Production of Low Trans-Fatty Acid Margarine by Plasma Hydrogenation

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การผลิตมาการีนที่มีกรดไขมันทรานส์ต่ำด้วยพลาสมาไฮโดรจีเนชัน

น.ส.กุลนันทน์ ภูประสิทธิ์

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กุลนันทน์ ภูประสิทธิ์ : การผลิตมาการีนที่มีกรดไขมันทรานส์ต่ำด้วยพลาสมาไฮโดรจีเนชัน. (Production of Low Trans-Fatty Acid Margarine by Plasma Hydrogenation) อ.ที่ปรึกษาหลัก : รศ. ดร.ดุลยพงศ์ วงศ์แสวง

มาการีนเป็นวัตถุดิบที่ใช้กันอย่างแพร่หลายในอุตสาหกรรมอาหารและเบเกอรี่ จึงได้ทำการศึกษาโดยใช้เทคโนโลยีพลาสมาอุณหภูมิต่ำแบบไดอิเลคทริคแบริเออร์ดิสชาร์จพลาสมาในการผลิดมาการีนเพื่อไม่ก่อเกิดไขมันทรานส์ได้ประสบความสำเร็จเป็นอย่างดี ด้วยกระบวนการการผลิตแบบใหม่นี้ ไม่ใช้สารเคมีเป็นตัวเร่งปฏิกิริยาจึงเป็นมิตรต่อสิ่งแวดล้อมมาก อีกทั้งยังสามารถผลิตมาการีนได้ที่อุณหภูมิห้องและความดันบรรยากาศจึงง่ายต่อการจัดการทำให้มีต้นทุนสำหรับอุปกรณ์ที่ใช้ในกระบวนการผลิตต่ำลง งานวิจัยนี้ได้ศึกษารูปแบบกการจัดเรียงขั้วอิเล็กโทรดซึ่งแบ่งเป็น 2 แบบ ได้แก่ แบบแผ่นคู่ขนานและแบบเข็มครอบด้วยท่อแก้ว จากการทดลองพบว่าการใช้อิเล็กโทรดแบบแผ่นคู่ขนานพบไขมันทรานส์ 1.44% และอัตราการเกิดไขมันทรานส์อยู่ที่ 0.07% ต่อเปอเซนต์การลดลงของค่าไอโอดีน ซึ่งต่ำกว่าวิธีการผลิตมาการีนโดยทั่วไปที่ใช้สารเคมีเป็นตัวเร่งปฏิกิริยาและผลิตที่อุณหภูมิสูง ความดันสูงอยู่ถึง 6.12 เท่า ในขณะที่การเรียงอิเล็กโทรดแบบเข็มครอบด้วยท่อแก้วมีอัตราการเกิดปฏิกิริยาไวกว่าแบบแผ่นคู่ขนานและไม่ก่อให้เกิดไขมันทรานส์ ซึ่งเป็นจุดประสงค์หลักในการศึกษาวิจัยครั้งนี้ ดังนั้นการจัดเรียงขั้วอิเล็กโทรดแบบเข็มครอบด้วยท่อจึงเป็นรูปแบบที่เหมาะสมในการผลิตมาการีนมากว่าแบบแผ่นคู่ขนาน จากผลการวิเคราะห์เศษฐศาสาตร์โดยพิจารณาเฉพาะค่าน้ำมันปาล์ม, ค่าไฟฟ้าที่ใช้ในการผลิตพลาสมา และก๊าซไฮโดรเจนที่เกิดปฏิกิริยาไฮโดรจิเนชันนั่น ทำให้ต้นทุนในการผลิตมาการีนในแบบแผ่นคู่ขนานมีต้นทุน 1.56 ดอลลาร์สหรัฐต่อลิตร ซึ่งต่ำกว่าแบบเข็มที่ครอบด้วยท่อแก้วอยู่ถึง 8.25 เท่า เมื่อเปรียบเทียบกับราคามาการีนที่มีขายทั่วไปในประเทศไทยจะมีราคาที่ 2.40 – 4.50 ดอลลาร์สหรัฐต่อลิตรจึงถือว่ามีความคุ้มทุนในการผลิต ทั้งนี้ ต้นทุนการผลิตส่วนใหญ่มาจากค่าไฟที่ใช้ในการสร้างสถานะพลาสมา หากต้องการเพิ่มประสิทธิภาพในการผลิตสามารถทำได้โดยการออกแบบระบบการจ่ายไฟให้ได้ผลรวมของกำลังไฟฟ้าที่ใช้ต่ำลงก็จะลดต้นทุนการผลิตได้อีก

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Kunlanan Puprasit : Production of Low Trans-Fatty Acid Margarine by Plasma Hydrogenation. Advisor: Assoc. Prof. DOONYAPONG WONGSAWAENG, Ph.D.

Margarine is a widely used raw material in the food and bakery industry. A successfully novel technique for refined palm olein hydrogenation to free *trans*-fat margarine production using non-thermal dielectric barrier discharge (DBD) plasma has been demonstrated. The new green method does not use chemicals as a catalyst, thus making it extremely environmentally friendly. This also performs well at room temperature and atmospheric pressure making it easier to manage. Two-electrode arrangement patterns were studied in this research: parallel plate and needle-in-tube. The results showed that using the parallel plate electrodes, 1.44% *trans*-fat (was detected) and a trans-fat generation rate of only 0.07% per percent reduction in iodine, 6.12 times lower than conventional margarine production methods use chemicals as a catalyst, operated at high temperature and pressure. At the same time, the needle-in-tube electrode arrangement did not detect *trans*-fats and had a higher reaction rate than the parallel-plate configuration. Zero *trans*-fat is the main objective of this research study. Thus, the needle-in-tube was more suitable for margarine production by hydrogenation than the parallel-plate configuration. Production estimates were made considering only the cost of raw materials, electricity and H_2 gas. The parallel-plate DBD plasma costed 1.56 USD per liter, which was 8.25 times cheaper than the needle-in-tube DBD plasma, which costed 12.87 USD per liter. Consequently, the majority of the

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Kunlanan Puprasit

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CHAPTER 1

INTRODUCTION

1.1 Relation of the research articles

This dissertation explored innovative methods to produce *trans*-fat free margarine using the plasma hydrogenation technique. Dielectric barrier discharge plasma (DBD) is the simplest way to generate high-potential plasma that can operate at room temperature and ambient pressure. The optimal condition was obtained by studying various parameters: types of oil, hydrogen gas concentration, reaction temperature, gas-filled gap size, reaction time, electrode geometry, and cost analysis. All parameters covered the scope of the dissertation and as an outcome two papers were published. The first publication is titled "non-thermal dielectric barrier discharge plasma hydrogenation for productions of margarine with low *trans*-fatty acid formation," and the second is titled "margarine production with no *trans*-fatty acid formation by non-thermal plasma hydrogenation with needle-in-tube configuration." These publications illustrate the successful *trans*-fat free margarine production with different reaction chambers and transformer designs which are the significant parameters that directly affect the *trans*-fatty acid formation. All articles are part of the dissertation.

1.2 Background and statement of the problem

Margarine was developed with the primary purpose of being a substitute for butter since the Napoleon III era. The first margarine in 1869 consisted of beef tallow churned with milk [1, 2]. Nowadays, margarine is made chiefly from vegetable oil, including corn, cottonseed, safflower, sunflower, soy and palm, which contain unsaturated fatty acids of 75 – 90% [3] and remain in a liquid phase at an ambient temperature. To produce margarine, one must transform unsaturated fatty acids, liquid to solid or semi-solid phase depending on the purpose of use, whether it is for cooking or baking purposes. Three primary processes are used in industry to improve oil/fat properties, especially in margarine production: interesterification, fractionation and hydrogenation [1, 4]. Interesterification is a process that requires either a chemical or an enzymatic catalyst [4]. Catalysts need to be separated from the product generating wastewater, which is not environmentally friendly. The fractionation process is a crystallization process to separate species based on melting point [4] and the physical force required to increase heat and mass transfer. Many units are required in the process making it complicated and expensive to maintain. Hydrogenation is the process to study in this dissertation.

Hydrogenation is a chemical process that converts liquid oils to semi-solid or solid fats by adding elemental hydrogen across the unsaturated bond [5]. These usually required catalysts for the reaction to operate under average temperature and pressure conditions. In traditional margarine production, they use the hydrogenation process by mixing oil with an appropriate catalyst (0.01 – 0.08 % of nickel). Afterwards, a high temperature (150 – 235°C) and a high pressure (up to 3 atm) process is conducted in a pressure chamber with the presence of small hydrogen gas bubbles. This is done for about 1 – 4 h in order to achieve the IV reduction from 132 to 90 [3]. Other catalysts such as platinum, palladium and copper can also be used[4]. Unfortunately, the catalyst and the high-temperature conditions generate harmful *trans*-fatty acids, or *trans*-fat, above 50% of which are total fat, depending on the starting oil and the hydrogenation conditions. This is usually done by converting unsaturated fatty acid chains usually existing as the *cis* isomer into the *trans* isomer. The higher the hydrogenation temperature, the more formation of *trans*-fat[6, 7].

Consequently, the food industry must invent solutions to lower *trans* content. Some of these solutions include an alternative hydrogenation method; the low-temperature electrocatalytic process, which has a lower final content of less than 6% *trans*-fat [8]. It has improved margarine potential by using the different catalysts and the design of the hydrogenation reactor, such as the reactor with more distribution of H_2 at low temperature [9, 10]. More recent methods include the partial hydrogenation process in liquids oils, in which a solution of oil and solvent are bought to a super-critical state and subsequently hydrogenated with a chemical catalyst. This method produced the content of *trans* fat to less than 0.3% [11]. It means the fat or oil that uses a partial hydrogenation process has a probability of getting low TFA and is more harmless than the traditional hydrogenation process. Because the *trans* configuration of the double-bonded carbon atoms is more stable than the *cis* one, the activation energy (temperature) is required for the conversion.

Approximately 540,000 deaths annually can be attributed to the intake of industrial-produced *trans*-fatty acid. High *trans*-fat intake increases the risk of dying from a variety of causes by 34%, coronary heart disease deaths by 28%, and coronary heart disease by 21% [12]. Due to the effect on lipid levels, *trans*-fatty acids raise the blood's low-density lipoprotein (LDL) cholesterol level posing significant risk factors for: hypertension, Alzheimer's disease, and obesity[13-17]. In May 2018, the World Health Organization (WHO) asked governments to eliminate artificial *trans*-fat from the global food chain by 2023 and mentioned that removing *trans*-fat from processed foods could prevent the deaths of millions of lives every year [18]. Nonetheless, *trans*-fat is still present naturally in minute quantities in some foods such as meat, dairy products from ruminants and commonly used cooking oils.

Plasma is the fourth state of matter, an electrically conducting medium consisting of roughly equal numbers of positively and negatively charged particles.

Excited and neutral species can also be present in plasma [19]. Many methods are used to generate plasma, such as heating gas to an extremely high temperature, applying high-power microwave (typically 2.45 GHz) [19], radio frequency (RF; typically 13.56 MHz) [20], electron beam or high voltage to a plasma chamber containing gas at a pressure substantially less than 1 atmosphere. Plasma can also be generated at atmospheric pressure with ambient temperature by the dielectric barrier discharge(DBD) plasma process[21]. The DBD plasma system consists of two high voltage electrodes separated by a dielectric material. The electrodes connect to a high voltage, high-frequency power supply to pass the alternating electric current through a working gas (such as H_2) to generate a plasma phase [21]. Energetic electrons in the plasma will collide with gas molecules, generating excited species and free radicals, which are chemically-active species [21]. When atomic hydrogen is in physical contact with unsaturated bonds of fatty acids, hydrogenation should occur similar to catalyst-based hydrogenation at high temperature and high pressure [22-24]. Applying parallel-plate and needle-in-tube DBD plasma to a liquid usually results in a slight temperature increase because the temperature of this non-thermal plasma is low.

In the present study, the novel application of the non-thermal, parallel-plate DBD plasma for hydrogenating vegetable oils at atmospheric pressure and near room temperature without using a catalyst to produce margarine with the absence of *trans*-fatty acid formation was proposed.

1.2 Objective

To produce low *trans*-fats margarine by hydrogenation of vegetable oil using non-thermal plasma.

1.3 Scope of the study

1) Margarine production using DBD plasma

2) Margarine production from soybean oil and refined palm olein cooking oil feedstocks

3) Studied parameters are as follows:

- H_2 concentration: 5 - 100%
- Reaction temperature: 30, 50, 80 and 100 °C
- Reaction time: 2 – 20 h.
- Electrode geometry

4) Perform production cost analysis

1.4 Expectation

1) Obtain the new and environmentally-friendly technology to produce low *trans*-fats margarine using DBD plasma at low temperature and atmospheric pressure without a catalyst.

2) The plasma hydrogenation technique will exhibit low cost and offer the possibility for industrial-scale applications.

CHAPTER 2

LITERATURE REVIEW

2.1 Margarine

Margarine was first invented by a French chemist in 1869 following Napolean III's request to seek for a low-cost substitute for butter for his armies and French workers, and this firstly-invented margarine composed of beef tallow and milk [2]. Nowadays, margarine, made from vegetable oils, has been considered as a cheap substitute to butter, which is made from animal milk. Margarine is a water-in-oil emulsion containing at least 80 w% fat. Fats and oils are one of important ingredients for the food industry. Vegetable oils, which contain unsaturated fatty acids of 75 - 90%[25] are liquid at room temperature, while fats, which have high content of saturated fatty acids, are solid at room temperature. Thus, to produce margarine, vegetable oil must be modified to become solid or semi-solid, depending on the desired final functionalities. There are three main processes that have been used by the edible oils industry to harden oils to desirable degrees, which are hydrogenation, interesterification and fractionation [4].

2.2 Hydrogenation

The melting point of vegetable oils can be increased by undergoing the hydrogenation process to transform liquid vegetable oils into solid/semi-solid fats [26]. During the traditional hydrogenation process, oil mixed with an appropriate catalyst such as 0.01 – 0.08 % nickel is heated to high temperature (150 – 235°C) and high pressure (up to 3 atm) [27, 28] in a pressure chamber in the presence of small hydrogen gas bubbles. Other catalysts such as platinum, palladium and copper can also be used [4]. About 1 – 4 hours is required to achieve a reduction in the iodine value (an indicator of unsaturation degree of oil) from 130 to 90 [27, 28] the typical value of commercial partially hydrogenated soybean oil. Under this harsh condition, hydrogen gas will be dissociated to form hydrides on the catalyst surface and each hydrogen atom will be incorporated into the double bonds of the unsaturated fatty acids, which are split up on the catalyst surface, turning them into single bonds and resulting in a partially hydrogenated oil (PHO) [29]. Vegetable shortening and margarine are good examples of PHOs. Hydrogenated oils, which have good properties for culinary purposes, are easy to use, inexpensive to produce, and are cheap alternatives to animal fats. The reduced number of the double bonds also results in a long shelf life, reheating stability, desirable textures of baked products as well as less susceptibility to oxidation, hydrolysis, and polymerization [27]. The level of hydrogenation can be controlled to produce desirable properties of finished products [28]. However, complete hydrogenation is not desirable since the product will be too solid at room temperature and not suitable for culinary purposes. After the hydrogenation process, citric acid is added to eliminate nickel soaps as well as bleaching and deodorizing [30]. The hardened oil must also be re-refined to remove the catalyst in the oil.

Unfortunately, the catalyst and the high temperature condition required for traditional hydrogenation inevitably results in the formation of the harmful trans fatty acids (TFAs, conventionally called trans fats) [31, 32] by conversion of unsaturated fatty acids normally existing as the cis isomer into the trans isomer. The higher the hydrogenation temperature, the more formation of trans-fat [25]. This is because the trans configuration of the double bonded carbon atoms is actually more stable than the cis one, and an activation energy (temperature) is needed for conversion. Trans fatty acids tend to raise LDL cholesterol and lower HDL cholesterol [33], which pose significant risk factors for cardiovascular diseases (heart disease and strokes), diabetes, high blood pressure, Alzheimer's disease and overweight, for example. The United States Food and Drug Administration (US FDA) estimates that by replacing partially hydrogenated fatty acids with saturated, cis-mono- or poly-unsaturated fatty acids, about 1,180 – 7,510 coronary events and 490 – 3,120 deaths from heart diseases can be prevented each year [34]. Eventually, in June 2015, the FDA has removed PHOs from the list of safe foods [34]. The World Health Organization estimates that if the trans fat is eliminated from the food industry worldwide by 2023, about 10 million lives could be saved. (Trans fat is still present naturally in some food such as meat, dairy products from ruminants and repeatedly used cooking oil.) Figure 1 demonstrates the cis and trans isomers.

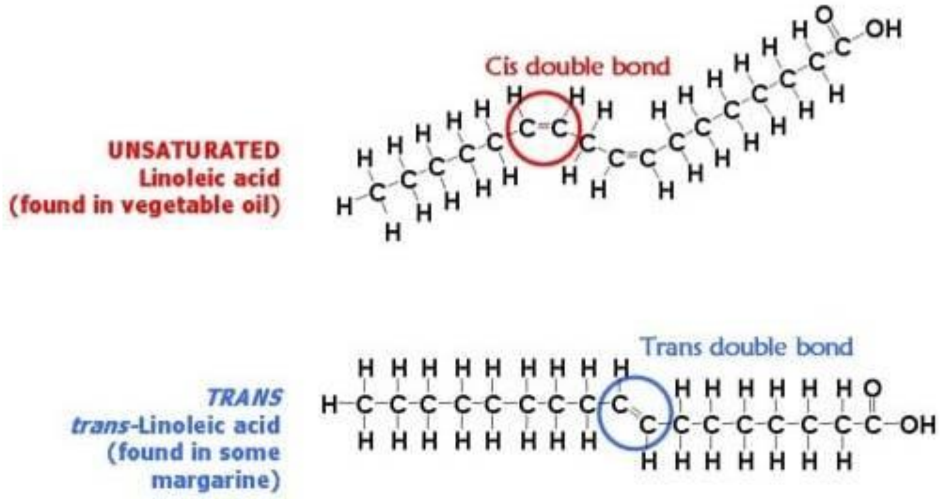

Figure 1 Cis and trans isomers

Source: https://www.healthline.com/nutrition/why-trans-fats-are-bad#section1

2.3 Plasma and basis properties

Plasma was discovered by Sir William Crookes in 1879. Most people realize that there are three states of matter: solid, liquid, and gas. However, when the gas is heated adequately (~ 24,000 °C) that the atoms collide with each other and knock their electrons off, a plasma is formed, so the plasma is regarded as the “fourth state of matter”[35]. The states of matter related to temperature and energy are shown in Fig. 2.

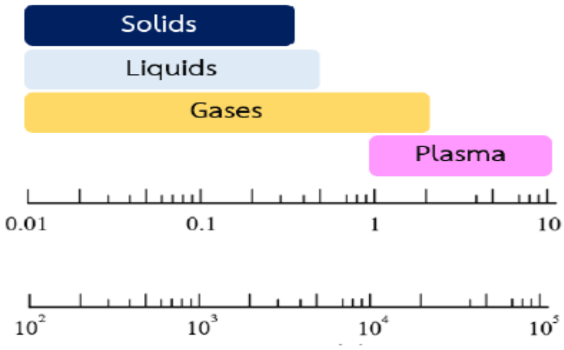

Figure 2 The physical states of matter including solid, liquid, gas and plasma [36]

To generate plasma, the gases should receive the energy that is higher than the ionization energy of those gases to strip an electron away from atoms or molecules. Figure 3 demonstrates the first ionization energy of elements which is different in atomic number. The plasma state consists of free electrons, positive ions and excited species with the number of positively charged ions approximately equal to negatively charged electrons. About 99% of the matter in the universe is in the plasma state. For instance, naturally occurring plasmas are lightning, northern lights, nebulae and the sun. The following is interesting properties of plasma

- Plasma can react to electromagnetic fields and conduct electricity, for it consists of charged particles. However, most gases in plasma are electrical insulators.
- Plasma has an uncertain shape or volume.
- When plasma gets exposed to a magnetic field, it may assume structures, including layers, filaments, and beams as can be obviously observed in plasma ball.

