of DBD systems, a microwave plasma generator was also employed for the hydrogenation of biodiesel. Wongjaikham et al. [66] found that the optimal time for the hydrogenation of 300 mL palm biodiesel to meet the standard was 3 h, which was considered less reaction time per unit volume of the reactant than the DBD plasma system due to the higher plasma density achievable in microwave plasma. Thus, microwave plasma is promising for the expansion of the production capacity.

3.4. Hydrogen Plasma Generation and Probable Mechanisms of Plasma Hydrogenation

A general principle of plasma generation is to supply an electric field (high-frequency electromagnetic field in the cases of microwave and RF discharge plasmas) to a neutral gas. The electric field transmits energy to the unbound electrons which participate in oscillation and collision with the hydrogen gas molecules, transferring some of the energy and causing bound electrons to escape from the orbital band to form a large number of free electrons. These free electrons then collide with molecules and ions in a chain reaction, generating the plasma species in the system. The plasma species comprising energetic free electrons, ions, neutral species, excited species, and photons are created which behave as reactive species to react with the studied reactants. By the electron-impact processes to form low-temperature hydrogen plasma, the excitation, dissociation, and ionization reactions according to Eqs. (1), (2), and (3) - (5), respectively, can be created throughout the application of the electric (or electromagnetic) field.

$$e^- + H_2 \rightarrow H_2^* + e^- \tag{1}$$
$$e^- + H_2 \rightarrow 2H + e^- \tag{2}$$
$$e^- + H \rightarrow H^+ + 2e^- \tag{3}$$
$$e^- + H_2 \rightarrow H_2^+ + 2e^- \tag{4}$$
$$e^- + H_2 \rightarrow H + H^+ + 2e^- \tag{5}$$

For the excitation, an electron-molecule collision forms an electronic state with an energy of 8.8 eV. The hydrogen molecule is in the excited state and subsequently decays into two hydrogen atoms with an average energy of 2.2 eV each. With the electronic energy obtaining 11.5 eV, the hydrogen molecule is activated as a second excited state (according to Eq. (1)). The molecules then return to ground level and release energy in the form of UV radiation. When the electronic energy reaches 11.8 eV, hydrogen molecules may be driven to the bound states, and then decomposes into two atomic hydrogens, each having an average energy of 2.2 eV (according to Eq. (2)). When the electronic energy reaches 12.6 eV, the hydrogen molecule can be driven to an excited state and returns to the ground state after releasing an ultraviolet photon [95].

For ionization, it occurs when the hydrogen atom/molecule is sufficiently energized. When the hydrogen atoms present in the system gain energy of 13.6 eV, ionization takes place according to Eq. (3). When molecular hydrogen is energized to 15.4 eV, the molecule is ionized according to Eq. (4). Additionally, when the hydrogen molecule is given energy of 18.1 eV, an electrolysis reaction takes place in the system according to Eq. (5), producing approximately 5 eV of energy each. When the plasma system is subjected to pressures ranging from tens to thousands of Pa, the dissociation rate is approximately ten folds greater than the ionization rate. However, the generation of H^+ requires more energy than H_2^+ , so the major ionization pathway is via the reaction shown in Eq. (4) [95].