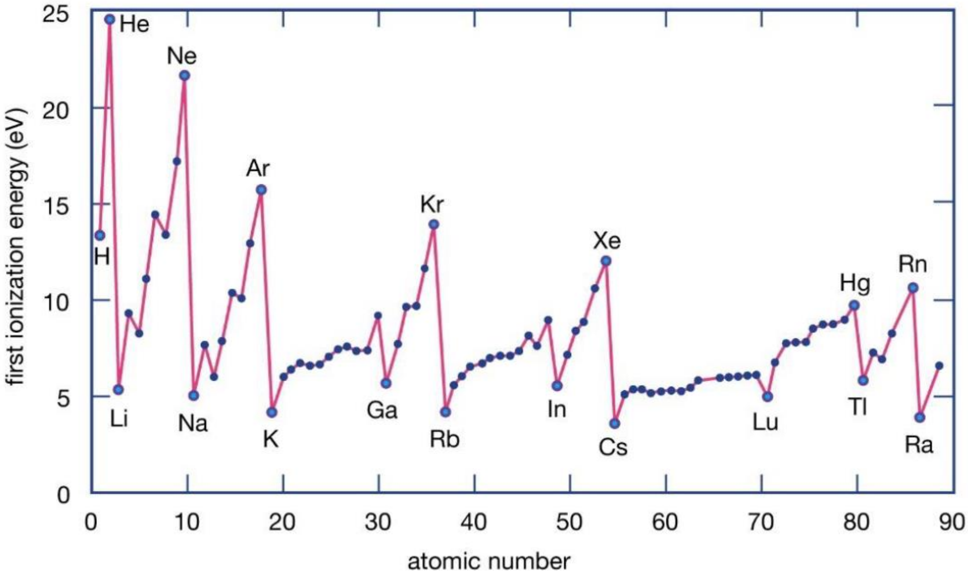

Figure 3 Ionization energy of different elements[37]

In general, the plasma density is about 107 – 1020 number of species/cm3. One of the important factors is the degree of ionization. This value refers to the fraction of the number of electrons (ne) to the total number of atoms or molecules (nt) as presented in eq.(1). In addition, the degree of ionization varies in line with temperature when pressure is constant[25]

$$\propto = \frac{n_e}{n_t} \qquad (1)$$

The gases fed to generate plasma will be excited and ionized, the following presents the ionization process of hydrogen [38].

When the hydrogen is in molecules (H_2), there are two types of ionization process:

1) $H_2 + e^- \rightarrow H_2^+ + 2e^-$ 15.37 eV (2)

2) $H_2 + e^- \rightarrow H^+ + H + 2e^-$ 18 eV (3)

To produce atomic hydrogen directly from hydrogen molecule, the energy needed to add into the system should be over 15 eV. As for atomic hydrogen with a proton and electron, the energy required to remove the electron from a hydrogen atom in the ground state is

3) $H + e^- \rightarrow H^+ + 2e^-$ 13.6 eV (4)

2.3.1 Types of plasma

Types of plasma can be widely divided into three types: Low-pressure non-equilibrium, atmospheric pressure non-equilibrium and high-current equilibrium plasma.

Low-pressure non-equilibrium plasma

The operating pressure of this type is in the range of 10–2 to 10–3 mbar by using pumping down to reduce the pressure to eliminate the air gas and then the gases used to generated plasma were flowed into the system by Mass Flow Controller with stable condition. Finally, the plasma will take place at operating power with high frequency generator and setting conditions. This plasma type is appropriated to apply to works that need well controlled and reproducible technique[39]

Atmospheric pressure non-equilibrium plasma

Most plasma forms are atmospheric pressure plasma such as corona discharges, it should be performed in a very small inter electrode spacing about -1 mm; dielectric barrier discharges known as DBD plasma, there is dielectric material covered between two high voltage electrodes; glow discharge, it is the stable discharges produced in He, Ar or N_2; atmospheric pressure plasma jet (APPJ) and so on. The utilizations of this plasma involve the medical or industrial equipment sterilization, surface modification, surface of film treatment, water treatment, surgery [39].

High-current equilibrium plasma

Equilibrium plasma refers to hot plasma. This plasma occurs at high temperature, so it is utilized in arc welding, electric arc melting, DC arc furnaces, nuclear fusion electricity production, applications in space, plasma torch, arc gas heaters etc [39].

2.4 Dielectric barrier discharge plasma

Dielectric Barrier Discharge (DBD), also known as barrier discharges or silent discharges, has been used in numerous industries especially applying to ozone generation and in CO_2 laser, excimer lamps which are the recent development. The DBD is non-equilibrium or cold plasma that can be generated at atmospheric pressure; in addition, the design and the construction of this plasma system are not complicated compared to other techniques that need low or high pressure to operate. The geometry, operating conditions and materials of DBD can be adjusted. Importantly, many works using DBD in laboratory scale have the possibility to establish in commercial scale.

Typically, the electrodes configuration of DBD plasma is in planar and cylindrical pattern as shown in Figure 4 The system can have one or two dielectric boundaries. A discharge is similar to the discharge operated in between two conductive materials: metal electrodes; however, the DBD cannot be supplied the power with DC voltages because it needs the alternating electric field to force the moving of currents. The designing and matching of the DBD configuration to the power supply should be considered carefully due to its limitation of current properties. As for the DBDs current, the sinusoidal, square-wave currents between line frequency and microwave frequencies or with special pulsed waveforms are the signal sources to generate the current of the DBD. In the cases of use on a large scale, the operating frequencies of power supply should provide in the ranges of 0.5-500 kHz [35]

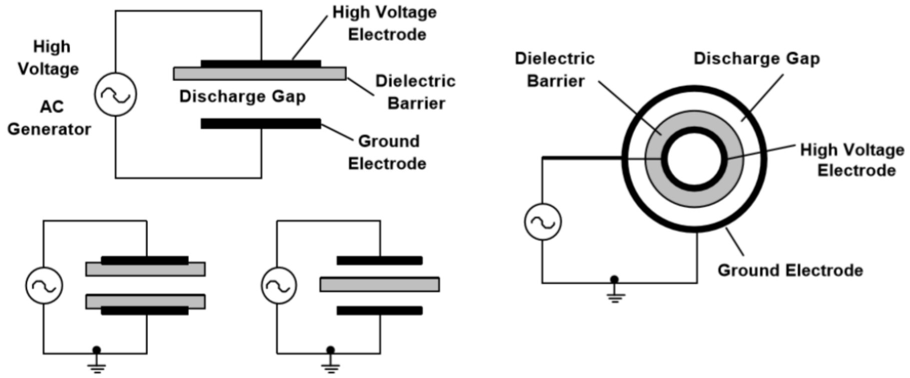

Figure 4 The electrode configuration of DBD [40]

2.4.1 Filamentary dielectric-barrier discharges

When the gases decompose in a small gap of DBD electrodes at atmospheric pressure, the phenomenon called “microdischarge” occurs. Once the spacing between two electrodes gets the high voltages with sufficient energy to drive the ionization of gases, the electrons generated in the system will be accelerated in an electric field to increases their energy until equal to, or more than that in ionization energy of gases. As long as the high voltage has been supplied to the system, the ionization by electron has still taken place that causes the increase of energetic electrons. Since the speed of electrons is faster than that of ions, they can reach an anode electrode in a nanosecond, while the ions are still in the gap between electrodes. There is the internal electric field between electrons and slow ions that influences the reduction of electric field and then the current filament or microdischarge is formed [40, 41] Figure 5 demonstrates microdischarge in atmospheric air plasma for 20 ms. There are experiments that study on microdischarge properties. Table 1 shows the air discharge parameters in 1 mm electrode gap

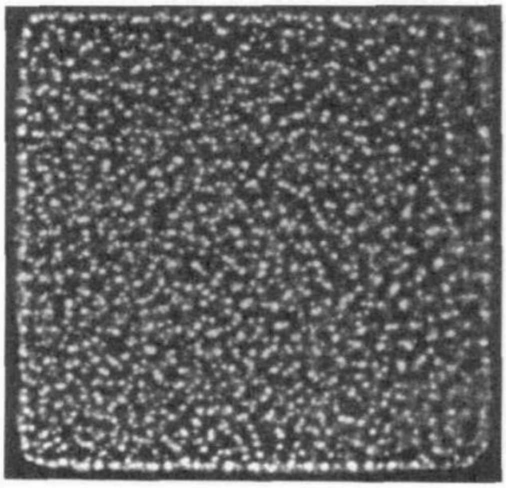

Figure 5 Microdischarge in air plasma with the exposure time 20 ms [41]

Table 1 The parameter of microdischarge properties[40]

Parameter	Value	Parameter	Value
Duration (s)	10^{-9}-10^{-8}	Total Charge (C)	10^{-10}-10^{-9}
Filament radius (m)	~10^{-4}	Electron density (m^{-3})	10^{20}-10^{21}
Peak current (A)	0.1	Mean electron energy (eV)	1-10
Current density (A/m^2)	10^6-10^7	Filament temperature	~average gas temperature in the gap

Dielectric barrier discharge configuration can generate homogenous diffuse discharges at atmospheric pressure, but it is complicated and tricky to control the homogeneous glow discharges because of many reasons: the changes of electrode pattern or some parameters of applied voltages can be the cause that filamentary discharge mode changes to be more stable.

2.5 Advantage and limitations of plasma technology applied to chemical reaction

A novel method for partial hydrogenation of vegetable oils without the formation of the harmful trans fatty acids is proposed. The technology to be used is the atmospheric pressure and low temperature dielectric barrier discharge (DBD) plasma torch, which does not require the use of a catalyst. A DBD plasma stream can be generated with minimum effort and requires low power to operate. Moreover, spray nozzles will be installed to generate tiny oil droplets to increase the surface contract with plasma to significantly increase the reaction kinetic.

If a mixture of hydrogen and helium gases are used to generate DBD plasma, hydrogen atoms (which are free radicals), among other species, will be generated. When the generated plasma physically contacts vegetable oil, the highly chemically-active hydrogen radicals should hydrogenate the double bonded carbons, achieving hydrogenation. Without the use of a catalyst and the near room temperature of the plasma, the cis isomer will not be converted into the trans isomer.

This environmentally-friendly hydrogenation process using DBD plasma torch is not complicated, non-energy intensive, low maintenance and low cost. This prototypical system could ultimately lead to commercial applications for large-scale hydrogenation facility for the food industry in the future. Moreover, this research supports the “Food for the Future” industry in Thailand’s 10 target industrial groups.

Table 2 compares the expected benefits of the proposed hydrogenation process using the DBD plasma torch to the conventional hydrogenation, interesterification and fractionation processes (some information will be explained in more detail later in the Preliminary Hydrogenation Study section).

Table 2 Expected benefits of the proposed hydrogenation process using DBD plasma torch compared to conventional hydrogenation, interesterification and fractionation processes

Aspect	Proposed hydrogenation process using DBD plasma torch	Conventional partial hydrogenation	Interesterification	Fractionation
Trans fatty acids formation	None	Substantial	None	None
Saturated fatty acid formation	Some	Some	Substantial	Substantial because needs to be followed by interesterification
Catalyst required	No	Yes	Yes	No, but needs to be followed by interesterification which uses catalyst
				Friendly, but needs to be

Environmental aspect	Very environmentally-friendly. No catalyst required. No wastewater and no oil loss	Friendly	Produces waste water and results in oil loss	followed by interesterification
Safety	Poses low risk level of high voltage (can easily be insulated and protected). Atmospheric condition, no possibility of explosion.	High T and high P conditions	Catalysts very reactive and must be handled with extreme care. Catalyst in contact with water can explode.	Safe, but needs to be followed by interesterification
Economics	Preliminary economic analysis reveals that the proposed technique requires up to 50% less energy compared to the current process.	---	---	---

The following summarizes the positive aspects of the proposed hydrogenation process using DBD plasma torch:

- Very environmentally-friendly
- Plasma acts as an effective catalyst. No physical catalyst is required.
- No catalyst separation/recycling after the process. No wastewater
- Reaction can proceed at slightly above room temperature
- System not complicated, easy operation and low maintenance
- Not capital-intensive
- Not energy-intensive
- Operating costs expected to be low
- All components of the system available domestically
- Could lead to commercial applications for large-scale hydrogenation facility for the food industry in the future

The limitations:

- Difficult to control the reaction mechanism
- Difficult to prevent continuing reactions due the action of highly energetic electrons
- Difficult to control the bonds that will be excited or ionized

2.6 Literature Review

Extensive literature review found only one publication that is directly related to plasma hydrogenation of vegetable oil as follows.

Ximena V. Yepez et al[25]. studied high-voltage atmospheric cold plasma (HVACP) hydrogenation of soybean oil without formation of trans-fatty acids. Their HVACP system is essentially a DBD system which can generate high voltage output of up to 130 kV at 60 Hz. The experiments were performed at 90 kV with the power setting of 200 W. In their setup, 2 electrodes are separated 52 mm apart with two dielectric sheets between. A container of 10 mL soybean was placed on one dielectric sheet. Soybean oil was exposed to hydrogen and nitrogen plasma at room temperature and the treatment reduced the iodine value from 133 to 92 over a period of 12 hours. The reduction in the iodine value was similar to the traditional soybean oil hydrogenation process. Moreover, saturated fatty acids increased by 12% and unsaturated fatty acids decreased by 16.2%. Trans-fatty acids were not detected. It was explained that atomic hydrogen is likely responsible for hydrogenation. The authors noted that because there was no need for pressure, elevated temperature or catalyst, the process requires up to 50% less energy compared to the current process. It was also noted that the production speed is low, and the reaction kinetic must be improved.

The present proposal differs and is a significant improvement to the work of Ximena V. Yepez et al. on the following aspects as shown in Table 3 (some information will be explained in more detail later in the Methodology section and the Preliminary Hydrogenation Study section).

Table 3 Comparison of the present proposal to the work of Ximena V. Yepez et al.[25]

Aspect	This proposal	Ximena V. Yepez et al.
Plasma generation technique	DBD plasma torches	DBD plasma generated between two parallel electrodes.
Plasma contact	Will use DBD plasma torches to blow plasma stream into oil and use spray nozzles to spray oil droplets onto plasma. This	The oil remained still in the reaction chamber. Plasma only contacted with the

	plasma generating method will also produce plasma covering the entire surface of the oil. These effects will greatly enhance the oil-plasma contact area and should significantly increase the reaction kinetic.	stationary oil surface.
Adjustment of high voltage frequency	With the proposed DBD power supply, the frequency of the high voltage output can be adjusted as desired. A higher frequency than 60 Hz will generate DBD plasma more effectively and efficiently.	Fixed line frequency (60 Hz)
High voltage level	Up to 15 kV (maximum output of the neon sign transformer). At this voltage, a DBD plasma stream can be easily generated. This poses lower risk of electrical shock as well as lower equipment cost to handle high voltage.	90 kV

Temperature	The hot plate stirrer under the oil container will allow temperature control of the oil. Also, during the preliminary experiment (discussed later in the Preliminary Hydrogenation Study section), this plasma generating technique heated up the oil only slightly (37°C). Low temperature ensures no trans-fat formation and preserves the oil quality and nutrients.	Treatment of 2 hours showed an increase in temperature up to 60°C
Safety	The plasma torch with a free-standing copper wire at the end is a very safe design. Even if someone touches the end of the free-standing copper wire, the person will not be electrically connected to the high voltage wire.	The designed parallel-plate DBD plasma reactor required a very high voltage to generate plasma because of the large separation distance between the electrodes. Thus, a highly-dangerous voltage was present.
Power requirement	Preliminary study indicated that <u>treatment of 10 mL of oil required power of only 40 W</u>. If	<u>200 W to treat 10 mL of oil</u>

Hydrogenation efficiency	10 L of oil will be treated in one time, it should require 40 kW of power. This is a significant improvement over Ximena V. Yepez et al.’s work and should be easily adoptable to the industrial scale. Preliminary study indicated that the acid value of soybean oil was reduced to 63 and 65 for the hydrogenation temperature of 37 and 80°C, respectively, for the treatment time of only 4 hours. (The lower the iodine value, the better in terms of hydrogenation efficiency.)	Achieved the iodine value of 92 over the hydrogenation period of 12 hours

CHAPTER 3

Non-Thermal Dielectric Barrier Discharge Plasma Hydrogenation for Production of Margarine with Low *Trans*-Fatty Acid Formation

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Abstract

A novel technique for refined palm olein hydrogenation with very low *trans*-fatty acid formation using non-thermal dielectric barrier discharge (DBD) plasma with parallel-plate configuration has been successfully demonstrated. This green technique does not require catalyst and is highly environmental-friendly. With 15% H_2: 85% He mixed carrier gas concentration ratio and initial 31^{o}C (rising to 50^{o}C due to plasma), after 4 h of plasma hydrogenation, iodine value (IV) was reduced from 60.89 to 48.39 and detected *trans*-fat was 1.44%. This represents *trans*-fat generation rate of only 0.07% per % decrease in IV, which is about 6.12 times lower than a conventional method relying on high temperature, high pressure and catalyst. About 8 h was required to produce margarine with texture closest to commercial margarines. Acid value (AV) reduced from 0.47 to 0.27%, or 43% reduction, after 12 – 20 h of treatment, significantly indicating that plasma hydrogenation can also help extend shelf life of oil or margarine. Large portion of DBD plasma hydrogenated refined palm olein can, thus, be mixed with palm olein and interesterified palm olein to produce margarine with overall *trans*-fatty acid content no higher than regulatory requirement. Continuous production scheme was presented. This novel plasma hydrogenation technique offers promising possibility for commercial utilization by edible oils industry.

Keywords: Margarine; *Trans*-Fatty Acid; Dielectric Barrier Discharge Plasma; Hydrogenation

3.1 Introduction

Margarine was first invented by a French chemist in 1869 following Napolean III's request to seek a low-cost substitute for butter for his armies and French workers, and this firstly-invented margarine composed of beef tallow and milk [2]. Nowadays, margarine made from vegetable oils has been considered as a cheap substitute to butter, which is made from animal milk. Vegetable oils, which contain unsaturated fatty acids of 75 – 90% [3], remain liquid at ambient temperature while fats, exhibiting high saturated fatty acids content, exist in a solid state. Thus, to produce margarine, vegetable oil must be modified to become solid or semi-solid, depending on the desired final functionalities. Three main processes have been used by the edible oils industry to harden oils to desirable degrees: hydrogenation, interesterification and fractionation [1, 42].

The hydrogenation of oils is the addition of hydrogen atoms to unsaturated bonds to produce a more saturated group with the triglycerides resulting in modification of the chemical and physical properties of oils; for example, the room-temperature texture can become firmer, hard or even brittle [27]. The saturated triglycerides also increase the oil melting point [15]. During the traditional hydrogenation process, oil mixed with an appropriate catalyst such as 0.01 – 0.08 % of nickel is heated to a high temperature (150 – 235°C) and a high pressure (up to 3 atm) in a pressure chamber in the presence of small hydrogen gas bubbles, and about 1 – 4 h is required to achieve the IV reduction from 132 to 90 [3], the typical value of commercial partially hydrogenated soybean oil. Other catalysts such as platinum, palladium and copper can also be used [42]. Under this harsh condition, hydrogen gas is dissociated to form hydrides on the catalyst surface. Hydrogen atoms are incorporated into the unsaturated fatty acid chains, altering the chemical structure of the oil, to convert them into simple bonds [27]. Vegetable shortening and margarine are good examples of partially hydrogenated oil (PHO). Hydrogenated oils, which have good properties for culinary purposes, are easy to use, inexpensive to produce and are cheap alternatives to animal fats. The reduced number of the unsaturated bonds also results in long shelf life, reheating stability, desirable textures of baked products, as well as less susceptibility to oxidation, hydrolysis and polymerization [27]. The degree of hydrogenation can be varied to produce desirable properties of finished products. However, complete hydrogenation is not desirable since the product is too solid at room temperature and not suitable for culinary purposes. After the hydrogenation process, citric acid is added to extract nickel soaps as well as to bleach and deodorize [15]. The hardened oil must be re-refined to remove the catalyst present in the oil.

Unfortunately, the catalyst and the high-temperature condition required for traditional hydrogenation inevitably generate harmful *trans*-fatty acids (TFAs, conventionally called *trans* fats) by conversion of unsaturated fatty acid chains normally existing as the *cis* isomer into the *trans* isomer. The higher the hydrogenation temperature, the more formation of *trans*-fat [6]. This is because the *trans* configuration of the double-bonded carbon atoms is more stable than the *cis* one, and the activation energy (temperature) is required for the conversion. *Trans*-fatty acids (*trans*-fat) raise the low-density lipoprotein (LDL) cholesterol level, posing significant risk factors for cardiovascular diseases, hypertension, Alzheimer's disease, and overweight [13-17], for example. In May 2018, the World Health Organization (WHO) asked governments to eliminate artificial *trans*-fat from the global food chain by the year 2023 and mentioned that removing *trans*-fat from processed foods could protect almost millions of lives from heart attacks and related death every year [18]. Nonetheless, *trans*-fat is still present naturally in minute quantities in some foods such as meat, dairy products from ruminants and repeatedly used cooking oil.

Plasma consists of a mixture of electrons, ions, excited molecules/atoms and neutral gas[19]. Plasma can be artificially generated by several means such as heating gas to extremely high temperature or applying high-power microwave (typically 2.45 GHz)[20], radio frequency (typically 13.56 MHz) [20], electron beam or high voltage to gas at reduced pressure substantially less than 1 atm. Plasma can also be generated and maintained with minimal effort under atmospheric pressure and near ambient temperature by the process called parallel-plate dielectric barrier discharge (DBD), where plasma is produced at the space between two electrodes separated by a dielectric material, which is responsible for a self-pulsing operation [43] with a high voltage, high-frequency electrical power. Energetic electrons in the discharge filaments generated in the gap between the dielectric barrier and the electrode make a collision with gas molecules generating plasma. If the gas in the gap contains hydrogen, atomic hydrogen, which is a very reactive free radical, could be generated [21]. When atomic hydrogen is in physical contact with unsaturated bonds of fatty acids, hydrogenation should occur similar to catalyst-based hydrogenation at high temperature and high pressure [22-24]. Applying parallel-plate DBD plasma to a liquid usually results in a small temperature increase because the temperature of this non-thermal plasma is low.

There has been only one reported study on cold plasma hydrogenation of edible oil pioneered by Ximena V. Yepez et al [3]. High-voltage atmospheric cold plasma (HVACP) hydrogenation of soybean oil without the formation of *trans*-fatty acids was investigated. The HVACP system was essentially a DBD system that can generate high voltage output of up to 130 kV at 60 Hz. The experiments were performed at 90 kV with the power setting of 200 W. In the setup, two electrodes were separated 52 mm apart with two dielectric sheets in between. A container of 10 mL soybean oil was placed on one dielectric sheet. Soybean oil was exposed to hydrogen and nitrogen plasma at room temperature and the treatment reduced the IV from 133 to 92 over a period of 12 h. The reduction in the IV was similar to the traditional soybean oil hydrogenation process. Moreover, saturated fatty acids increased by 12% and unsaturated fatty acids decreased by 16.2%. *Trans*-fatty acids were not detected. It was explained that atomic hydrogen was likely responsible for the hydrogenation. The advantage of this process was no need for high pressure, elevated temperature, or a catalyst, requiring up to 50% less energy compared to the current process. However, the production speed was low and the reaction kinetic would need to be improved.

In the present study, the novel application of the non-thermal, parallel-plate DBD plasma for hydrogenating vegetable oils at atmospheric pressure and near room temperature without the use of a catalyst to produce margarine with very low *trans*-fatty acid formation was proposed. The present study used a high voltage, high-frequency power source of much lower power (10 kV maximum open-circuit voltage and 30 mA maximum closed-circuit current) than the research pioneered by Ximena V. Yepez et al. [3], presenting a simpler, safer and more economical system. The effects of vegetable oil type, H_2: He mixed carrier gas concentration ratio, temperature and reaction time were explored. Two types of vegetable oil, i.e. refined palm olein and soybean oil, were studied. Refined palm olein is the most used type of cooking oil in Thailand. Palm olein or a mixture of palm olein and coconut oil has been the main feedstock for margarine production in the country. Soybean oil has been the main starting material for hydrogenation in other countries [44], so it was also chosen for the study. Soybean oil is also used abundantly in Thailand, but not as much as palm olein because of its higher price. The main outcome of the research is a novel production method of healthier margarine, and the knowledge gained from this research will benefit the global society.

3.2 Materials and methods

3.2.1 Chemicals

Two types of vegetable oil, refined palm olein cooking oil and soybean oil, were studied. Fresh refined palm olein of Morakot brand was obtained from a local department store in Bangkok, Thailand. Soybean oil of Morakot brand was obtained from the same department store. They were directly used from the retail bottles without any treatment or purification. H_2 and He gases were of UHP (Ultra High Purity) grade. For determination of IV, the following chemicals of analytical reagent grade were used: cyclohexane obtained from Loba Chemie Pvt., Ltd., sodium thiosulfate 5-hydrate purchased from KEMAUS, potassium iodide obtained from Ajax Finechem, and a starch solution made from corn starch of Superfine brand obtained from a local department store in Bangkok, Thailand. For the determination of AV, the following chemicals of analytical reagent grade were used: diethyl ether obtained from RCI Labscan, ethanol and potassium hydroxide obtained from KEMAUS and phenolphthalein obtained from Ajax Finechem.

3.2.2 DBD plasma reactor system set-up

A non-thermal parallel-plate DBD plasma hydrogenation chamber was constructed with the drawing illustrated in Fig.6. The DBD plasma system comprises of two high voltage electrodes made from aluminum plates connected to the output of a high voltage, high-frequency power supply. The power supply was an adjustable neon sign transformer of Cool Neon brand, model NG.B410ET1, with the maximum output of 10 kV and 30 mA at 25 kHz (fixed frequency). The upper electrode was installed inside an 800 mL reaction chamber made of clear borosilicate glass with the thickness at the bottom of the glass chamber of 3 mm. A glass dielectric plate of 2 mm in thickness was attached to the oil-facing side of the electrode. The lower electrode was placed underneath the reaction chamber on top of a hot-plate stirrer to provide stirring of the oil in the chamber as well as temperature increase if required. The upper electrode with the attached dielectric plate was raised 12 mm from the bottom surface of the reaction chamber to provide space for vegetable oil in the chamber. The oil volume for each run was 25 mL, measured in a 50-mL graduated cylinder as follows. After the oil was slowly poured into the graduated cylinder and after entrained air bubbles floated to the surface, more oil was gradually added until the required volume was reached. The oil was slowly poured into the reaction chamber and a few minutes were allowed for the oil sticking to the graduated cylinder surface to fall to the reaction chamber as much as possible. Without stirring the oil, the gap distance between the glass plate and the surface of the oil was 5 mm and the total spacing between the two electrodes was 17 mm. As 800 rpm of magnetic stirring was applied to every run, the oil surface became wavy and the gap size fluctuated all the time. The H_2/He gas mixture was admitted into the chamber at the top with the total flow rate of 800 mL/min for every run controlled by mass flow controllers. A thermocouple was installed to allow temperature observation. To condense any oil vapor leaving the system with the exiting gas, a condenser cooled by tap water was installed.

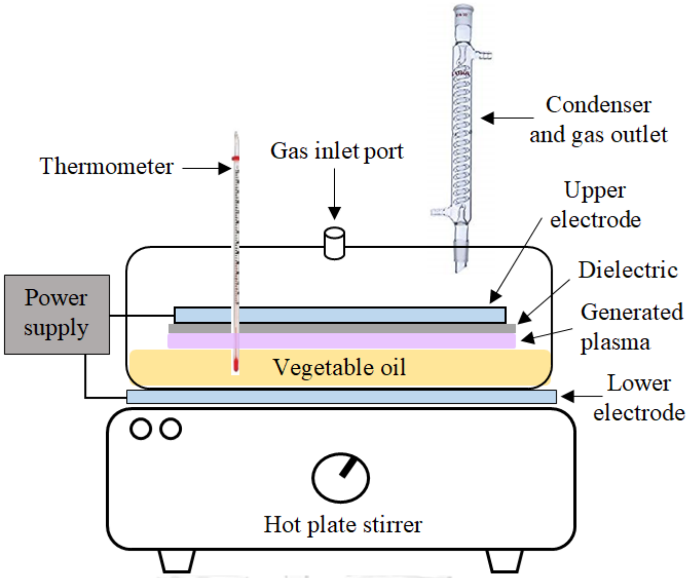


Figure 6 Drawing of constructed DBD plasma hydrogenation chamber

3.2.3 Hydrogenation and evaluation

Hydrogenation studies of the vegetable oils were performed by varying the following process parameters: type of vegetable oil (refined palm olein and soybean oil), H_2: He mixed carrier gas concentration ratio (5% H_2: 95% He to 25% H_2: 75% He), temperature (31 – 100°C) and reaction time (1 – 20 h). Unless otherwise explicitly stated, experiments were performed independently in triplicate and the average values are presented with the error bars representing the standard deviation. For every run, the total gas flow rate of 800 mL/min was fixed. The output of the high voltage, high-frequency power supply was adjusted to the same highest level for every run. Because the condenser was vented to the atmosphere, the pressure inside the chamber was always 1 atm. A mixture of H_2 and He gas was used as a working gas because H_2 provided a hydrogen source for hydrogenation. Helium was used because it can sustain DBD plasma much more effectively than H_2 [45]. N_2 was not chosen to eliminate any possibility of nitrogen-containing compound formation (such as nitride or cyanide) in the edible product.

Evaluations of IV, AV and slip melting point (SMP) on the hydrogenated oil samples were performed locally in the laboratory. Evaluation of IV was based on the IUPAC 1987 standard [46], which can be summarized as follows. The sample weighting 0.2 g was mixed with 15 ml cyclohexane and 25 mL Wijs solution. The reaction was allowed to proceed in the dark for 1 h and was terminated with 20 mL potassium iodide and 150 mL distilled water. The 0.1 N sodium thiosulfate solution was used for titration. The IV can be calculated from the formula: $IV = [(V_1-V_2) \times N \times 12.69] / M$, where V_1 is the volume of sodium thiosulfate titration in the blank, V_2 is the volume of sodium thiosulfate titration in the sample, N is the normality of $Na_2S_2O_3$ and M is the sample weight. Evaluation of AV followed IUPAC 1987 [46] as follows. The sample weighting 2 g was mixed with 25 mL diethyl ether and 25 mL 95% ethanol, and 0.5 mL of 0.1% phenolphthalein solution was added. The 0.1 M potassium hydroxide solution was used for titration. The AV can be calculated from the formula: $AV = (V \times 5.16) / W$, where V is the volume of the potassium hydroxide solution and W is the weight of the sample. The determination of SMP was based on PORIM 1995 [47], which relied on measuring the temperature at which a frozen sample started to melt. Evaluation of the texture of samples was performed using Shimadzu EZ-X texture analyzer (speed 10 mm/min, indentation 2.5 mm, $23 \pm 2^{\circ}C$) at Nation Science and Technology Development Agency, Thailand. The fatty acid composition of the hydrogenated oil samples was investigated by Shimadzu GC-2010 Plus with a DB-WAX capillary column with a flame ionization detector. Individual fatty acid content, which can reveal *cis* and *trans* isomer compositions, was analyzed using the GC-MS technique at Research and Service Laboratory, The Halal Science Center, Chulalongkorn University.

3.2.4 Effect of temperature

Temperature generally plays a significant role in chemical reactions including plasma-catalyzed hydrogenation kinetics. As the hydrogenation reaction is exothermic [48], low temperatures should promote the equilibrium conversion, while high temperatures can accelerate the reaction kinetics. The effect of hydrogenation temperature at 30, 50, 80 and 100°C was evaluated. For the 30°C case, a simple water container with cooling water from an aquarium chiller was installed around the reaction chamber to maintain 30 ± 1°C during the experiment. For 50°C, the reaction started at room temperature of about 31°C and rose to 50 ± 1°C in about 25 min due to the deposition of thermal energy from the plasma onto the oil. The temperature then stabilized at this value through the end of the experiment. Thus, for this 50°C case, neither heating nor cooling provision was required. For the 80°C case, the oil was first heated to 60°C by the hot plate stirrer. With the application of the plasma and constant heating form the hot plate stirrer, the temperature rose to 80 ± 1°C in about 25 min and stabilized through the end of the experiment. The 100°C case was similar to the 80°C case except that the oil was first heated to 80°C by the hot plate stirrer and that the temperature stabilized at 100 ± 1°C through the end of the experiment

3.3 Results and discussion

3.3.1 Different oil types

In the first experiment, the hydrogenation responses of the two oil types, refined palm olein and soybean oil, were compared. The processing gas concentration ratio was 15% H_2: 85% He. The initial temperature of the oil was that of the laboratory (about 31°C). After 25 min into the reaction, the temperature increased to roughly 50°C and stabilized through the end of the 2 h run, clearly indicating that the oil was not substantially heated up by the generated plasma. Oil sampling was performed every 30 min. Fig. 7 shows the generated plasma with refined palm olein.

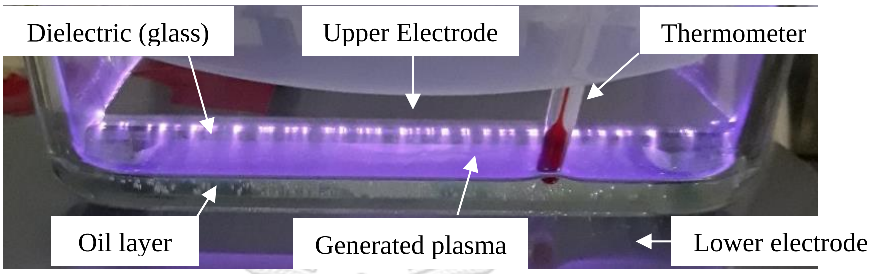
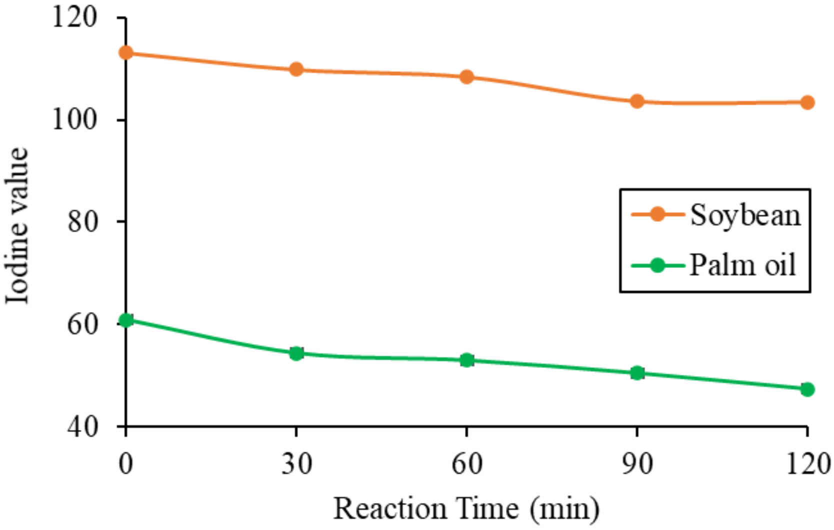


Figure 7 Generated plasma during refined palm olein hydrogenation

Fig. 8(a) demonstrates the evaluated IV of the hydrogenated oils as a function of reaction time



(a)

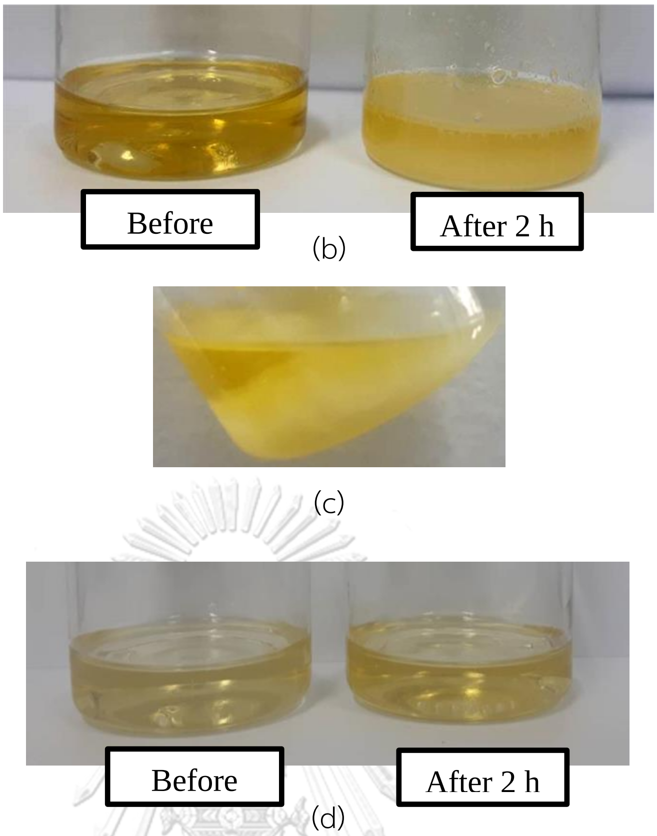


Figure 8 (a) IV of hydrogenated oils (25 mL oil volume, mixture of 15% H_2*:85% He and initial temperature 31°C), (b) Refined palm olein before and after 2 h of hydrogenation, (c) coagulation of whitish solid substance at bottom and (d) Soybean oil before and after 2 h of hydrogenation*

IVs at 0 h represent that of new, un-hydrogenated oils. These values correspond quite well with the literature-reported numbers (130 – 132 for soybean oil [49] and 53.1 for refined palm olein [46]). In this first experiment, the observed decreases in IVs with reaction time for both oil types were statistically significant (error bars barely visible because of the very small SD). The reduction in IVs did indicate that the vegetable oils can be successfully hydrogenated using the studied non-thermal, parallel-plate DBD plasma. The occurrence and extent of the hydrogenation can also be confirmed in Fig. 8(b) showing the fresh refined palm olein and the 2 h hydrogenated refined palm olein. The oil color became noticeably lighter, indicating hydrogenation [5]. Moreover, there is a coagulation of whitish solid substance at the bottom of the container as depicted in Fig. 8(c). The substance, when heated, dissolved into liquid and returned to solid again after setting at room temperature. The substance represented solidified refined palm olein from successful hydrogenation. For the case of soybean oil, although the IV decreased similar to the case of refined palm olein as shown in Fig. 8(a), visual observation found no solidification and the oil color became more intense as demonstrated in Fig. 8(d). Two hours of hydrogenation was not sufficient for soybean oil to reach a solidified state. Palm oil contains approximately 50% saturated fatty acids, 39% monounsaturated fatty acids and 10% polyunsaturated fatty acids [50]. Soybean oil contains approximately 16% saturated fatty acids, 24% monounsaturated fatty acids and 60% polyunsaturated fatty acids [51]. The lower IV of refined palm olein than that of soybean oil at the initial reaction time shown in Fig. 8(a) confirms this. This indicates that refined palm olein is more readily saturated and that it takes a longer time for soybean oil to reach a higher saturated fatty acid ratio to become solid.

In terms of reaction kinetics for soybean oil hydrogenation, when compared to the research of Yepez and Keener [3] who performed hydrogenation of 10 mL soybean oil via the high-voltage atmospheric cold plasma (HVACP) technique with results showing that the IV of soybean oil was reduced from 132 to 124.8 in 2 h of reaction time (a reduction rate of 3.6/h assuming linear kinetics), the present result shows a reduction of the IV from 113.09 to 103.46 in 2 h or a reduction rate of 4.8/h. Soybean oil hydrogenation of 25 mL using the parallel-plate DBD plasma method appears to exhibit a faster kinetic response than the HVACP technique, offering a significant improvement over the HVACP method.