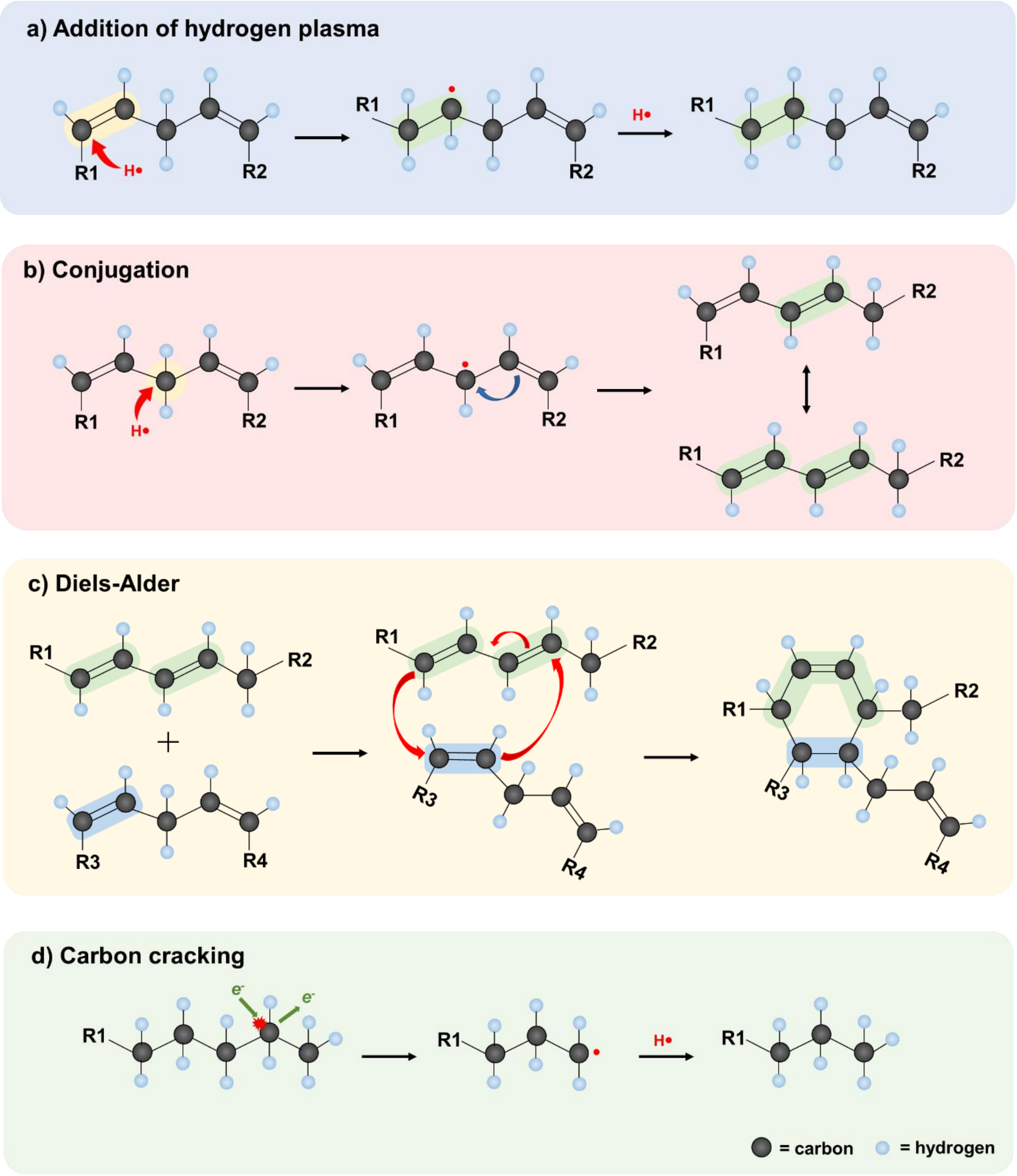


Fig. 6. Probable plasma hydrogenation mechanisms of fatty acid chains (a) addition of hydrogen plasma or hydrogenation, (b) conjugation reaction, (c) Diels-Alder polymerization, and (d) carbon cracking reaction. R1, R2, R3, and R4 indicate the remaining alkyl portions of the fatty acid or methyl ester

Table 2. Parameters and properties of synthesized products.