3.3.2 Effect of H2: He ratio

As the results in section 2.3.1 indicate successful hydrogenation for refined palm olein in 2 h, it was selected to perform the rest of the studies. The effect of H_2 concentration in the mixed carrier gas is demonstrated in Fig. 9.

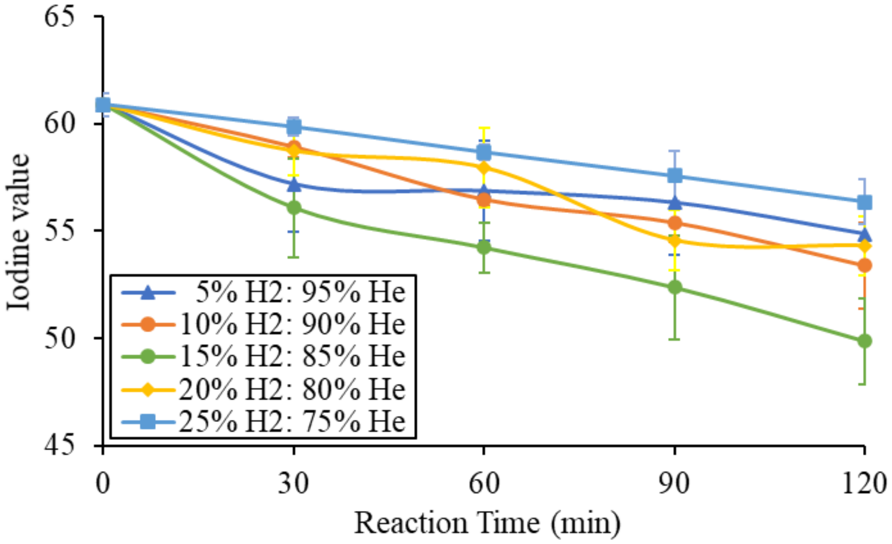
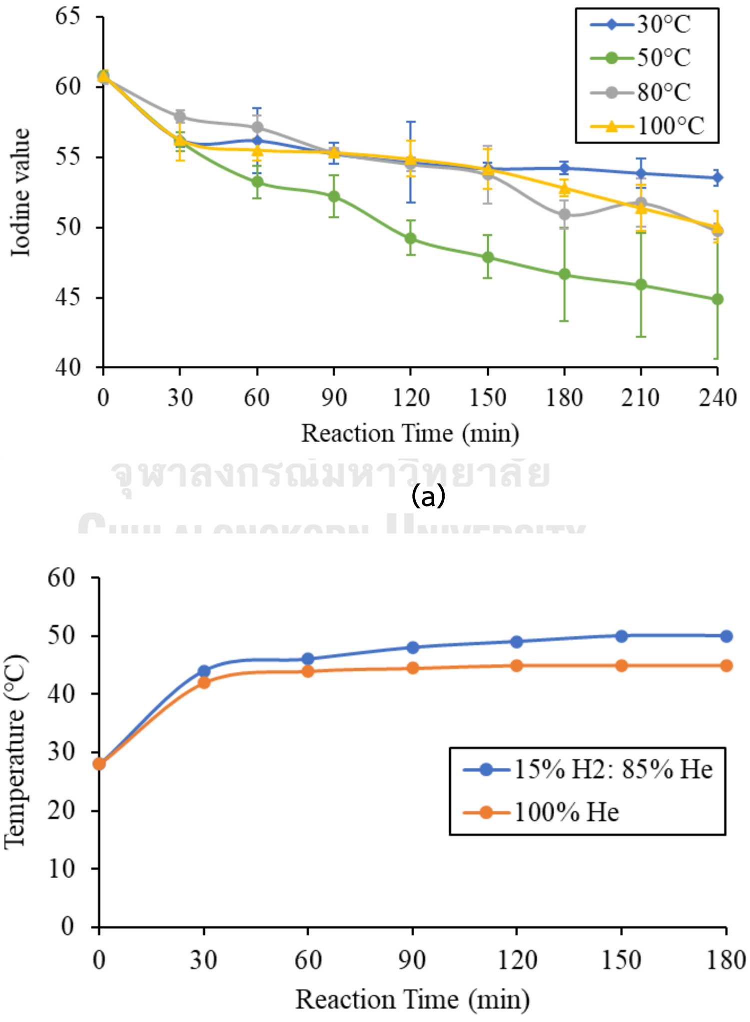


Figure 9 Effect of H_2: He ratio on IV (25 mL refined palm olein and initial temperature 31°C)

For every hydrogen gas concentration, the IV decreased with increasing reaction time. This is expected as more reaction time means more generated hydrogen radicals reacting with remaining unsaturated-bonded carbon atoms on the fatty acid chains. Although the H_2 concentration appears to exhibit no clear trend on the IV reduction, the results clearly show that 15% H_2: 85% He yields the fastest hydrogenation kinetics at every reaction time with good statistical significance. Lower hydrogen concentrations of 10% and 5% resulted in less hydrogen free radicals present, so hydrogenation proceeded at a slower pace. The higher hydrogen concentrations (20 and 25%) showed the poor hydrogenation response, especially the 25% content. This was likely because at high hydrogen gas concentrations, the large amount of generated hydrogen free radicals experienced smaller mean free paths and recombination became significant, effectively resulting in less atomic hydrogen being present in the system to interact with vegetable oil [52]. A dedicated measurement of the presence of atomic hydrogen will be required to confirm this hypothesis.

3.3.3 Effect of temperature

The influence of hydrogenation temperature in the range of 30 – 100°C was evaluated with the fixed 15% H_2: 85% He mixed carrier gas concentration ratio as shown in Fig. 10(a).



(a)

(b)

Figure 10 (a) Effect of reaction temperature on IV (25 mL refined palm olein and mixture of 15% H_2: 85% He) and (b) oil temperature history showing DBD plasma heating effect (25 mL refined palm olein and initial temperature 28°C)

Results reveal that the studied temperature of 50°C provided the fastest hydrogenation rate with good statistical significance as the IV reached the lowest value of 44.88 after 4 h. This finding on the effect of temperature is highly convenient for the production standpoint because no external heating or cooling of the reaction chamber is required -- heating comes mainly from the plasma process. However, it is understood that a different steady-state temperature from 50°C may be achieved in a dissimilar setup because of different degrees of heat loss as well as heat dissipation mechanisms to the surrounding. Although hydrogenation is an exothermic reaction in nature [48], the heating of the oil comes mainly from plasma heating as can be proven by the following simple experiment. Pure He was used as a processing gas to generate DBD plasma over refined palm olein (with no hydrogenation taking place) as well as 15% H_2: He gas mixture (to allow hydrogenation to take place). The temperature history of the oil was recorded every 30 min for up to 3 h as shown in Fig. 10(b). The experiment was performed one time. At the end of the 3 h experiment, the temperature gradients as increased from room temperature (28°C) due to plasma heating alone and due to hydrogenation and plasma heating was 19 and 22°C, respectively. Based on the sensible heat equation of $Q = mC_p\Delta T$, where Q is the thermal energy supplied to a mass m with thermal capacity at constant pressure of C_p resulting in the temperature increase of ΔT, with the same m and C_p for both cases, the ratio of Q due to hydrogenation + plasma heating to plasma heating alone was 22/19 = 1.16. The hydrogenation provides a small contribution of about 16% of thermal energy to the system.

For the 80 and 100°C cases, the reduction in the IV was similar to one another but still less than the 50°C case. This corresponds to the fundamental understanding that an exothermic reaction should be carried out at a reduced temperature to drive the reaction forward. High temperature is also not suitable for margarine production as it promotes *trans*-fat formation as well as decomposition of temperature-sensitive vitamins present in oil [53].

The 30°C case appeared to show the slowest reaction rate after 30 min of reaction time. The IV became constant at around 53 – 55 after 120 min into hydrogenation, indicating that hydrogenation no longer took place or proceeded very slowly. The most likely explanation is that the cooled oil at 30°C was much more viscous than at higher temperatures (65.37 cSt at 30°C and 27.06 cSt at 50°C [54]), making physical exchange between the oil underneath the surface layer and that at the surface layer much more difficult. Since plasma hydrogenation only took place on the surface of the oil, the mass transfer limitation severely restricted the reaction. A more effective method than simple magnetic stirring employed in the study should be explored to promote effective mass transfer to the surface layer of the oil.

3.3.4 Effect of reaction time

With the findings of the optimal process variables from the previous sections, the hydrogenation study was carried out up to 20 h with sample collection every 4 h to determine the reaction time that refined palm olein became solidified. A plot of the IV vs. reaction time is depicted in Fig. 11, and Fig. 12 displays the samples collected every 4 h.

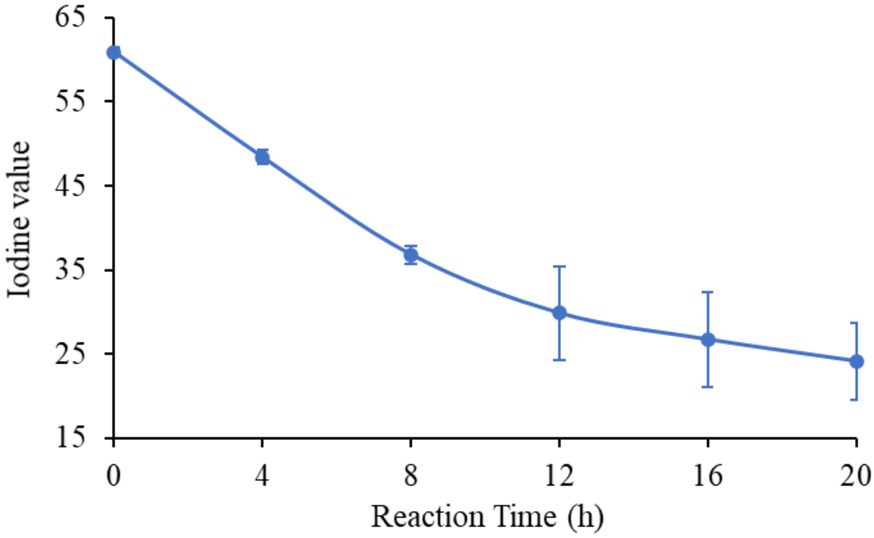


Figure 11 IV vs. reaction time (25 mL refined palm olein, mixture of 15% H_2*: 85% He and initial temperature 31°C)*

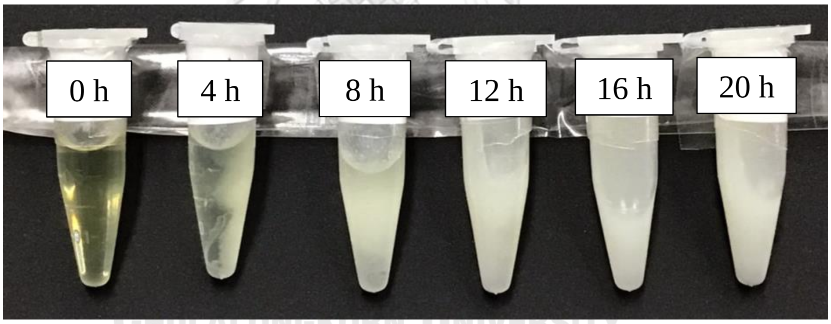


Figure 12 Collected oil samples (25 mL refined palm olein, mixture of 15% H_2*: 85% He and initial temperature 31°C)*

At 4 h, the refined palm olein was visually observed to remain liquid, although the IV decreased substantially and the color became lighter. It is also important to note that the IV at 4 h in Fig. 11 was 48.39, while the value at 4 h in Fig. 10(a) was 44.88, indicating that the studied parallel-plate DBD plasma hydrogenation is fairly reproducible. At 8 h, the oil appeared to be a solid/semi-solid phase, corresponding to the IV of 36.80. Results of the texture analysis of the samples compared to two margarine brands of Imperial and Tesco, which are widely commercially available in Thailand, are shown in Fig. 13. It can be seen that the hydrogenation time of 8 h (or slightly beyond 8 h) produced margarine with the texture closest to the commercial ones. Over-hydrogenation at 12 h and beyond resulted in a too firm product unsuitable for culinary purposes.

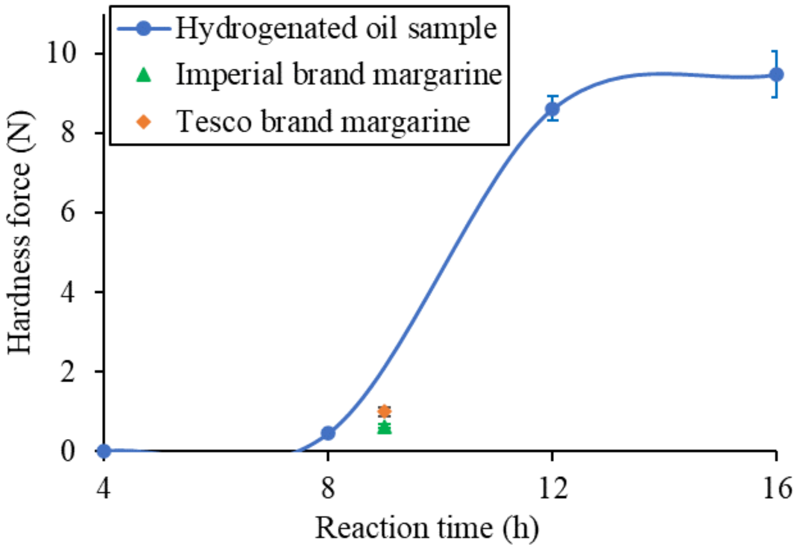


Figure 13 Texture analysis of hydrogenated oil samples (25 mL refined palm olein, mixture of 15% H_2: 85% He and initial temperature 31°C) compared to commercially available margarines

The SMP values shown in Fig. 14 at 8 and 12 h were 17.67 and 28℃, respectively, which were quite close to those of many studies: 5 – 10 ℃ for refrigerated products, 20 – 30 ℃ at ambient condition and 35 ℃ at oral melting temperature[55], as well as 31.2 – 34.9 ℃ [56] for margarine in Turkey markets and 32 – 41.3 ℃ [57] for margarine in Iranian markets. The evaluated SMP value is also consistent with the IV (Fig. 11). Low IV meant high saturated fat content, corresponding to high SMP. The SMP at 12 h was within the range at ambient condition while the SMP at 8 h was slightly below the range. As the texture analysis results (Fig.13) suggested the hydrogenation time of about 8 h, plasma hydrogenation of refined refined palm olein for about 8 h, 15% H_2: 85% He process gas mixture at initial temperature 31°C (increasing to 50°C from plasma heating) appears to be the most suitable condition to produce margarine using the designed non-thermal DBD plasma system.

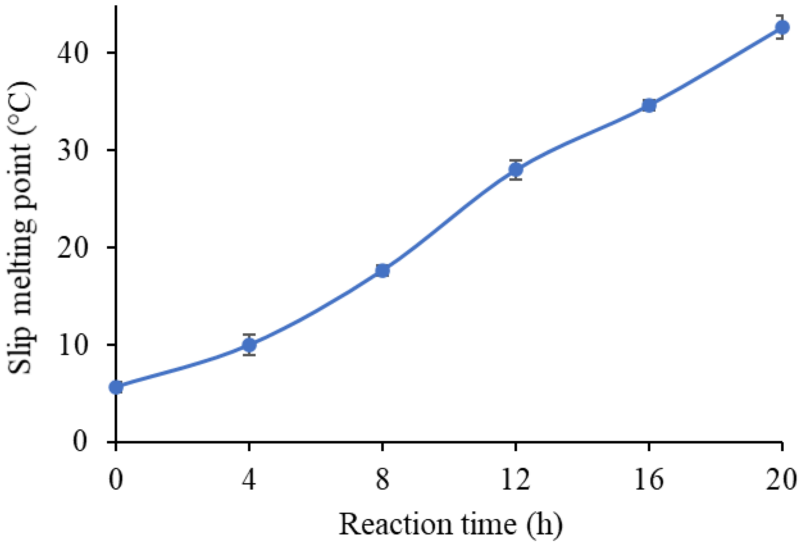


Figure 14 SMP vs. reaction time (25 mL refined palm olein, mixture of 15% H_2: 85% He and initial temperature 31°C)

The hydrogenation kinetics from 0 – 8 and 12 – 20 h appeared to be different as can be seen in Fig. 6. From 0 – 8 h, the oil essentially remained mostly in a liquid state, so mass transfer from the magnetic stirring action between the oil underneath the surface layer and that at the surface layer was still effective. From 12 h onward, as the refined palm olein became much more viscous and became semi-solid/solid-like material and as available unsaturated bonds became less abundant, mass transfer became severely hindered and the chance that unsaturated-bonded carbon atoms would come into physical contact with the generated hydrogen radicals in the plasma gap significantly reduced with increasing reaction time.

A plug-in power meter was employed to measure the energy consumption of the high voltage, high-frequency power supply. At the finish of the 20 h run, the measured energy consumption was only 0.437 kWh. This translates into only 21.85 W of instantaneous power consumption by the power supply, assuming constant power consumption through the run. Although as much as 8 h was required to treat refined palm olein to the desired degree of hydrogenation with desirable texture, the very low reported power consumption suggested that the increasing power of DBD should reduce the operation time.

GC-MS was employed to evaluate the fatty acids composition of the new refined palm olein and the hydrogenated oil at 4 and 12 h. Table 4 presents the analysis results up to eicosenoic acid (C20:1n-9) as fatty acids beyond this are either not detected or present at only a fraction of a percentage. Also, C4:0 and C6:0 are not shown because they are not detected in any of the analyzed oil samples.

Table 4 GC-MS results of individual fatty acids composition of fresh refined palm olein and hydrogenated oil (25 mL, mixture of 15% H_2: 85% He and initial temperature 31°C)

Fatty acid	Composition (%)		
	Fresh refined palm olein	DBD plasma hydrogenation for 4 h	DBD plasma hydrogenation for 12 h
C8:0	0.01	-	0.02
C10:0	0.02	-	0.02
C12:0	0.22	-	0.38
C14:0	1.08	0.89	1.51

C15:0	0.04	0.03	0.06
C16:0	33.26	39.47	35.80
C16:1	0.23	0.13	0.11
C17:0	0.10	0.05	0.18
C17:1	-	-	-
C18:0	5.54	5.51	18.85
C18:1n-9 *trans*	-	1.44	5.24
C18:1n-9 *cis*	43.58	43.39	32.87
C18:2n-6 *trans*	-	-	-
C18:2n-6 *cis*	13.18	8.19	4.05
C18:3n-6	0.03	-	-
C18:3n-3	0.15	0.10	0.02
C20:0	0.41	-	0.69
C20:1n-9	0.12	-	0.05

For the fresh refined palm olein, 17 types of fatty acids were detected with the highest composition being oleic acid (C18:1 n-9 *cis*) of 43.58%, followed by palmitic acid (C16:0) of 33.26%. No *trans*-fat was found. For the hydrogenated refined palm olein at 4 h, 18 types of fatty acids were found with the highest composition being oleic acid (C18:1 n-9 *cis*) of 43.39%, followed by palmitic acid (C16:0) of 39.47%. C18:1 n-9 *trans* of 1.44% was detected. For the hydrogenated refined palm olein at 12 h, 17 types of fatty acids were found with the highest composition being palmitic acid (C16:0) of 35.80%, followed by oleic acid (C18:1 n-9 *cis*) of 32.87%. C18:1 n-9 *trans* of 5.24% was detected.

When comparing the fatty acids composition of the fresh refined refined palm olein to that of the hydrogenated oil, it can be observed that palmitoleic acid (C16:1), oleic acid (C18:1n-9 *cis*), linoleic acid (C18:2n-6 *cis*), γ-linolenic acid (C18:3n-6) and α-Linolenic (C18:3n-3) was reduced, while lauric acid (C12:0), myristic acid (C14:0), pentadecanoic acid (C15:0), palmitic acid (C16:0), margaric acid (C17:0) and stearic acid (C18:0) increased. This clearly illustrates that the mono-, di- and tri-unsaturated fatty acids decreased while the saturated chains increased. These are the expected direct results of hydrogenation on the unsaturated bonded carbon atoms. It is interesting to note that C12:0, C14:0, C15:0, C16:0 and C17:0 also increased substantially. Except for C16:0, these saturated fatty acids don't have the unsaturated precursors in the refined palm olein, so the increase must be attributable to the DBD plasma application. Yepez and Keener [3] also detected the presence of C16:0 in soybean oil hydrogenation experiments using the HVACP technique although the un-treated oil did not consist of the mono- and tri-unsaturated fatty acid precursors. A hypothesis can be given that because the microfilament discharges and species present in the plasma, e.g., free electrons, positive helium ions and atomic hydrogen, were in direct physical contact with the refined palm olein, any of them with sufficient energy could have broken the longer fatty acid chains to become the shorter ones. A study on the exact mechanism is deferred to a future publication.

Although C18:2n-6 *trans* was not detected in any of the analyzed oil samples in Table 1, C18:1n-9 *trans* of 1.44% at 4 h and 5.24% at 12 h became present in the hydrogenated oil. As a comparison, slightly hydrogenated refined palm olein through a conventional method relying on high temperature (180 – 200°C) and a catalyst

(0.06 – 0.2% of fresh nickel/oil level) generated *trans*-fatty acid of 7.15% when palm olein was slightly hydrogenated to reduce the IV from 55.2 to 46.0 [58], or a reduction of 16.67%. This conventional hydrogenation produces *trans*-fat at a rate of 0.429% per % decrease in the IV. In the present study, the IV was reduced from 60.89 to 48.39 at 4 h, or a reduction of 20.54%. This represents the *trans*-fat generation rate of only 0.07% per % decrease in the IV, which is about 6.12 times lower than that of the conventional method [58], offering a substantial improvement over the conventional method. The results indicate that the applied low-temperature DBD plasma hydrogenation technique can successfully hydrogenate refined palm olein with much less *trans*-fatty acid generation than the conventional production. Thus, a large portion of DBD-plasma hydrogenated refined palm olein can be mixed with palm olein and interesterified palm oil to produce margarine with the overall *trans*-fatty acid content no higher than the regulatory requirement.

Because the steady-state bulk temperature of the oil during the plasma hydrogenation was only about 50°C, the *trans* isomer should not be formed due to the slightly elevated treatment temperature. A hypothesis can be given that because the microfilament discharges as well as active species present in the plasma, e.g., free electrons, helium ions and atomic hydrogen, were in direct physical contact with the refined palm olein, any of them could have imparted sufficient energy locally to covert the *cis* isomer into the *trans* one. Similar to the increase in the number of shorter saturated chains, a study on the exact mechanism for the formation of the *trans* isomer is deferred to a future publication. Once the exact mechanism is revealed, DBD plasma hydrogenation with an appropriately modified reactor setup can be performed to produce truly *trans*-fat-free margarine.

The AV is one of the basic indicators of the product property [59], which indicates the acid content in fats or oils given by the amount of free fatty acids derived from the hydrolytic deterioration (rancidity) of the triacylglycerol. This transition takes place under unsuitable treatment and preservation of the fats. From the experimental results illustrated in Fig. 15, the AV reduced from 0.47 to 0.27%, or a 43% reduction, after 12 – 20 h of treatment, significantly indicating that the plasma hydrogenation can also help extend the shelf life of oil or margarine. This is highly advantageous for food storage, which helps reduce food costs, offers healthier food and protects the environment by reducing food waste [60]. W.S. Abdul-Majeed et al. [61] used flying non-thermal DBD jet plasma for biodiesel production from waste cooking oil (WCO). It was discussed that energetic electrons, radicals and other species in the plasma played a role in the destruction of free fatty acid chains present in WCO. Similarly, in the present investigation, free electrons, radicals and other species present in the generated DBD plasma must have destroyed the free fatty acid constituents in refined palm olein, resulting in a reduction of the AV with treatment time.

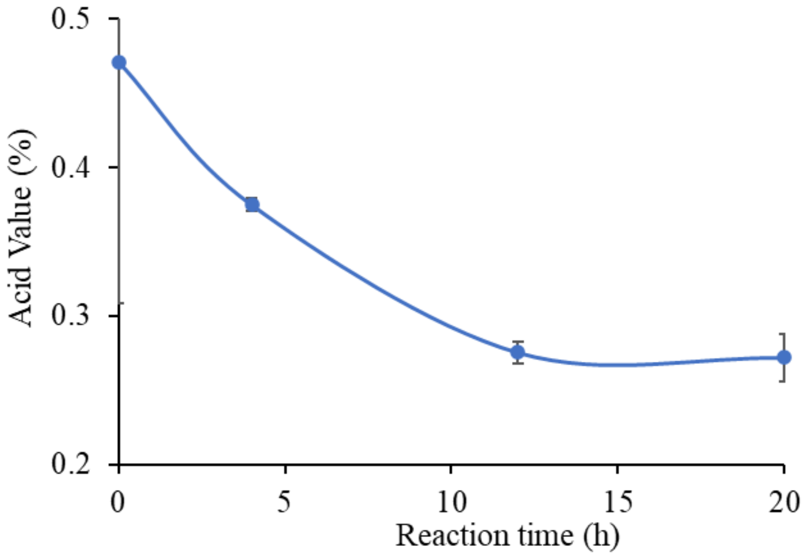


Figure 15 AV vs. reaction time (25 mL refined palm olein, mixture of 15% H_2*: 85% He and initial temperature 31°C)*

3.4 Preliminary suggestion on continuous production system design

Although the production capacity of the present study is low because the power consumption was only 21.85 W, a continuous process could be designed together with a more powerful power supply to generate DBD plasma with higher intensity. As a preliminary suggestion, a refined palm olein layer can be carried on a long conveyor belt acting as a lower electrode. With appropriate conveyor speed and size, oil layer thickness and DBD plasma intensity, the oil to be removed at the end of the conveyer belt can have the optimum plasma-contacting residence time with the appropriate degree of hydrogenation. The operation ensures nearly isothermal conditions. The processed oil could be directly packed for further blending with other ingredients as no catalyst removal procedure would be required. In a closed production system, to minimize the costs of processing gases, He and H_2 can be recycled and only periodic replenishment of H_2 was necessary to maintain the optimal H_2 partial pressure. As the system operates under atmospheric pressure, a non-complicated recirculating pump operating at 1 atm with a sufficient flow rate is required to perform simple gas recirculation.

The present study demonstrates that the non-thermal DBD plasma can be successfully employed to hydrogenate refined palm olein with good reaction kinetics and very low *trans*-fatty acids generation. The technique offers a promising possibility for commercial utilization by the edible oils industry.

3.5 Conclusions

The non-thermal dielectric barrier discharge (DBD) plasma with parallel-plate configuration has been successfully demonstrated to hydrogenate refined palm olein with very low *trans*-fatty acid formation. The mixed carrier gas concentration ratio of 15% H_2: 85% He, initial temperature 31^{o}C (rising to 50^{o}C due to plasma) and 8 h of hydrogenation provided the fastest reaction rate and desirable product. After 4 h of hydrogenation, the IV was reduced from 60.89 to 48.39 and the detected *trans*-fatty acid was 1.44%, presenting the *trans*-fat generation rate of only 0.07% per % decrease in the IV, which is about 6.12 times lower than the conventional catalyst-based technique. About 8 h was required to produce margarine with texture closest to commercial margarines. The AV reduced from 0.47 to 0.27%, or a 43% reduction, after 12 – 20 h of treatment. A continuous process together with a more powerful power supply to generate DBD plasma could be designed to increase the production capacity of the present study.

CHAPTER 4

Improved Hydrogenation Process for Margarine Production with No *Trans* Fatty Acid Formation by Non-Thermal Plasma with Needle-in-Tube Configuration

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Abstract

Non-thermal dielectric barrier discharge (DBD) plasma with needle-in-tube configuration was used to improve hydrogenation reaction for *trans*-fat free margarine production. Refined palm olein was used as raw material with operating conditions at ambient pressure, room temperature (29°C) and no catalyst. Effects of hydrogen gas (H_2) concentration, input power, gas flow rate, discharge gap size and reaction time on fatty acid compositions and properties of hydrogenated refined palm olein after plasma treatment was evaluated. Lowest iodine value (IV) was achieved with reduction from 60.75 to 23.56 with increase in saturated fatty acid composition from 40.82±0.05 to 68.70±0.07 % and decrease in unsaturated fatty acid composition from 59.11±0.12 to 31.39±0.01% under the condition of 0.5 L/min gas flow rate with 100% H_2, 40 W input power, 0.5 cm gap size and 15 h reaction time. In addition, no *trans*-fat was detected by GC-MS analysis. Slip melting point (SMP) was increased from 9.33±0.5 to 36.33±0.5°C. Acid value (AV) was reduced from 0.47±0.02 to 0.32±0.03 mg KOH/g oil. Texture of produced margarine was similar to that of commercial one. Generated hydrogen free radicals were hypothesized to perform hydrogenation by reacting with carbon-carbon double bonds (π-bonds), converting poly- and monounsaturated fatty acids into saturated ones. This highly effective catalyst-free plasma hydrogenation system can be used as alternative, environmentally friendly and economically feasible method to produce *trans*-fat free margarine.

Keywords: *Trans*-fat free margarine; *Trans*-fatty acid; Non-thermal plasma; Hydrogenation; Tesla coil

4.1 Introduction

Margarine was invented by Hippolyte Mège-Mouriés in 1869 [1] with the purpose to replace butter which had high consumption and was expensive at that time. The first margarine was made from beef tallow churned with milk [2]. At present, margarine is manufactured by combining emulsion of water and a vegetable oil such as soybean [62], corn, canola, olive or palm oils [58, 63] containing unsaturated fatty acids of 75 – 90% [3, 64]. These unsaturated fats must be made more saturated to produce a more solid content providing a melting behavior and texture close to those of butter [62]. The physical and chemical enhancements can be achieved through hydrogenation, interesterification and fractionation [1, 42].

Hydrogenation refers to an addition of hydrogen atoms onto unsaturated carbon double bonds (π-bonds) of fatty acid chains to become saturated ones. Hydrogenated oils are simple to produce and inexpensive alternatives to animal fats. Higher melting points, firmer texture, increased oxidation stability, as well as enhanced shelf life are typical features of hydrogenation products [1, 15, 65, 66]. With conventional hydrogenation, a catalyst is necessary in the process to make the reaction more efficient such as 0.1-0.15% nickel catalyst at 180-200 °C and 1-3 atm, requiring 1-4 h to reduce iodine value (IV) from 130 to 90 [27, 28]. Various catalysts have been employed including platinum, palladium, copper and palladium on activated carbon, diatomite, etc. [27, 67, 68]. Under this condition, the hydrogen molecule is adsorbed on the catalyst surface where it is dissociated into hydrogen atoms. This atomic hydrogen then reacts with the unsaturated fatty acid chain and transforms the structure from a double bond into a single bond [27, 69]. Using a catalyst combined with high temperatures in the hydrogenation process causes *trans* fatty acid formation [6]. *Trans*-fatty acids or *trans*-fat increase low-density lipoprotein (LDL), increasing the risks of various diseases such as cardiovascular diseases, hypertension, Alzheimer's disease, heart disease and stroke, diabetes and certain cancers [13-15, 17, 21]. The World Health Organization (WHO) has an announcement in May 2018 to completely remove *trans-fat* from processed foods by 2023 that could help millions of people who die from the aforementioned diseases every year [18].

Non-thermal or cold plasma is defined as a thermodynamic non-equilibrium plasma because of the difference in temperature between electrons and heavy particles [70, 71]. As the lightweight electrons reach higher kinetic energy (temperature) faster than the heavy particles [72], the electron temperature in non-thermal plasma is higher than that of the heavy particles (molecules, ions) that are close to room temperature. Cold plasma can be generated at ambient pressure or under low pressure [73] by several types of systems depending on the application used such as dielectric barrier discharges (DBD), corona discharges, microwave plasma, radiofrequency discharges, atmospheric glow discharges, high voltage pulsed discharge and jet plasma [70, 73, 74].

For margarine production, a thermal (high temperature) plasma is not preferred due to the *cis* isomer having a high tendency to be transformed into the *trans* isomer. Therefore, non-thermal plasma is required. Non-thermal plasma is a partially or fully ionized gas consisting of photons, excited or neutral atoms and molecules, free radicals, ions and free electrons. One type of non-thermal plasma is a DBD plasma, which can be generated and maintained at room temperature and atmospheric pressure. A typical DBD plasma system consists of two high voltage electrodes separated by a dielectric material. The plasma is formed by the passage of an alternating electric current through a working gas between the two electrodes. The working gas consisting of hydrogen gas (H_2) can generate atomic hydrogen which is a highly reactive free radical [21]. Thus, plasma can function similarly to a conventional catalyst by producing atomic hydrogen directly in the plasma field. The major advantage of plasma hydrogenation over conventional catalyzed hydrogenation is that this green process can be performed at atmospheric pressure and low temperatures in the absence of a catalyst. The processes and waste generated from catalyst preparation, utilization, removal, reactivation and final disposal are eliminated, presenting a novel and environmentally friendly approach to hydrogenate liquid substances.

DBD plasma requires a high voltage, high-frequency electric power. Several types of generators can be employed as an electric power source, of which a tesla coil is one alternative. In 1890, Nikola Tesla invented a tesla coil [75], which is essentially an electrical resonant transformer circuit to produce high voltage and high frequency with low currents. The output has a frequency between 50 kHz and 1 MHz [76-79]. Nowadays, tesla coils have been developed and used in a wide range of applications such as x-rays, electrical lighting and wireless energy transfer for electrical power transmission and industries [80].

There have been a few reported studies on the non-thermal hydrogenation of vegetable oils. Firstly, Yepez et al. [3]developed a process known as high-voltage atmospheric cold plasma (HVACP) hydrogenation of soybean oil with no detectable *trans*-fat formation. The experiment was performed at room temperature to avoid the *trans* isomer that can occur at high temperatures. Yepez et al. [81] performed another investigation on the effect on soybean oil after non-thermal hydrogen plasma treatment. Using the same transformer as in the previous study, the result revealed that unsaturated fatty acids decreased, saturated fatty acids increased and an insoluble portion in the solid fraction increased. It was concluded that two reactions of polymerization and hydrogenation occurred during the plasma treatment. Puprasit et al. [82] investigated margarine production via refined palm olein hydrogenation employing a DBD plasma with a parallel-plate configuration. No catalyst was used in the experiment. After 8 h of the plasma treatment, the resulting texture was closest to that of commercial margarine. For a shorter 4 h of plasma treatment, 1.44% of *trans*-fat formation was detected, which was about 6.12 times lower compared to the conventional hydrogenation with a catalyst technique operating at high temperatures and high pressure. These three pieces of literature highlighted the successful applications of catalyst-free low-temperature plasma for vegetable oil hydrogenation.

In the present study, a novel, catalyst-free and non-thermal DBD plasma with a needle-in-tube configuration for hydrogenating refined palm olein under ambient conditions to produce *trans*-fat-free margarine was investigated. A tesla coil powered by a DC power supply was employed to generate high voltage, high-frequency output to produce plasma. The studied parameters were: H_2 and helium (He) mixed carrier gas concentration ratio, input power, gas flow rate, gap size between the tip of the needle electrode and the oil surface, and reaction time. Refined palm olein was used to investigate because it presents the most used cooking oil type in Thailand. The success of this research will help increase the commercial value of domestic refined palm olein.

4.2 Materials and methods

4.2.1 Chemicals

Refined palm olein of the Morakot brand was obtained from a local supermarket in Bangkok, Thailand. The plastic bottled oil was used directly without any pretreatment. H_2 and He gases of Ultra High Purity (UHP) grade distributed by Alternative Chemical Company were used for plasma generation and hydrogenation. The following chemicals were used for evaluation of IV and acid value (AV): 0.1N Wijs solution distributed by RCI Labscan, 99.5% cyclohexane distributed by Loba Chemie

Pvt., Ltd., 99.5 – 101% sodium thiosulfate 5-hydrate distributed by KEMAUS, 99% potassium iodide distributed by Ajax Finechem, a laboratory-produced starch solution, diethyl ether distributed by RCI Labscan, 95% ethyl alcohol and potassium hydroxide distributed by KEMAUS, and phenolphthalein distributed by Ajax Finechem.

4.2.2 Needle-in-tube DBD plasma reactor and tesla coil transformer system set-up

A drawing of the needle-in-tube plasma reaction chamber is illustrated in Fig. 16. The 350 mL chamber was made of borosilicate glass with a bottom thickness of 3 mm. The locking lid was made of polypropylene (PP) which can resist heat up to 150 °C. Three holes were drilled into the lid as demonstrated in Fig. 17. The hole no. 1 presented the quartz tube position for plasma generation. The hole no. 2 was for a thermometer insertion to observe the temperature. The hole no. 3 was for the gas outlet. It is important to note that although in the present laboratory-scale investigation the working gases were discharged into the atmosphere, for commercial production in a closed semi-batch system, the exhaust H_2 can be supplied back to the system via a simple recirculating pump operating at a low speed, atmospheric pressure and relatively low temperature, recirculating 100% of the working gas. The quartz tube (ID = 8 mm, OD = 10 mm) was installed at the center of the lid (hole no. 1) with the end opening submerging approximately 1 mm into the oil to contain the generated plasma and to introduce the plasma to bubble through the oil, enhancing the physical contact. This configuration was supposed to have a better performance than the parallel-plate configuration where most of the generated plasma might not contact the oil before leaving the system. A stainless-steel needle electrode of 1 mm in diameter and 15 cm in length was inserted into the quartz tube through a gas inlet port. All insertions were airtight. An aluminum ground plate of dimensions

15×20 cm was placed beneath the reaction chamber and was on a hot-plate stirrer to provide circulation. The high voltage, high-frequency power supply system consisted of two components. The first component was a regulated DC power supply (UNI-T, model UTP3315TFL-II), which provides a maximum output of 30 V and 5 A to supply direct current (DC) power to a tesla coil system, the second component. The adjustable voltage output of the DC power supply controlled the generated high voltage from the tesla coil, which was measured by a high voltage probe connected to a digital oscilloscope (Tektronix, model TDS 2012). The refined palm olein volume for each experiment was 25 mL, measured in a 50 mL graduated cylinder. 200 rpm of magnetic stirring provided efficient mixing for every run. The flow rates of H_2 and He gases were controlled by digital mass flow controllers (Unit Instruments, model UFC-1000, calibrated for each gas). The system setup is shown in Fig. 18 and the generated plasma is displayed in Fig. 19.