Feedstock	Type of catalyst/ plasma	Optimal studied parameter			Property of synthesized product				Yield efficiency	Ref.
		Reaction time/ Temperature	Input power (W)	Discharge voltage (kV)	Fatty composition (%)	IV (g I_2/100 g oil)	OS (h)	CP (°C)	(mL/J)	
Catalytic hydrogenation										
Sunflower oil	Pd/C in ultrasonic reactor	2 h 30°C	150		Sat = NS Unsat = NS *Trans* = NS	87.2 (from 141.6)	-	-	1.07×10^{-5}	[99]
Soybean oil	Pd/C in ultrasonic reactor	1 h 30°C	100		Sat = NS Unsat = NS *Trans* = NS	95 (from 135)	-	-	3.05×10^{-5}	[100]
Jatropha oil FAME	Raney-Ni in microwave reactor	30 min 85.7°C	150		Sat[a] = 19.60 Unsat = 58.70 *Trans* = 21	70 (from 101.5)	45.6	1.37	3.74×10^{-5}	[22]
Cottonseed FAME	Raney-Ni in ultrasonic reactor	40 min 80°C	180		Sat[a] = 36.33 Unsat = 52.03 *Trans* = 10.96	72.2 (from 108.7)	-	-	1.79×10^{-5}	[101]
Soybean FAME	Pd-Pt/MCM-41 (1:1)	4 h 100°C			Sat[a] = 7.35 Unsat = 52.5 *Trans* = 6.03	-	65	7	-	[102]
Palm FAME	Pd/SBA-15	4 h 100°C			Sat[b] = 51.35 Unsat = 40.54 *Trans* = 7.70	-	27.9	13	-	[103]

Plasma hydrogenation										
Soybean oil	DBD plasma (parallel plate)	12 h 60°C	200	90	Sat = 32.2 Unsat = 65.7 *Trans* = ND	91.9 (from 130)	-	-	1.16×10^{-6}	[72]
Soybean oil	DBD plasma (parallel plate)	6 h < 50°C	NS	80	Sat = 22.5 Unsat = 33.3 *Trans* = 0.3	84 (from 130)	-	-	3.79×10^{-6}	[93]
Palm oil	DBD plasma (parallel plate)	8 h 50°C	21.85	NS	Sat = 54.65[c] Unsat = 36.94[c] *Trans* = 5.24[c]	36.8 (from 60.89)	-	-	3.97×10^{-5}	[73]
Palm oil	DBD plasma torch (needle in the tube)	15 h 50°C	40	0.603	Sat = 67.22 Unsat = 31.40 *Trans* = ND	23.56 (from 60.75)	-	-	1.16×10^{-5}	[76]
Soybean FAME	DBD plasma (parallel plate)	5.5 h 58°C	2.45	NS	Sat = 52.79 Unsat = 42.50 *Trans* = 3.67	67.4 (from 128)	10	11	6.94×10^{-5}	[65]
Palm FAME	DBD plasma (parallel plate)	5 h 38°C	100	2.1	Sat = 51.85 Unsat = 43.58 *Trans* = ND	43.5 (from (50.2)	20	16	1.67×10^{-4}	[10]
Palm FAME	DBD plasma torch (needles in tubes)	1 h 90°C	100	3.36	Sat = 55.83 Unsat = 43.08 *Trans* = ND	43.8 (from 50.6)	23.5	16	8.50×10^{-5}	[75]
Palm FAME	Microwave plasma	3 h 30°C	500	NS	Sat = 61.90 Unsat = 36.40 *Trans* = ND	40.1 (from 50.2)	21.6	16	5.55×10^{-5}	[66]
Beef jerky	RF plasma (atmospheric pressure)	5 min ~ 70°C	200	NS	Sat = 45 Unsat = 44.50 *Trans* = ND	-	-	-	-	[86]
Chia flour	RF plasma (low pressure)	15 min NS	60	2	Sat = 16.54 Unsat = 80.72 *Trans* = 0.24	-	-	-	1.85×10^{-4} (g/J)	[87]

Sat: C16:0, C18:0; Unsat: C18:1-*cis*, C18:2-*cis*, C18:3; *Trans*: *trans*-C18:1;