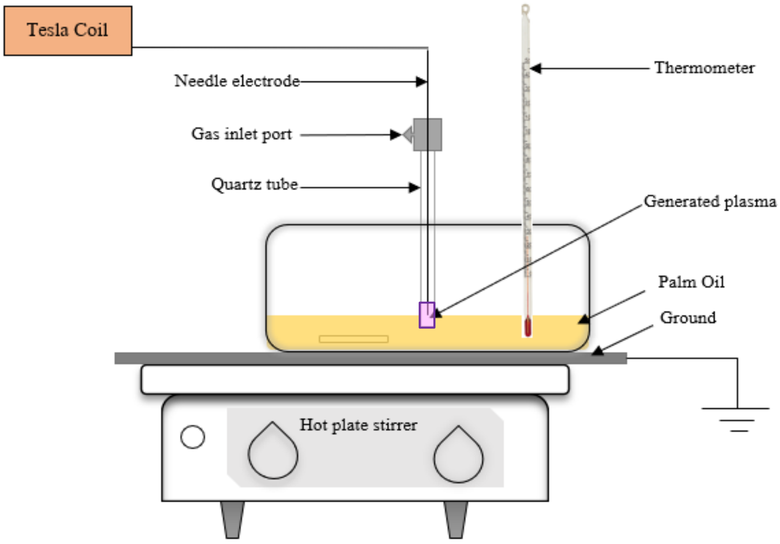


Figure 16 Drawing of constructed needle-in-tube DBD plasma hydrogenation chamber

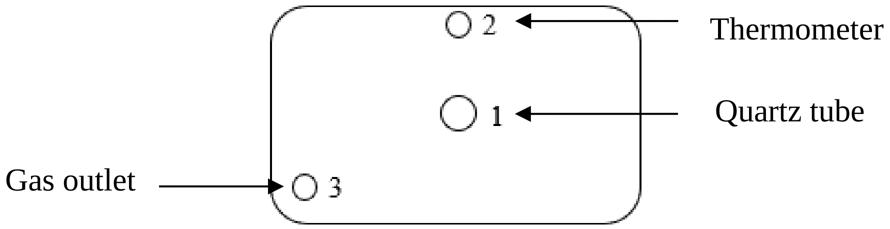


Figure 17 Lid top view

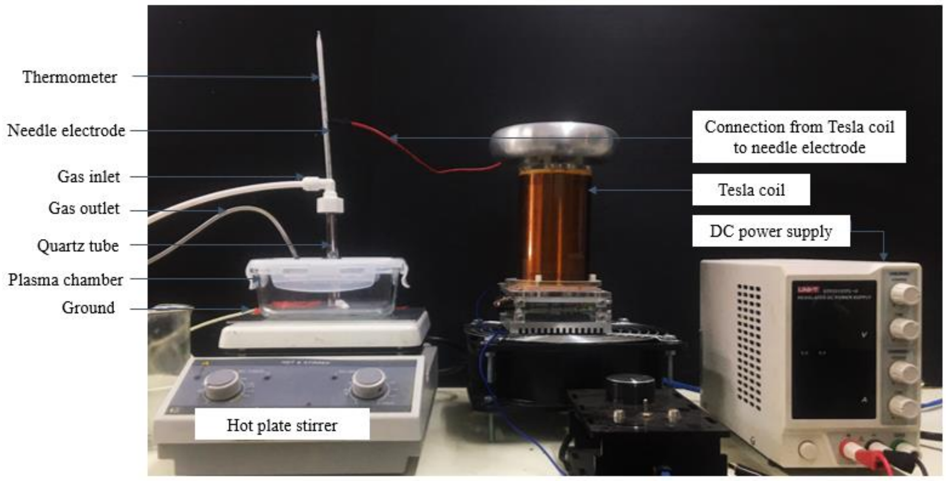


Figure 18 Picture of needle-in-tube DBD plasma chamber and high voltage, high-frequency power supply system

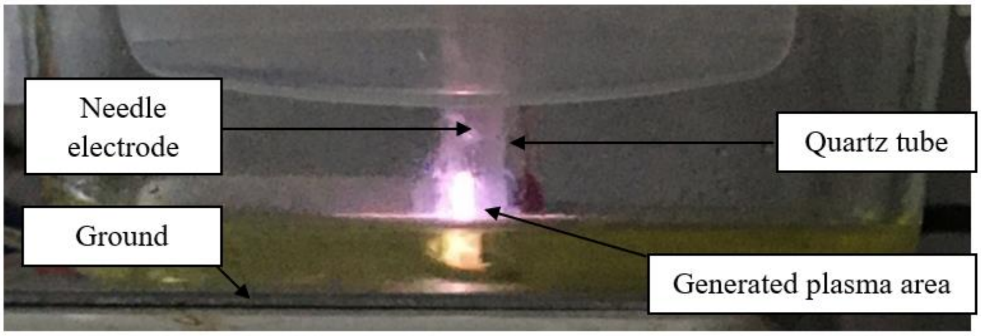


Figure 19 Generated plasma

4.2.3 Hydrogenation and evaluation

Five parameters were evaluated as follows: H_2: He mixed carrier gas concentration ratio (25 - 100% H_2), input power (20 - 80 W), total gas flow rate (0.25 - 1.5 L/min), gap size between the needle tip and the oil surface (0.25 – 1 cm) and reaction time (0 - 15 h). The parameters used in each trial were defined in Table 5. He gas was chosen as the carrier gas because it was more effective in plasma generation than H_2 gas [46]. Other gases, for example, nitrogen gas (N_2), were not chosen because of the possibility of nitride or cyanide formation, presenting harm to the environment and the human body. All experiments were performed independently triplicate. The reported values represent the averages, and the error bars show one standard deviation of the data. IBM SPSS STATISTICS® version 22.0 (IBM Corp., Armonk, N.Y., USA) with Tukey HSD's test was used to analyze statistical data. The p-value of < 0.05 is considered statistically significant. The subgroup (a, b, c and d) of the result was used to provide the significant differences. After the plasma treatment of each experiment, the sample was collected after 3-5 min of continuous stirring by a magnetic stirrer to ensure homogeneity. Each sample was collected at a minimum of 3 positions in the plasma chamber to represent the average of the whole material.

Table 5 Experimental parameters

Experiment No.	Parameters						
	H_2 concentration (%)	Input power (W)	Gas flow rate (L/min)	Gas-filled gap size (cm)	Reaction time (h)	Voltage** (V)	Current** (A)
1	0	40	1	0.5	0.5	15.40±0.1	2.60
2	25					16.00±0.2	2.50
3	50					16.67±0.1	2.40
4	75					17.23±0.2	2.35
5	90					17.55±0.2	2.30
6	100					17.90±0.1	2.26
7	100*	20	1	0.5	0.5	13.5±0.01	1.50
8		40				17.90±0.1	2.26
9		60				21.50±0.01	2.80
10		80				23.65±0.02	3.40
11	100*	40*	0.25	0.5	0.5	17.55±0.1	2.30
12			0.5			17.57±0.1	2.29
13			1			17.65±0.1	2.26
14			1.5			17.67±0.1	2.27
15	100*	40*	0.5*	0.25	0.5	17.67±0.1	2.25
16				0.5		17.57±0.1	2.29
17				1		17.45±0.2	2.33
18	100*	40*	0.5*	0.5*	15 (Sampling every 3 h)	17.70±0.2	2.29

* Most effective condition of each parameter

** Voltage and current outputs from DC power supply

Evaluations of IV, AV and SMP

After plasma treatment, the treated refined palm olein properties were assessed with an IV, AV, and slipping melting point (SMP), with each triplicate determination.

The IV was used to measure the degree of unsaturated oil reacting with iodine. By following the IUPAC 1987 standard [46], 0.2 g of the sample was mixed with 25 mL Wijs solution and 15 mL cyclohexane. The mixed solution was placed in the dark for 1-2 h and the reaction was discontinued by adding 150 mL distilled water and 20 mL potassium iodide. Titration with a 0.1 N sodium thiosulfate solution with a starch solution as an indicator was performed.

The AV indicates the presence of acidity in the oil which can be evaluated following the IUPAC 1987 standard [46] as follows: 2 g of the sample was mixed with 25 mL 95% ethanol and 25 mL diethyl ether and was subsequently titrated with a 0.1M potassium hydroxide solution with 0.5 mL of a 0.1% phenolphthalein solution as an indicator.

The SMP is defined as the melting point of oil and fat which can be determined based on PORIM 1995 [47]. An open-ended capillary tube was used to contain the solid (fat) and the temperature that the sample started to melt was recorded as the SMP.

Texture Analysis

The texture is one of the most important properties of margarine relative to the amount of solid content [2] that is used to identify the type of margarine. Different techniques can be employed to determine this characteristic of margarine by analyzing consistency, hardness, and spreadability [83]. In the present study, hardness was chosen to be evaluated. The hardness values were measured using a texture analyzer (Shimadzu, model EZ-X). The sample was tested using male and female 45° cone probes with 50 N compression force. The male cone penetrated the sample contained in the female cone with a 13 mm distance with 10 mm/min speed, 2.5 mm indentation, 50 N and 22 ± 2°C testing temperature [82] at the Nation Science and Technology Development Agency, Thailand. Triplicates of the sample were evaluated.

Fatty acid composition

The fatty acid composition of the hydrogenated oil samples was analyzed at the Research and Service Laboratory, The Halal Science Center, Chulalongkorn University using the gas chromatography-mass spectrometry (GC–MS) technique together with an in-house method modified following the Journal of Lipid Research, vol. 27, 1986. A gas chromatography (Trace 1310, Italy) with a TR-FAME column was utilized to analyze the percentage of fatty acid composition, including the percentages of *cis*- and *trans*-isomers. In brief, 3 g of the blended sample (if the sample is solid, it needs to blend first) in a screw cap tube was added with 12 mL of 2:1 v/v dichloromethane: methanol solution. The mixture was vortexed every 15 min for 1 h. A 0.1M KCl solution was added to the mixture at approximately 20% of the total volume and was centrifuged at 2,000 rpm for 10 min. The upper phase was discarded, and the solution was taken to perform methylation. The methylation procedure was performed by pipetting 200 µL of the sample into a screw cap tube and adding 1 mL of 0.5 mol/mL NaOH-methanol. The mixture was heated to 100°C for 15 min and was cooled down to room temperature. 2 mL of BF_3-methanol (14%) was added with heating and cooling down. 500 µL of hexane and 5 mL of saturated NaCl solution were added and the mixture was centrifuged at 1,000 rpm for 5 min at 25°C. The upper phase was taken to inject into the GC-MS. Duplicates of the sample were evaluated.

4.3 Results and discussion

4.3.1 Effect of H_2 gas concentration

The effect of H_2 concentration (25, 50, 75, 90 and 100%) in the mixed carrier gas with a comparison of statistically-significant differences ($p < 0.05$) grouped with letters a-d is demonstrated in Fig. 20. In addition, as the error bars in Fig. 20 indicate, there is a statistically significant difference between all investigated percentages of H_2 except for 25 and 50% H_2 which are not statistically different. The experimental condition was 1 L/min total gas flow rate, 29°C initial temperature, 40 W input power, 0.5 cm gas-filled gap size and 30 min reaction time. The trend with H_2 concentration was obvious -- the higher the H_2 concentration, the faster the hydrogenation reaction as more hydrogen atoms were present in the system and became hydrogen plasma. During the initial 30 min of plasma treatment, at 100% H_2 concentration, hydrogenation occurred the fastest as the IV was decreased from 60.75 to 52.89. The reaction rate based on the reduction in the IV was calculated to be 7.86 IV unit/30 min, which was higher than that of the previous investigation of Puprasit et al. (2020) who employed DBD plasma with a parallel-plate configuration achieving the reaction rate of 6.13 IV unit/30 min. At 25, 50, 75 and 90 % H_2, the reaction rate was 3.43, 4.03, 4.8 and 6.48 IV unit/30 min, respectively, signifying the advantage of high H_2 concentrations. Although the He gas interrupts the recombination of hydrogen atoms [46], with the IV reduction rate being higher than that of the parallel-plate configuration, the chance of recombination became much less and no He dilution was required.

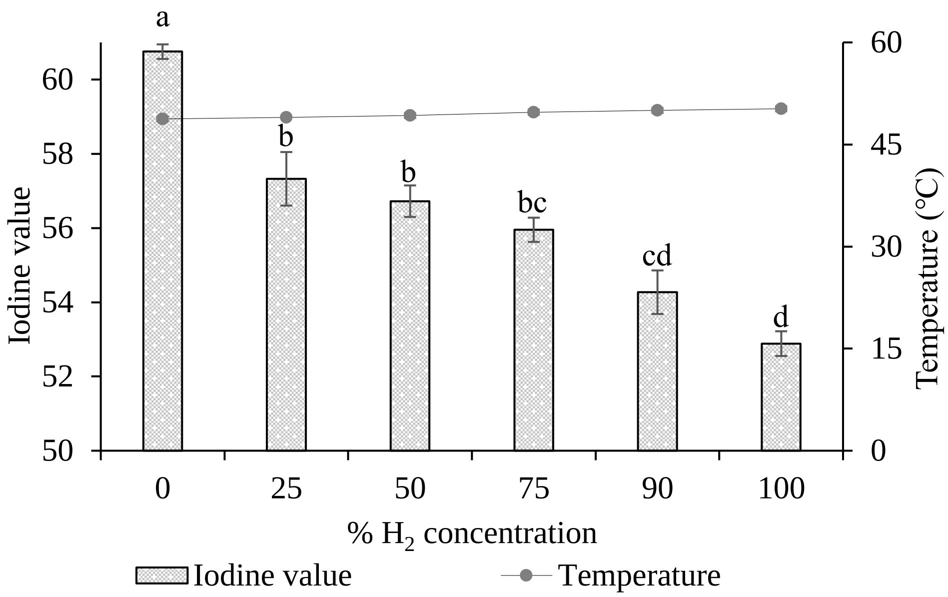


Figure 20 Effect of H_2 concentration on IV and temperature at end of reaction (25 mL refined palm olein, 29°C initial temperature, 1 L/min total gas flow rate, 40 W input power, 0.5 cm gas-filled gap size and 30 min reaction time)

By observing the 30-minute oil temperature history for each H_2 concentration as illustrated in Fig. 20, the case of 100% He showed the lowest temperature (48.75±0.35°C) while 100% H_2 exhibited the highest one (50.25±0.35°C) with a statistically significant difference. At 30 min, the temperature increased with increasing H_2 concentration with the corresponding decrease in IV. As hydrogenation is exothermic, the highest reaction rate results from 100% H_2 released heat the most. Although this is not desirable from the *trans*-fat generation point of view, the oil temperature at 30 min was still low (about 50°C) and should not cause any *cis-trans* isomerization. As concluded earlier that pure H_2 was the optimal parameter, this finding was highly beneficial, meaning that no He gas was required, so did the requirement to maintain an optimal H_2: He ratio all the time, making the process convenient to operate and control.

4.3.2 Effect of input power

The effect of input power (20, 40, 60 and 80 W) with a comparison of statistical significance is demonstrated in Fig. 21. The experimental condition was 1 L/min H_2 gas flow rate, 100% H_2 gas concentration, 29°C initial temperature, 0.5 cm gas-filled gap size and 30 min reaction time. As can be observed, the lowest IV was obtained from 40 W of input power, which was reduced from 60.75 (feed oil) to 52.89. The reaction rate based on the reduction in the IV was calculated to be 7.86 IV unit/30 min. At 20, 60 and 80 W, the reaction rate was 3.07, 6.96 and 5.57 IV unit/30 min, respectively. Referring to the input power (voltage × current output of the DC power supply) vs. Tesla coil discharge voltage shown in Fig. 22, 40 W of input power resulted in the Tesla coil's discharge voltage of 0.603 kV. The higher the input power, the higher the discharge voltage and the supposedly higher plasma density. This is because more H_2 molecules were quickly dissociated into free radicals [84]. However, the results also revealed that the hydrogenation performance became degraded when the input power was greater than 40 W, meaning that fewer hydrogen atoms were added to the unsaturated carbon double bonds. This is explained by the increase in temperature when the increase in input power. The temperature at the end of the 30-min reaction for each power level was also recorded and is shown in Fig. 21. The temperature rose from 48.5±0.70 to 61±0.70 and 74.75+0.35°C when the input power was increased from 40 to 60 and 80 W, respectively. As the hydrogenation rate depends on temperature according to Arrhenius' law [85], higher temperatures (as a result of higher input power) should promote the reaction rate to become faster. High temperatures should not increase the H_2 solubility in the investigated gas-liquid phase reaction as the hydrogenation was always performed at atmospheric pressure (0.1 MPa) [86]. High temperatures may result in greater desorption, decreasing the reaction rate. Sancheti et al. (2017) and Zuo et al. (2022) have reported that the IV of hydrogenation reaction could be increased (decrease in reaction rate) when the temperature was increased. Also, the increasing IV at 40, 60 and 80 W in the present investigation showed no statistical difference.

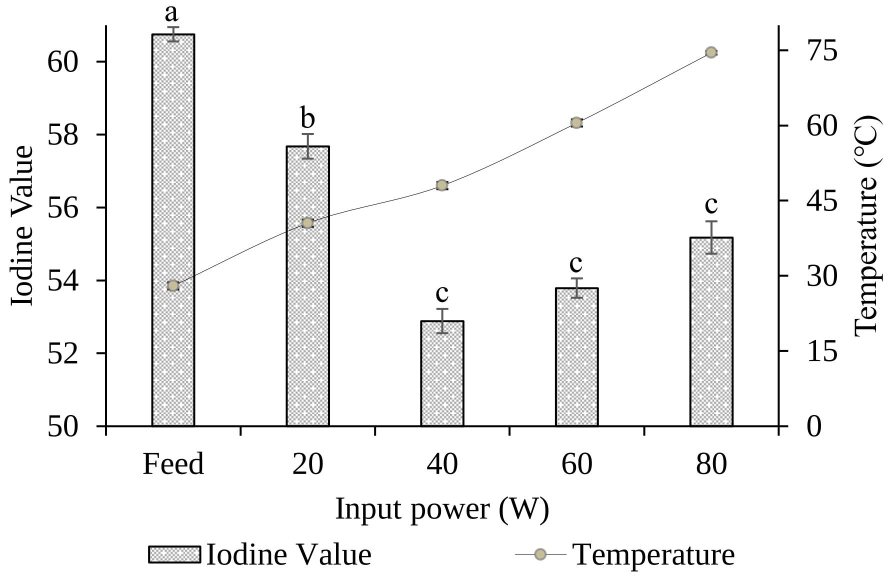


Figure 21 Effect of input power on IV and temperature at end of the reaction (25 mL refined palm olein, 29°C initial temperature, 1 L/min gas flow rate, 100% H_2 gas concentration, 0.5 cm gas-filled gap size and 30 min reaction time)

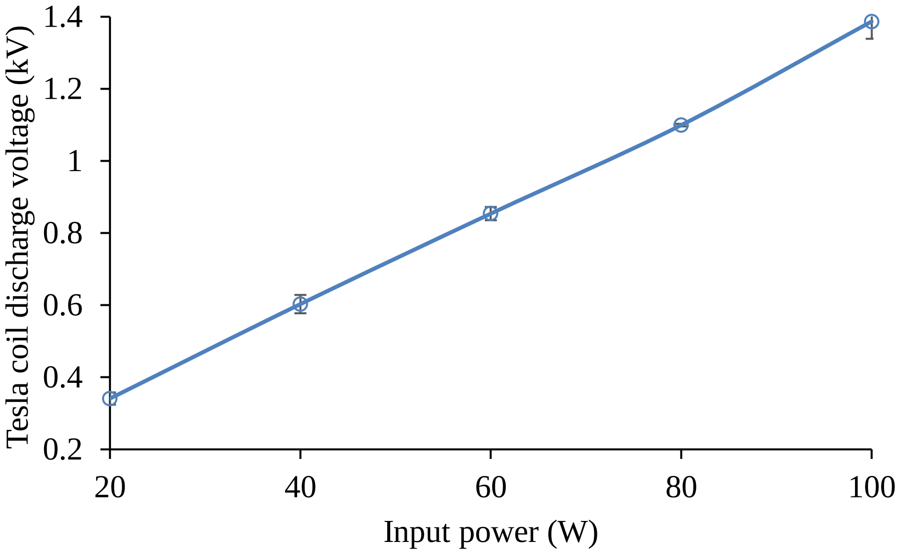


Figure 22 Relationship between input power and tesla coil discharge voltage

4.3.3 Effect of gas flow rate

The effect of gas flow rate (0.25, 0.5, 1 and 1.5 L/min) with a comparison of statistical significance is demonstrated in Fig. 23. 40 W input power, 100% H_2, 29°C initial temperature, 0.5 cm gas-filled gap size and 30 min reaction time were the set conditions. At the end of the plasma treatment, the temperature rose to about 50°C for all conditions, indicating that different gas flow rates did not affect the temperature during the treatment. The lowest IV was obtained from the 0.5 L/min case, which was reduced from 60.75 (feed oil) to 51.66. The reaction rate based on the reduction in the IV was calculated to be 9.09 IV unit/30 min. At 0.25, 1 and 1.5 L/min, the reaction rates were 6.55, 7.86 and 6.43 IV unit/30 min respectively. The hydrogenation reaction occurred less at a lower flow rate (0.25 L/min) due to less H_2 gas being supplied into the quartz tube and correspondingly less atomic hydrogen being generated in the system to react with the refined palm olein. At higher flow rates of 1 and 1.5 L/min, the effect of enhanced gas flow velocity must have carried hydrogen atoms (and hydrogen molecules) out of the quartz tube too quickly to be ineffective physical contact with the oil. Besides, the thermal fluctuation in the discharge area induced the gas expansion and hence lowered the gas density. Increasing the flow rate affects the length of the plasma and the flow pattern of the hydrogen atoms [87]. In other words, the higher the flow rate, the longer the plasma length. At high flow rates, it was most likely that the hydrogen atoms were dispersed throughout the area, shortening the exposure time to the unsaturated carbon bonds. It was also possible that high flow rates created holes through the oil layer surrounding the quartz tube allowing hydrogen free radicals to leave the system unreacted. Based on the statistical analysis, the increase from 0.5 to 1.5 L/min was less significant difference in the IV value as well as their temperature.