[a] only C18:0; [b] Total saturated fatty acids; ND = Not detected; NS = Not specified;

[c] Report at a reaction time of 12 h

The resulting hydrogen plasma species can only react with the reactant at the surface; the reaction is a 2-phase system between hydrogen plasma and liquid oil. It has been reported that higher pressure can increase the solubility of hydrogen gas in vegetable oil following Henry's law [96, 97]. The report also revealed that at 50°C and atmospheric pressure, hydrogen gas can dissolve at about 0.035 mL/g-oil which is not much [96]. There is no literature report on the dissolution of atomic hydrogen in vegetable oil. Thus, it could be said that the dissolution of plasma species in vegetable oil is likely negligible. In addition, during the hydrogenation operation, adequate stirring should be provided to increase the physical contact and enhance the reaction rate. As mentioned above, dissociation takes place more than ionization. Indeed, Yepez and the group [93] reported that the stability of H^+ (proton) and H radical (hydrogen atom with one unpaired electron) are comparable. Therefore, the main species in hydrogenation plasma are atomic hydrogen or hydrogen radicals and hydrogen ions which play a significant role in any proposed process. The proposed mechanisms involved in the hydrogenation of fatty acid compounds using hydrogen plasma are presented in Fig. 6 which can be categorized into four routes as follows:

1. Addition of hydrogen plasma or hydrogenation: A hydrogen radical reacts at the π bond of the C=C position of the unsaturated fatty acid compounds which is readily reactive, and the unstable state C−C* position is incorporated with another hydrogen radical resulting in a stable single carbon bond (C−C).
2. Conjugation: Any atomic hydrogen can react with polyunsaturated fatty acid compounds (C18:3 and C18:2) at the bis-allylic position which is the most susceptible position leading to double bonds shifting. As a result, the *cis* position can be converted into the *trans* position.
3. Diels–Alder polymerization: This is a consequence of the conjugation reaction that easily facilitates polymerization when exposed to air. During conjugation formation, the unstable carbon−carbon double bonds of the unsaturated chain react with the double bonds of another chain to form a pericyclic reaction. However, under normal conditions without conjugation, the double bond is not reactive to be polymerized due to the existence of allyl hydrogens, which are effective radical traps [98].
4. Carbon cracking: In the plasma region, a large number of energetic electrons and photons are produced. These electrons and photons often possess high enough energy to break the terminal carbon−carbon single bond of the long-chain fatty acid compounds such as 18:0 into short-chain ones like C16:0. Then, the unstable cleaved hydrocarbon chain reacts with a hydrogen atom to form a stable state.

3.5. Properties of Synthesized Products by Chemical Catalysts and Plasma Catalysis

Table 2 presents a summary of the optimal conditions and product properties from selected studies on the hydrogenation of oil compounds.

Hydrogenation of fatty acid compounds is a significant process in fats and oils manufacturing because of its numerous applications, including modifying the oil's physical properties for specific uses and increasing its oxidation stability. The requirement of product properties depends on the intended use purposes conforming to international standards. From Table 2, a comparison between catalyzed hydrogenation and plasma hydrogenation, various optimal parameters such as reaction duration and temperature, including different types and amounts of feedstock, all affect the properties of the synthesized product differently. It can be seen that when using the same reactant, the catalytic hydrogenation required less time than plasma hydrogenation based on the equivalent final IV levels, and vice versa in terms of reaction temperature.

After hydrogenation, the fatty acid or methyl ester composition, IV, OS, and cloud point are related. When the carbon double bonds of unsaturated fatty acids are hydrogenated to form single bonds, the saturation fraction becomes higher. Unsaturated fatty acids are converted into saturated fatty acids; for example, C18:3 is hydrogenated into C18:2, C18:1, and C18:0, respectively. The hydrogenation time depends on the type of reactant used. The reactants with more unsaturated fatty acids composition take a longer time to react than those with less unsaturated fatty acids to obtain the same amount of saturated fatty acids. An important fatty acid formed during the partial hydrogenation process that has a negative effect is *trans* fatty acids (TFA). The primary cause of TFA formation is high-temperature processing. For the hydrogenation of vegetable oil for culinary purposes, such as the production of margarine and shortening, TFA's detrimental aspect has been reported to decrease “good cholesterol” (HDL-C) and elevate “bad cholesterol” (LDL-C). Though saturated fat is the most common dietary malefactor for raising LDL-C, TFA and dietary cholesterol also play a significant role. From Table 2, it can be noticed that the catalyzed hydrogenation of vegetable oils produces approximately 5 times more TFA than plasma hydrogenation. This is most likely due to the much lower treatment temperature of plasma hydrogenation.

The IV is an index used to indicate the unsaturation of lipid materials. It is defined as the number of grams of iodine uptake to the oil's double bond per 100 g of oil sample [104]. Oils with high IVs are highly unsaturated and have a great susceptibility to oxidation. Each type of vegetable oil has a different IV. For instance, in soybean oil, palm oil, sunflower seed oil, canola oil, and coconut oil, the IVs are 124 – 139, 44 – 55, 118 – 141, 105 – 126, and 6 – 11, respectively [105-107]. The widely used standard method for determining IV is the wet chemical method using Wijs solution by titration technique [108]. After atomic hydrogens are added to any C=C bonds of the oil, the IV decrease, enhancing thermal and oxidative stability. Hydrogenated vegetable oils with various IVs are used in many fields for different purposes, such as IVs of 70 for all-purpose shortening and 95 – 110 for pourable oil applications [4]. For hydrogenated biodiesel, IV can be issued as an indicator of polymerization. The requirement of the EN 14214 standard states that the IV should not exceed 120 g I_2/100 g-biodiesel [108]; more than that, there is a tendency for ketones and aldehydes compound formation, affecting the engine over long-term use.

The OS is one of the major parameters affecting biodiesel applications. It refers to compounds that are stable against oxidation; i.e., saturated fatty acids are stable to oxygen and do not undergo oxidation. Unsaturated compounds tend to be oxidized easily. In the production of biodiesel fuel, if the OS value is low, the fuel quality will easily deteriorate especially under long-term storage [109]. When biodiesel is oxidized, the acidity increases and results in metallic materials in contact with biodiesel, especially the fuel tank, being easily corroded. Therefore, the hydrogenation of biodiesel will improve the OS by reducing the percentage of unsaturated methyl esters. In particular, polyunsaturated esters composition such as C18:3 and C18:2 negatively affect the OS [110]. The OS can be measured using the Rancimat method performed at 110°C. The American standard (ASTM D6751) and the European standards (EN 14213 and EN 14214) prescribe the OS values of biodiesel with a minimum induction period of 3 and 6 h, respectively [111]. For Thailand from 2009 onwards, the OS of B100 (100% biodiesel fuel) was set to be at least 10 h [112] since the feedstock used for biodiesel production is mainly palm oil, which already exhibits high oxidation resistance. Comparing catalyzed and plasma hydrogenation of biodiesel, it was found that catalyst-based hydrogenation can improve the OS value more than the use of plasma. This may be due to the high selectivity of the catalyst and the better control over the hydrogenation rate.