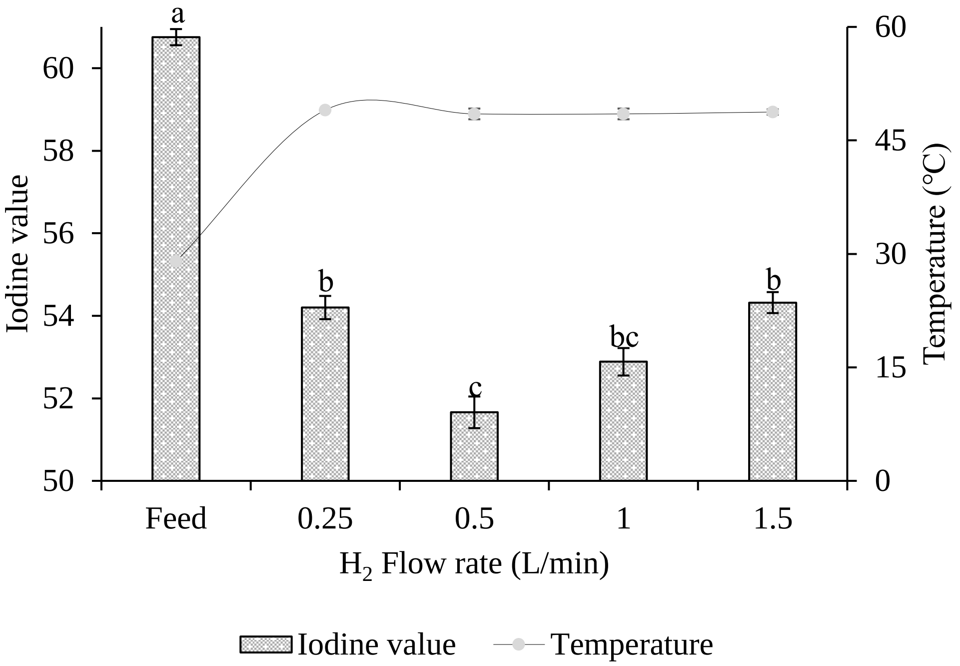


Figure 23 Effect of H_2 flowrate on IV and temperature at end of reaction (25 mL refined palm olein, 29°C initial temperature, 40 W input power, 100% H_2 gas concentration, 0.5 cm gas-filled gap size and 30 min reaction time)

4.3.4 Effect of gas-filled gap size

The effect of gas-filled gap size (0.25, 0.5 and 1 cm) with a comparison of statistical significance is demonstrated in Fig. 24. 1 cm was the largest gap size studied because plasma was difficult to generate with a larger gap size. 40 W input power, 100% H_2, 29°C initial temperature, 0.5 L/min gas flow rate and 30 min reaction time were the set conditions. The lowest IV was obtained from a 0.5 cm gap size, which was reduced from 60.75 (feed oil) to 51.50. The reaction rate based on the reduction in the IV was calculated to be 9.25 IV unit/30 min. At 0.25 and 1 cm gap size, the reaction rate was 5.02 and 7.14 IV unit/30 min respectively. It is a commonly known DBD plasma characteristic that a smaller gas-filled gap increases the plasma intensity and vice versa [88]. However, for the 0.25 cm gap, hydrogenation became less effective. The likely explanation is that as a lower breakdown voltage was required for a smaller gap size, the lower voltage was insufficient to effectively dissociate the H_2 molecules. The required lower voltage follows Paschen's law, $V_b = f(pd)$, [89, 90] where V_b is the breakdown voltage which is a function of pressure (p) and gap size (d). Thus, under the same atmospheric pressure, a smaller gap size required a lower breakdown voltage. Conversely, a wider gap size required a higher breakdown voltage, generating a lower density plasma and decreasing the temperature in the plasma chamber [91] as illustrated in Fig. 24. A constant power of 40 W was maintained for all gap sizes by appropriately adjusting the current output of the DC power supply.

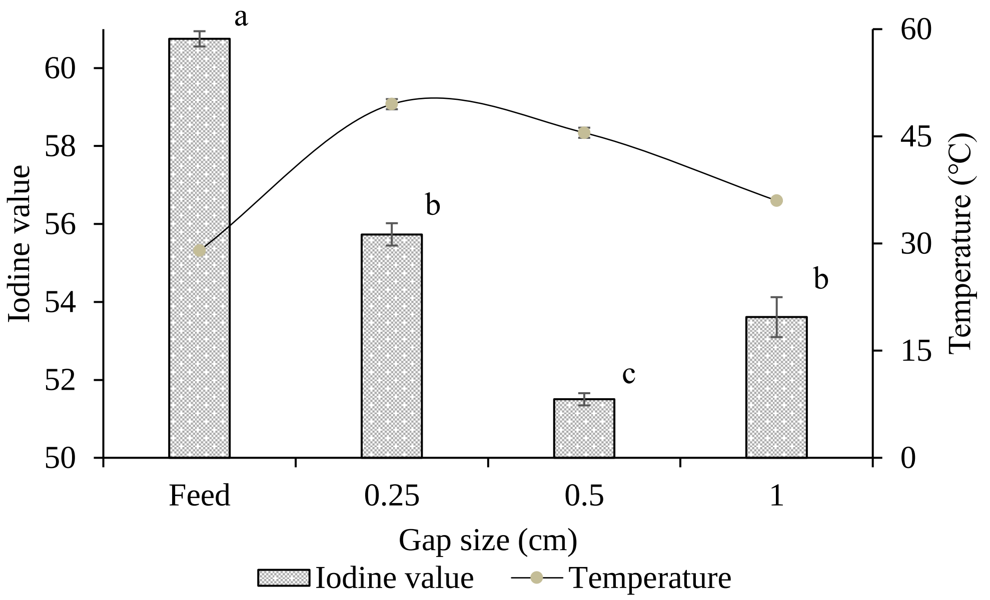


Figure 24 Effect of gas-filled gap size on IV and temperature at end of reaction (25 mL refined palm olein, 29°C initial temperature, 0.5 L/min gas flow rate, 40 W input power, 100% H_2 gas concentration and 30 min reaction time

4.3.5 Effect of reaction time

The effect of reaction time was investigated to determine the most suitable refined palm olein hydrogenation time in the designed plasma hydrogenation system. The appropriate conditions determined earlier were set as follows: 100% H_2 gas concentration, 29°C initial temperature, 40 W input power, 0.5 L/min gas flow rate and 0.5 cm gas-fill gap. The experiment was conducted continuously for up to 15 h with sample collection every 3 h to observe the transformation of the feed refined palm olein from liquid to semi-solid and finally to solid. The reduction of IV with reaction time is demonstrated in Fig. 25.

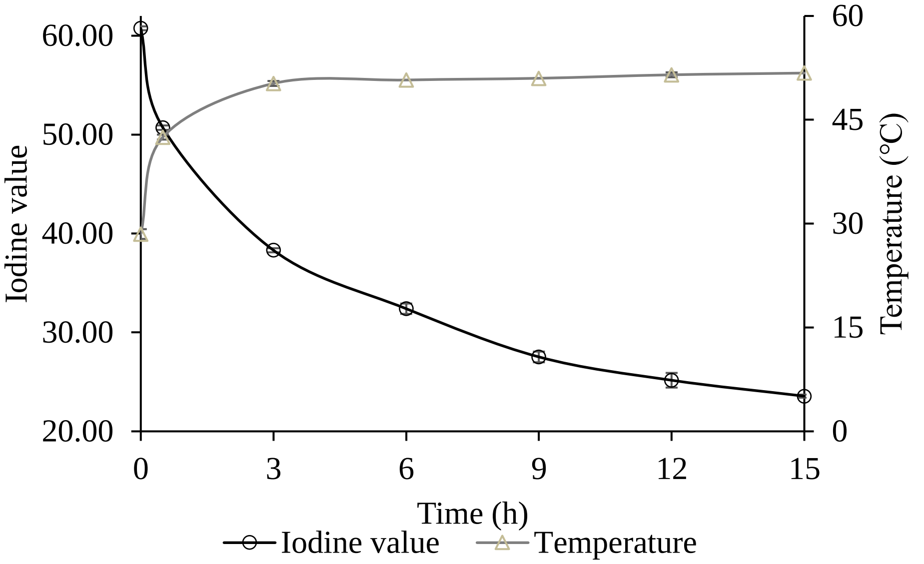


Figure 25 Effect of reaction time on IV and temperature (25 mL refined palm olein, 29°C initial temperature, 0.5 L/min gas flow rate, 40 W input power, 100% H_2 gas concentration and 0.5 cm gas-filled gap size)

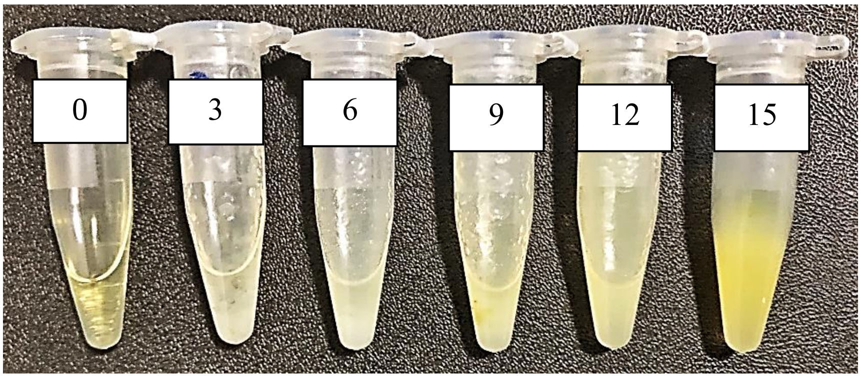


Figure 26 Collected hydrogenated refined palm olein samples (numbers indicate plasma treatment time (h) with 0 h being feed refined palm olein)

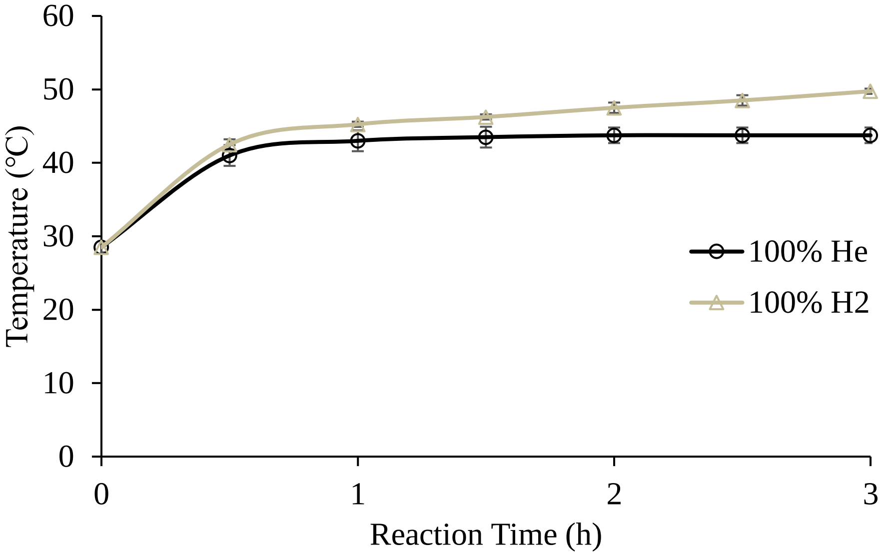


Figure 27 Temperature histories of 100% He and 100% H_2 cases

From the results of IV vs. reaction time, the IV effectively decreased with increasing reaction time implying that the fatty acids chains became more saturated. During 0 – 3 h of hydrogenation with the IV of 60.75 (feed oil) and 38.15 (3 h), the oil was still liquid. The color of the hydrogenated oil samples became pale at 3 and 6 h with the presence of small solid particles. However, from 9 to 15 h, the color became yellow again with more solid particles as depicted in Fig. 26. During 12 – 15 h of treatment time with the IV of 25.17 (12 h) and 23.56 (15 h), the oil finally became solidified. This much additional hydrogenation time resulted in a harder and finally spreadable product. As the oil became more and more viscous with plasma treatment time, the oil circulation in the region surrounding the quartz tube became more and more restricted. This implies that it would become harder to provide additional hydrogenation which is evident from Fig. 25 as the slope of the curve (i.e., the hydrogenation kinetics and mass transfer) reduced with reaction time. The effect of hydrogenation on the refined palm olein temperature is illustrated in Fig. 27, which shows the temperature histories for 100% He and 100% H_2 cases for up to 3 h. For the case of pure He, the temperature stabilized at about 44°C after 0.5 h. This was expected as no hydrogenation taking place. The thermal energy deposited by the plasma onto the oil was balanced with the dissipated energy to the environment, as well as the thermal energy carried away with the gas leaving the system. For the case of pure H_2, the temperature kept increasing to about 50°C after 3 h. The increase temperature was obviously from the exothermic hydrogenation reaction [82, 92]. In future experiments, it is advised to increase the stirring speed when the oil became thicker to enhance oil circulation and reduce the reaction time.

4.3.6 Properties of hydrogenated refined palm olein

Fatty acid composition

The fatty acid composition was evaluated by GC-MS. Table 6 shows the comparison of the fatty acid composition of fresh refined palm olein, the oil treated for 15 h in the needle-in-tube DBD plasma reactor of the present study with statistically significant differences in percent composition of saturated and unsaturated fatty acid, and the oil treated for 12 h in the parallel-plate DBD plasma reactor of the previous investigation [82]. The needle-in-tube configuration resulted in more saturated fat conversion than the parallel-plate configuration which was desirable. Most importantly, no *trans*-fat was detected.

Table 6 GC-MS results of individual fatty acids composition and properties of refined palm olein, hydrogenated oils in needle-in-tube DBD plasma reactor and parallel-plate DBD plasma reactor.

Composition (%)	Refined palm olein	Needle-in-tube DBD plasma (15 h)	Parallel-plate DBD plasma (12 h) [82]
Saturated	**40.82^{a}±0.05**	**68.70^{b}±0.07**	**57.66**
C8:0	0.01	-	0.02
C10:0	0.002	-	0.02
C12:0	0.22	0.33±0.01	0.38
C14:0	1.08	1.15	1.51
C15:0	0.04	-	0.06
C16:0	33.27±0.01	58.05±0.06	35.8
C17:0	0.1	-	0.18
C18:0	5.55±0.01	9.17	18.85
C20:0	0.41	-	0.69
C22:0	0.07±0.04	-	0.07
C24:0	0.08±0.01	-	0.08
Unsaturated	**59.11^{a}±0.12**	**31.39^{b}±0.01**	**42.34**
C16:1	0.23±0.01	-	0.11
C18:1 n-9 *trans*	-	-	5.24
C18:1n-9 *cis*	43.55±0.04	30.07±0.01	32.87
C18:2 n-6 *trans*	-	-	
C18:2 n-6 *cis*	13.16±0.42	1.33	4.05
C18:3 n-6	0.03	-	
C18:3 n-3	0.15	-	0.02
C20:1 n-9	0.12	-	0.05

unidentified peak	1.88± 0.04	-	
Properties			
SMP (°C)	9.33±0.5	36.33±0.5	21.67
AV (mg KOH/g oil)	0.47±0.02	0.32±0.03	0.28

* a, b is the subgroup to provide the significant differences

For the refined palm olein, 22 types of fatty acids were detected. The main types were 43.55±0.04% oleic acid (C18:1n-9 *cis*), 33.27±0.01% palmitic acid (C16:0), 13.16±0.42% linoleic acid (C18:2n-6 *cis*), 5.55±0.01% stearic acid (C18:0) and 1.88±0.04% unidentified peak. For the treated refined palm olein after the needle-in-tube DBD plasma application, 6 types were detected. The main types were 58.05±0.06% palmitic acid (C16:0), 30.07±0.01% oleic acid (C18:1n-9 *cis*) and 9.17% stearic acid (C18:0). The result clearly demonstrates the effectiveness of the plasma hydrogenation, with the total saturated content increasing by 68.27% in 15 h. A significant decrease in the unsaturated fatty acids especially oleic acid and a significant increase in the saturated fatty acids especially palmitic acid were observed, which directly resulted from hydrogen atoms adding into available carbon double bonds. Compared to Puprasit et al.'s [82] earlier report on refined palm olein hydrogenation with parallel-plate DBD plasma for 12 h, the saturated content was increased by 3.44%/h being 32.27% slower than the current work, and most importantly with 5.24% C18:1 n-9 *trans* being detected. Compared with conventional palm olein hydrogenation using 0.06-0.2% nickel catalyst at 180-200°C generating *trans*-fatty acid as much as 7.15% with the IV reducing from 55.2 to 46.0 with 4 kPa which was vacuum condition in 1.5 h [58], the novel catalyst-free plasma reactor is successful and is highly capable of refined palm olein hydrogenation at ambient conditions. It allows the reaction to occur gradually but efficiently without *cis-trans* isomerization in the system.

SMP and AV

The result of the SMP evaluation is demonstrated in Table 6. As a comparison with refined palm olein, the SMPs for needle-in-tube and parallel-plate configurations were 9.33±0.5 (refined palm olein), 36.33±0.5 (15 h) and 21.67 °C (12 h), respectively. The margarine synthesized in the needle-in-tube configuration was more culinary-suitable than that produced in the parallel-plate plasma reactor because the SMP was very close to the oral melting temperature of 35 °C [93] and the human body temperature of 37 °C, which is preferable for consumers to be able to melt in the mouth and increase the taste. According to the survey of margarine at the Turkish and Iranian markets, the melting values were in the range of 31-41 °C [56, 57]. Thus, the SMP of the produced margarine situates suitably in the range of commercial margarine.

The AV is one of the fundamental indicators to determine the amount of free fatty acids present in a fat [56]. The result of the AV analysis is shown in Table 6. As a comparison with refined palm olein, the AVs for needle-in-tube and parallel-plate configurations were 0.47±0.02 (refined palm olein), 0.32±0.03 (15 h) and 0.28 mg KOH/g oil (12 h), respectively. The AV of the present study was reduced by about 32%. The most likely explanation is that plasma dissociated free fatty acids. Cubas et al. (2016) converted industrial waste frying oil into biodiesel using corona discharge plasma. The findings were that the acid value was substantially reduced from 2.16 to 0.48 mg KOH/g without any free fatty acid pretreatment before feeding the oil to the reactor, implying that plasma eliminated free fatty acids in the oil. The reduction in the AV provides advantages to extending the shelf life of the margarine, reducing costs in various aspects such as production, storage and waste disposal [60].

Texture Analysis

The result of the texture analysis is shown in Fig. 28. The hardness force of 1.0125 N at 15 h of hydrogenation was obtained. The hardness force of commercial margarine brands 1 and 2 was 0.6251 and 0.9993 N, respectively. The previous investigation by Puprasit et al. [82] using the parallel-plate geometry found the hardness force at 8 h to be 0.4537 N, and at 12 and 16 h, the hardness force was more than 8 N, being outside the range of commercial margarine. The synthesized margarine of the present investigation exhibited a hardness force very close to that of commercial margarine brand 2.