Cold flow properties can be represented by the cloud point (CP) which is the temperature at which crystals become visible due to the formation of a cloudy suspension [113]. The fatty acid profile in biodiesel is dependent on the parent lipids. Transformation to biodiesel does not involve many composition changes. The concentration of high melting point and saturated long-chain FAMEs is the primary influence of CP. Thus, biodiesel with a high polyunsaturated fatty acid methyl esters proportion has a lower CP. Palm biodiesel contains high saturated methyl esters content leading to an average CP of 10 – 18°C [111, 114], whereas soybean biodiesel has a low concentration of saturated long-chain methyl esters providing better cold flow properties. Therefore, biodiesel derived from various oil feedstocks is suitable for use in different regions. After the hydrogenation of biodiesel, the unsaturated esters content decreases, which increases the CP value. If the resulting CP value is too high, this is unfavorable: wax crystals can form and coagulate at ambient temperatures below the CP, interrupting the fuel lines and filters and leading to problems in engine operation, as well as fuel starvation. Therefore, biodiesel both B100 and blended formulas must fulfill CP specifications of universal standards such as ASTM D 6751 (-3 – 12) or EN 14214 (≤ 16) [66]. In addition, the Economic Research Institute for ASEAN and East Asia (ERIA) recently defined the maximum CP as 16 °C. [103]. However, blending is another way to improve cold flow properties. Different countries have different blending formulas based on their usage and availability of feedstock suitable for their own country with diversified climatic conditions [8].

Yield efficiency refers to the ability of a system or product to perform its intended function using the least amount of energy possible. In other words, it is about achieving the same or better results while using less energy. Herein, it aimed to compare the yield efficiency of several plasma reactors. This efficiency can be calculated as the quantity of product divided by the energy supplied, as expressed in Eq. (6).

$$\text{Yield efficiency (mL/J)} = \frac{\text{Quantity of product (mL)}}{\text{Supplied energy (J)}} \quad (6)$$

Table 2 presents data on the yield efficiency of catalytic hydrogenation and catalytic-free hydrogenation using non-thermal plasma. The yield efficiency for hydrogenation utilizing catalysts is relatively consistent, with only minor differences observed at the level of the negative fifth power. A case study involving cutting-edge technologies, such as microwave and ultrasonic assistance with the use of a catalyst, showed that the yield efficicency was not particularly high. However, when compared to that of plasma-based hydrogenation without the aid of catalysts, it is apparent that the majority of plasma-based hydrogenation processes offers higher yield efficiency.

The yield efficiency of plasma hydrogenation is depending on the type of plasma used, as well as the configuration of the plasma reactor. Notably, even when the same type of plasma is employed, distinct yield efficiency values can be obtained. According to the data presented in Table 2, RF plasma generated in the reference [87] yields the highest yield efficiency of 1.85×10^{-4} g/J. This could be because this study only treated chia flour without hydrogenation into the substrate using low energy supply and short reaction time. However, other studies investigating hydrogenation of various raw materials found that parallel plate-type DBD plasma in the reference [10] demonstrated the highest yield efficiency of 1.67×10^{-4} mL/J. This is because the reactant flows continuously throughout the reaction process, ensuring that the hydrogen atoms thoroughly react with the precursor in less reaction time. Additionally, multi-needle DBD plasma is also effective (8.50×10^{-5} mL/J) due to the dense plasma filaments resulting in a shorter treatment time for the precursor.

Table 3. Pros and Cons of non-thermal plasma and catalytic hydrogenation.

Type of hydrogenation	**Pros**	**Cons**
Hydrogenation with catalyst	• Highly selective for reducing unsaturated fatty acids and increasing C18:1 formation • Well-controlled reaction	• Complicated catalyst preparation process • Most catalyst preparation steps require high temperatures and generate large amount of waste • Post-process separation of catalyst from product required • Most reactions carried out at high temperatures • Reaction carried out at high gas pressure, requiring equipment to withstand pressure • *Trans*-fatty acids formation during partial hydrogenation
Hydrogenation with plasma		
DBD plasma (Parallel plate)	• System easy to install and uncomplicated • Compact reactor size • Less energy consumption	• Mostly used at laboratory level • Plasma exhibits non-uniform micro discharge appearances • Product may be contaminated by electrode materials such as aluminum • Over time, plasma may cause deposition on electrodes
DBD plasma (Needle torch)	• High-density plasma • Easy to assemble • Compact reactor size	• Mostly used at laboratory level • Plasma appears like spark filament • Resulting in quite high reactant temperature • Product may be contaminated by electrode materials such as aluminum • Over time, plasma may cause deposition on electrodes
Microwave plasma	• Very high-density plasma • Can expand production capacity to industrial level • Uniform plasma • No electrode used, so no product contamination	• Expensive devices and equipment for plasma generation and control • Complex plasma generator system, requiring experienced operators • Must have microwave leakage detection and protection systems • Operate at reduced pressure, requiring vacuum system • High energy consumption

4. Positive and Negative Aspects Of Non-Thermal Plasma and Catalytic Hydrogenation

A comparison of the advantages and disadvantages of catalytic and non-thermal plasma hydrogenation processes is shown in Table 3.

The NTP technique provides more advantages over catalytic hydrogenation to produce saturated fatty acid chains derived from oils, lipids, and biodiesel because it can operate at lower temperatures and under atmospheric pressure. To scale up to a large production rate on an industrial scale, some NTP techniques such as parallel plate DBD and needle plate DBD require further configuration development to achieve higher plasma intensity for the high volume of feedstocks. Nevertheless, microwave plasma could be ready to scale up to an industrial scale. This technique requires a higher capital investment due to the expensive devices and equipment for plasma generation and control, as well as the microwave protection equipment for the safety aspect.

5. Conclusions and Future Perspectives

This article reviews the utilization of various non-thermal plasma technologies in lipid hydrogenation processes. The cutting-edge plasma technologies offer promising and reliable performances in hydrogenation, as well as relatively high energy efficiency. They can, therefore, be alternative methods with the potential to replace the conventional catalytic hydrogenation process. Several types of plasma have been investigated for the hydrogenation of fatty acid compounds, such as parallel-plate DBD plasma, DBD plasma torch, microwave plasma, and RF plasma, each of which has a different way of generating plasma. The applied strong electric (or electromagnetic) field results in the generation of hydrogen reactive species which readily react with the double bonds of carbon in the fatty acid chains. After the process, the resulting product exhibits more saturated fatty acid content and less unsaturated fatty acid content, showing greater oxidative stability. The formation of the *trans*-isomer is less than that of the traditional process, which is a very desirable discovery. The mechanism of hydrogen plasma generation as well as various possible routes involved in the hydrogenation are addressed including the addition of atomic hydrogen, conjugation, Diels–Alder polymerization, and carbon cracking. Non-thermal plasma technology is well known as a green technology because no chemicals and catalysts are used during the reaction, thereby minimizing chemical contamination as well as reducing the cost and environmental footprint of waste generation from the catalyst preparation, separation, regeneration, and final disposal processes. However, the existing plasma technology for lipid hydrogenation needs enhancements concerning the selectivity of the desired product and better cost-effectiveness.

Non-thermal plasma technology is now being applied in a hybrid plasma-catalytic chemical process either as a single-stage in-plasma catalysis or two-stage post-plasma catalysis configuration to increase the reaction rate, enhance the yield, and increase energy efficiency. In the near future, plasma technology could be developed as an integration process combined with other technologies such as photochemistry, electrochemistry and intensification; however, it still requires significant research and development from fundamental knowledge, such as understanding mechanism pathways, to design and development of the processes especially on scaling up the processes to pilot scale or industrial scale. Non-thermal plasma can also be used in other chemical processes to produce desired products or improve the properties/quality of several kinds of reactants.

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Wijittra Wongjaikham, photograph and biography not available at the time of publication.

Doonyapong Wongsawaeng, photograph and biography not available at the time of publication.

Kanokwan Ngaosuwan, photograph and biography not available at the time of publication.

Worapon Kiatkittipong, photograph and biography not available at the time of publication.

Suttichai Assabumrungrat, photograph and biography not available at the time of publication.