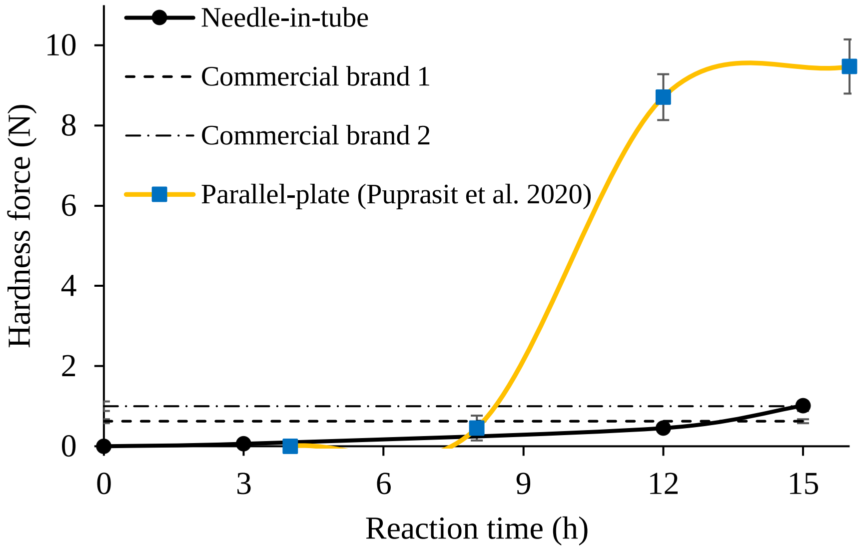


Figure 28 Result of texture analysis (25 mL refined palm olein, 29°C initial temperature, 0.5 L/min gas flow rate, 40 W input power, 100% H_2 gas concentration, 0.5 cm gas-filled gap size and 15 h reaction time)

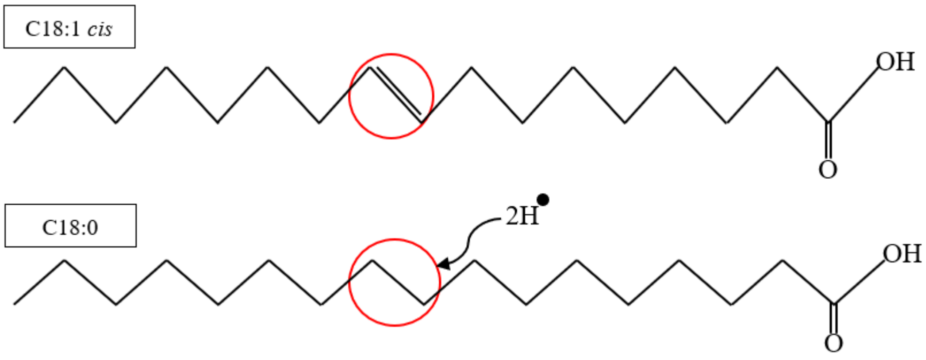
4.3.7 Proposed reaction mechanisms by DBD plasma

Four possible reactions are proposed to have occurred during the plasma hydrogenation: hydrogenation, conjugated double bond, Diels-Alder and cracking. The oil hydrogenation was achieved using the low-temperature plasma's unique properties where H_2 gas is energized sufficiently to allow dissociation into reactive species of hydrogen including H^+, H^{3+} and $H^\cdot$ which were the species normally generated in a cold plasma as reported in the study of Yepez et al. [81], as well as other active species such as energetic electrons, neutral and excited molecules/atoms that act as a catalyst in a chemical reaction [94]. The oil hydrogenation mechanism can be described by the fatty acid composition analysis in Table 6 and Fig. 29a. showing that the unsaturated fatty acids were decreased by the plasma treatment. The process started from the double bonds of fatty acid molecules being stimulated by the generated reactive species and the plasma photon. The hydrogen atoms which were close to the double bonds particularly at bis-allylic and allylic positions had a high probability to be dissociated into $H^\cdot$ free radicals causing the instability of molecules and the double bonds (π bonds) moving during this step. Then, the hydrogen radicals were allowed to incorporate at the π bonds becoming single bonds that were stable molecules.

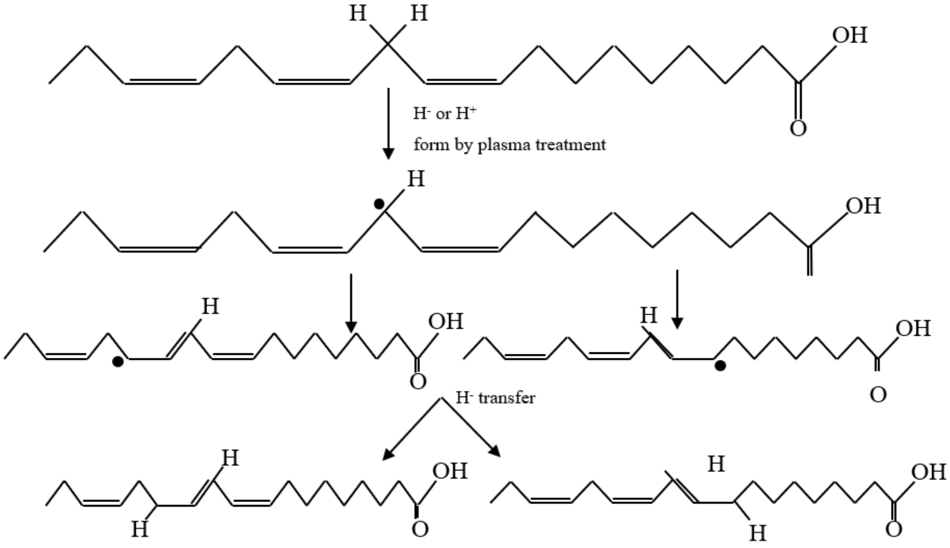
According to the concept, the carbon double bonds in C16:1, C18:1, C18:2, C18:3, and C20:1 were broken causing free radical formations which allowed hydrogen radicals incorporation into the single bonds which were called conjugated double bonds. A possible mechanism of conjugation double bonds is demonstrated in Fig. 29(b). When a conjugated double bond is formed, Diels-Alder was possible to occur between triglyceride molecules. In a 2009 patent titled “Cationic polymerization of biological oils with superacid catalysts” by Ionescu and Petrovic [95], it was reported that the cationic polymerization of soybean oil went through a pericyclic reaction like Diels-Alder. This was caused by the formation of conjugated double bonds on the hydrocarbon chain such as linoleic and linolenic [95]. Diels-Alder is presented in Fig. 29(c).

The cracking reaction was also discovered with the mechanism shown in Fig. 29(d). It should be noted that the unexpected increase in C16:0 was observed. It could be because the long chain of stearic acid (C18:0) has a tendency of breaking, becoming palmitic acid (C16:0) and ethyl radical (C_2H_5) [94]. Hao et al. (2018) studied the mechanism of hydrogenating heavy oil in a plasma-driven catalytic system. By experimenting with the ethyl radical reacting with a hydrogen atom at the end position of the side chain of the benzene ring (e.g., $-CH_3$ or $-C_2H_5$) compared with the ethyl radical reacting with the carbon atoms of the benzene ring, the result revealed that the radical was inclined to capture the hydrogen atom (barrier < 70 kJ/mol) rather than attack the carbon atoms of the side chain (barriers > 220 kJ/mol) probably forming into a bigger alkane (such as ethane) and a smaller alkyl-benzene. With this possibility, the ethyl radical could form gaseous molecules and flow out of the system with a continuous flow of H_2. A dedicated study to determine the extent of the reaction will be performed in a future investigation. In this present work, the increase of C16:0 was as much as 74.49%. This can be explained by considering the bond dissociation energy (BDE), which is the energy required to break a bond and form a molecule. In a normal alkane chain, it was reported that the weakest bond was C_2H_5–nC_iH_{2i+1} with 359.8 kJ/mol [96]. This implies that the ethyl group ($-C_2H_5$) in stearic acid (C18:0) was able to be split causing the increase in palmitic acid (C16:0) [88].

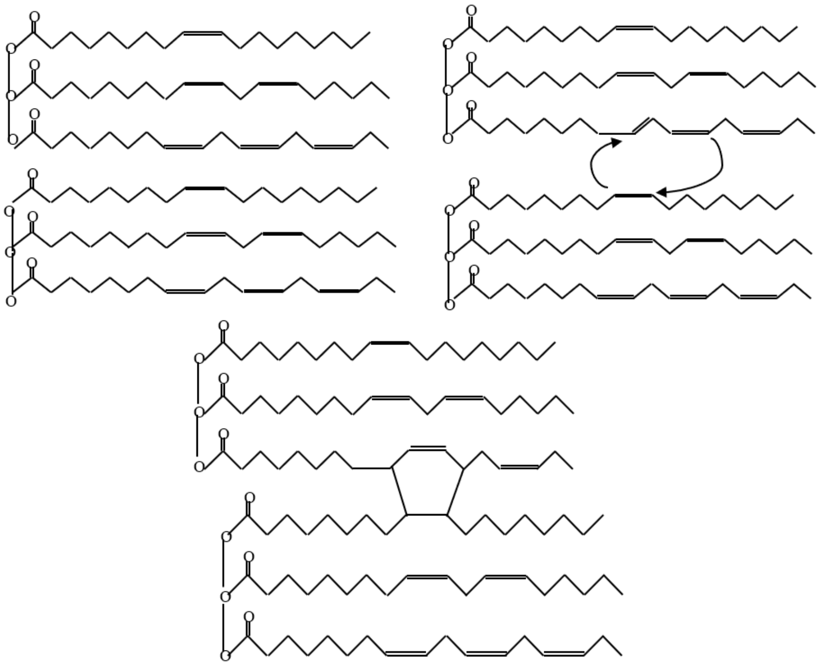
a) Hydrogenation



b) Conjugation



c) Diels-Alder



d) Cracking

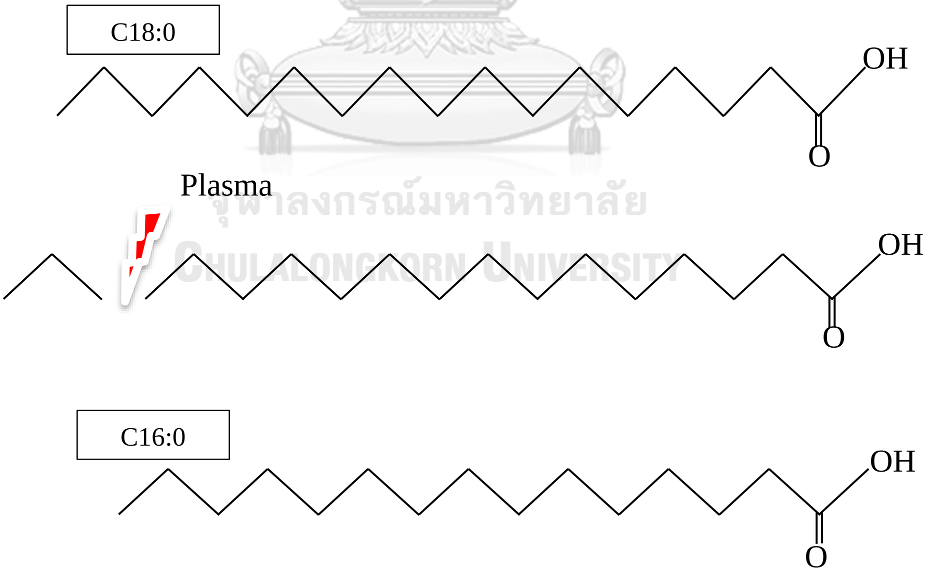


Figure 29 Proposed reaction mechanisms: a) hydrogenation, b) conjugation double bond, c) Diels-Alder and d) cracking

The new and effective method to produce *trans*-fat free margarine from refined palm olein utilized non-thermal plasma hydrogenation with the needle-in-tube DBD plasma reactor powered by a Tesla coil. In 15 h of treatment, the total unsaturated fatty acid content decreased by 31.39±0.007% while the total saturated fatty acid content increased by 68.695±0.067%. The IV, AV and SMP were 23.56 IV unit, 0.32±0.03 mg KOH/g oil and 36.33±0.5°C, respectively, with an almost perfect texture compared to commercial margarines. This novel hydrogenation method shows several advantages. It is simple and inexpensive to operate and maintain. It is also very environmentally friendly because no metal catalyst is required. The system operates at room temperature and atmospheric pressure, so equipment such as a heater, pressure chamber or vacuum pump is not required, providing operator safety.

4.4 Conclusions

The non-thermal DBD plasma with the needle-in-tube configuration powered by a Tesla coil has been successfully demonstrated to hydrogenate refined palm olein to produce *trans*-fat free margarine. The advantages of this configuration were the low-temperature reaction facilitating zero *trans*-fatty acids formation and tube configuration confining generated hydrogen free radicals within the tube and forcing them to bubble through the oil layer, significantly enhancing the probability of contact with the oil. Using 40 W input power, 0.5 cm gas-filled gap size, 100% H_2, 0.5 L/min H_2 gas flow rate, room temperature (29°C) and 15 h of reaction time for 25 mL refined palm olein in the absence of a catalyst provided the lowest IV (from 60.75 to 23.56) with the texture being very similar to that of commercial margarine. The generated hydrogen free radicals were hypothesized to perform hydrogenation by reacting with carbon-carbon double bonds, converting poly- and monounsaturated fatty acids into saturated ones. This novel and highly effective catalyst-free plasma hydrogenation system can be used as an alternative, environmentally friendly and economically feasible method to produce zero-*trans*-fat margarine. The application could extend further into the hydrogenation of other liquid-based processes such as biodiesel to increase the oxidation stability.

CHAPTER 5

5.1 Economic valuation assessment

An economic evaluation was conducted using the retail price of bottled refined palm olein oil, electricity cost and H_2 gas price—the variable cost excluding fixed costs: wage, reactor building, and facility construction costs. The cost of refined palm olein oil is 48 Thai baht per liter, based on the price at a local supermarket store in Bangkok. 25 mL was used in the experiment, so the refined palm olein cost was 0.0358 USD (exchange rate of 33.5 Thai baht/USD). The Thai electricity rate was 0.15 USD per kWh. The H_2 gas price was 76.66 USD per one 6-m^3 cylinder. The H_2 gas cost was calculated based on the amount of H_2 required for the hydrogenation reaction. It was calculated from the reduction percentages of unsaturated fatty acids (C18:1, C18:2, and C18:3) that were transformed into saturated fatty acids, as demonstrated in Tables 4 and 6. The ideal gas law ($n=pV/RT$) was used to calculate. This assumes that the discharged H_2 and He gas can be recycled using a recirculating pump.

Table 7 demonstrates the production cost by comparing parallel-plate DBD plasma and needle-in-tube DBD plasma methods. Therefore, by estimating the production cost, only the cost of electricity and H_2 gas is considered. The parallel-plate DBD plasma costs 2.99 USD per liter, which is 4.24 times cheaper than the needle-in-tube DBD plasma, which costs 12.69 USD per liter. Consequently, most of the cost were electricity related costs. With the treatment time of 12-15 h, it was expected that the electricity cost would be the most significant cost component. A further study attempting to reduce the treatment time or the power consumption of the transformer is highly recommended. A preliminary market survey revealed that commercial margarine in Thailand costs about 2.40 - 4.50 USD per liter, depending on the brand. Thus, the parallel-plate DBD plasma is more cost-effective.

Table 7 Production cost of margarine production using plasma technology

Composition (%)	**Parallel-plate DBD plasma**	**Needle-in-tube DBD plasma**
C16:0	35.8	58.05±0.06
C18:0	18.85	9.17
C18:1	32.87	30.07±0.01
C18:2	4.05	1.33
C18:3	0.02	0
Batch volume (mL)	25	25
refined palm olein cost per liter (USD)	1.43	1.43
Reaction time (h)	12	15
Power consumption (kWh)	0.26	1.89
Electricity rate (USD/kWh)	0.15	0.15
Electricity cost per liter (USD)	1.56	11.26
Reacted H_2 per liter refined palm olein oil (mL)	6.32	11.94
H_2 price per liter (USD)	0.0128	0.0128
H_2 needed to produce margarine (USD)	0.0000808	0.000152832
Total production cost per liter (USD)	2.99	12.69

CHAPTER 6

6.1 Conclusion

The non-thermal dielectric barrier discharge (DBD) plasma has been successfully demonstrated to hydrogenate refined palm olein with very low or non-*trans*-fatty acid formation without using catalysts. These depend on electrode geometry, a reaction chamber and high voltage transformer design. With a parallel-plate configuration powered by a Neon-sign transformer the detected *trans*-fatty acid was 1.44%, demonstrating the *trans*-fatty acid formation generation rate decrease of only 0.07% in the IV which was about 6.12 times less than the traditional catalyst-based methods. The optimal conditions were: 15% H_2, 85% He mixed carrier gas concentration, 31°C initial temperature (room temperature), 0.5 cm gas-filled gap size and 8h of reaction time and producing the texture closest to commercial margarine. *Trans*-fatty acid was performed in the parallel-plate configuration because the wide space to generate plasma causes high-temperature reaction distribution to oil. These high possibilities transform *cis* to *trans* formation. Whether a Tesla coil powers with the needle-in-tube configuration, *trans*-fatty acid was not detected in this method. In this method the optimal conditions were: 40 W power input, 100% H_2 gas, 0.5 cm gas-filled gap size, 0.5 L/min H_2 gas flow rate, 29°C initial temperature (room temperature) and 15 h of reaction time. Thus, the needle-in-tube configuration was more suitable for margarine production by hydrogenation than the parallel-plate configuration. This novel and highly effective catalyst-free plasma hydrogenation system can be used as an alternative. It is environmentally friendly and an economically feasible method to produce low *trans*-fat or zero-*trans*-fat margarine. The application could extend further into the hydrogenation of other liquid-based processes such as biodiesel to increase oxidation stability.

6.2 Limitation of research

The limitations of the study are as follows:

- The neon power supply was limited to only voltage adjustment. A power supply with adjustable frequency, current, and voltage was required.
- Difficulty to measure plasma density in a small chamber with refraction.
- The reaction was difficult to control because the temperature changed during the reaction. Temperature is an essential parameter for the hydrogenation reaction.
- A stirring system for circulation was required.

6.3 Suggestions for future work

As a result of the study, most of the production cost was electricity used in the plasma generation, and several variables are of interest to study and develop processes as follows:

- Develop a more efficient power supply system to reduce power loss.
- Increase or decrease the volume of oil in production, which might affect the speed of the reactions.
- Improve the temperature control system. The temperature was a sensitive parameter for margarine production by hydrogenation. Appropriate temperature control can increase the quality of margarine and decrease the probability of creating *trans*-fatty acid.
- Install more tubes and upper electrodes in the needle-in-tube configuration to increase production rate and reduce reaction time.

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Appendices

Appendix A

Supplementary Materials for Production Cost Estimation.

In the plasma method, the reaction relied on energy supplied and hydrogen radicals. Therefore, the cost is related to the electricity consumed by a power supply and hydrogen gas which are the variable cost excluding fixed costs: wage, reactor building, and facility construction costs. Assuming unreacted hydrogen and helium gases can be recirculated into the system, the hydrogen gas that participated in the reaction to transform the double bond into a single bond was calculated. This was estimated by considering the change in the number of moles of the double bonds including C18:1, C18:2, and C18:3 based on the ideal gas law ($n = PV/RT$). To find the number of unsaturated fatty acid molecules, the mole number was multiplied by Avocado's number of 6.02×10^{23}. All changes in unsaturated fatty acid were assumed to be a single bond, so C18:1, C18:2, and C18:3 needed to add 2, 4, and 6 atoms of hydrogen, respectively.

Volume used in experiment (25 mL)								
% Fatty acid composition	Fresh refined palm olein	Parallel-plate DBD plasma at 12 h	Needle-in-tube DBD plasma at 15 h	Convert % fatty acid composition to volume (mL) unit			Volume was charged to liter	
				Fresh refined palm olein	Parallel-plate DBD plasma at 12 h	Needle-in-tube DBD plasma at 15 h	Parallel-plate DBD plasma at 12 h	Needle-in-tube DBD plasma at 15 h
C16:0	33.27	58.05	35.8	8.32	14.51	8.95	0.00620	0.00063
C18:0	5.55	9.17	18.85	1.39	2.29	4.71	0.00091	0.00333
C18:1	43.55	30.07	5.24	10.89	7.52	1.31	0.00337	0.00958
C18:2	13.16	1.33	4.05	3.29	0.33	1.01	0.00296	0.00228
C18:3	0.18	-	0.02	0.05	-	0.01	-	0.00004